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Tracing Atmospheric Oxidation Through Organic Nitrates

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Tracing Atmospheric Oxidation Through Organic Nitrates

By

Chiu-Lin Lee

A dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Ronald C. Cohen, Chair
Professor Kristie A. Boering
Professor Allen H. Goldstein

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Tracing Atmospheric Oxidation Through Organic Nitrates

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by

Chiu-Lin Lee
Abstract

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Organic nitrates, chemicals with the formula RONO$_2$, are products of atmospheric oxidation of organic molecules in the presence of nitric oxide (NO) and of the oxidation of alkenes by the nitrate radical (NO$_3$). The formation of these organic nitrates results in removal of NO$_x$ (NO + NO$_2$) from the atmosphere and consequently suppresses the oxidative capacity of the atmosphere by terminating OH-initiated free radical chain propagation reactions and shifting the HO$_x$ radical balance towards HO$_2$ and away from OH. In addition, NO$_x$ removal lowers the NO$_3$ concentration in the evening and thus suppresses the nighttime formation of low vapor pressure compounds that condense to give secondary organic aerosol.

In this dissertation, I present the acquisition and analyses of novel laboratory measurements and field observations of the chemistry of RONO$_2$ species. I begin with a chamber experiment of the oxidation of three isomers of isoprene-derived hydroxy nitrates detected using chemical ionization mass spectrometry and thermal dissociation laser induced fluorescence. This study provides a direct experimental constraint on the lifetime and product yield of the single most important class of atmospheric organic nitrates. Guided by these laboratory measurements, I suggest a parameterization for use in global models of the oxidation rates and product yields of the 8 first-generation isoprene nitrate isomers formed in the atmosphere. I then turn to the role of condensed phase RONO$_2$ in constraining the composition and lifetime of atmospheric aerosol. I describe a laboratory study of the oxidation of a model system for atmospheric aerosol by NO$_3$ radical using ~100 nm particles of pure squalane or of pure squalene in a flow tube reactor coupled to a tunable VUV vacuum UV photoionization aerosol mass spectrometer. The results show that oxidation of squalane (a model for saturated organic aerosol) is too slow to be atmospherically relevant but that oxidation of squalene (a model for multi-unsaturated aerosol) proceeds at a very rapid rate—too rapid for it to be limited by diffusion in solid aerosol particles. The results indicate rapid movement of radical sites within the aerosol matrix and are suggestive that the aerosol is liquid rather than being solid or glassy, as some have suggested.

Organic nitrate formation is strongly affected by temperature, proceeding more quickly at low temperatures, in contrast to many other atmospheric reactions that slow when it is cold. To
investigate the role of organic nitrate chemistry at low temperature and to understand its role in wintertime production of ozone (O3) and organic aerosol, I measured the concentration of a variety of nitrogen oxides, including gas- and aerosol-phase RONO2, during the Uintah Basin Winter Ozone Study in Utah, USA, in 2012. I describe how the observations support that at low temperatures (~0°C) organic nitrate formation suppresses ozone formation and that the particulate organic nitrate budget can be closed using reactions of gas phase precursors.

I conclude with a detailed description of a novel instrument combining gas chromatography with thermal-dissociation laser induced fluorescence for detecting specific individual nitrates, which were used in the preparation of isoprene-derived hydroxy nitrates used in oxidation experiments mentioned above, and with some thoughts on the most interesting questions for future research on the links between RONO2, the oxidative chemistry of the atmosphere, and organic aerosol.
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Chapter 1.

Introduction

1.1. Overview

The chemistry of the Earth’s surface layer and of the troposphere has been dramatically modified by emissions from anthropogenic activities. In the troposphere, the chemistry is oxidative and occurs predominantly via chemical reactions initiated by the hydroxy radical (OH). Other less reactive or abundant oxidants include ozone (O₃), the nitrate radical (NO₃), and oxygen (O) atoms. As a result of these oxidation reactions, O₃ and particulate matter are produced near the surface, causing specific adverse effects on human and animal health, such as increased occurrence in cardiovascular and pulmonary diseases, and crop damage, upon exposure. Climate is also affected.

The mechanism of tropospheric O₃ production requires the participation of nitric oxide (NO) and solar radiation, resulting in the oxidation of organic molecules. Generally, NO is converted to nitrogen dioxide (NO₂) which photolyses on a time scale of ~2 minutes to yield NO and a ground state O atom, which then recombines with abundant oxygen molecules (O₂) in the atmosphere to produce O₃. The conversion of NO to NO₂ occurs by 2 pathways: reaction with O₃, which represents a null cycle since no net O₃ is produced (Figure 1), and reaction with organic peroxy radicals (RO₂) which produces net O₃ (Figure 2). For the null cycle shown in Figure 1, note that NO, NO₂ and O₃ reach a steady-state in the presence of sunlight, and the sum of NO and NO₂ is defined as NOₓ, which has a combined lifetime on the order of 4 hours. For Figure 2, note that, because the NO + RO₂ reaction rate constants are very insensitive to the nature of the R group, O₃ formation is a general feature accompanying most atmospheric oxidation of volatile organic compounds (VOCs) in the presence of NOₓ. The limiting agent is typically the availability of NO in remote regions, where NOₓ concentrations are low. However, in regions where high concentrations of NOₓ are present, such as urban areas or in plumes of industrial emissions or biomass burning, the O₃ formation rate is instead limited by the VOC consumption rate due to the competition between NO₂ and VOCs for the available OH. Reaction of OH with NO₂ yields HNO₃ and terminates the HOₓ (OH + HO₂) and NOₓ radical catalytic cycles. The non-linear behavior of O₃ formation rate versus NOₓ concentration makes prediction of regional O₃ concentrations difficult since exact knowledge of the spatial distribution of NOₓ concentrations, and the organic molecules present and their rate constants for reactions with OH are not generally available. In addition, rates of chain termination reactions leading to production of organic hydroperoxides or organic nitrates are also important and yet not well known.

NOₓ is emitted to the atmosphere as a byproduct of combustion, lightning or anaerobic respiration from microbes. Most analyses of atmospheric processes assume the only important process for removing NOₓ from the atmosphere is formation of HNO₃ followed by deposition. Recently, observational results, however, have indicated that the organic nitrogen oxides of the form RONO₂ (i.e. organic compounds containing the nitrooxy group) are as if not more
important than HNO₃ over most continental regions. These RONO₂ species form more rapidly than HNO₃ at low NOₓ (in the presence of VOCs) and are routinely found at similar concentrations as HNO₃. In addition, organic nitrates typically have lower solubilities than HNO₃, making them much more resistant to wet scavenging and are potentially longer lived in the atmosphere than HNO₃. As a result, they can be transported over long distances before subsequent oxidation to return NOₓ to the atmosphere. On the other hand, some RONO₂ species may be converted to HNO₃ by condensed phase reactions, and observations have indicated that certain RONO₂ may be removed even more rapidly than HNO₃ for which the mechanism responsible is not clear at this time. Thus, the various RONO₂ species represent a complex array of potential sources and sinks of NOₓ to the atmosphere.

The formation yield and fate of the major RONO₂ species produced in the atmosphere, i.e. those derived from isoprene and monoterpene oxidation, have received relatively little attention. The daytime formation pathway of RONO₂ begins with OH-initiated oxidation of an organic molecule, typically by addition to carbon double bonds or abstraction of hydrogen to generate an alkyl radical which reacts rapidly with O₂ to yield an RO₂ radical. In the presence of NO, the subsequent reaction RO₂ + NO generates an energy-rich adduct ROONO*. This adduct can be collisionally stabilized, which terminates the radical chain and gives RONO₂, or it can decompose to an alkoxy radical (RO) and NO₂, which produces net O₃. The temperature and pressure dependence of the RONO₂ yield depends on the number of carbon atoms in the RO₂ radical and on the substitution of other functional groups on the carbon backbone. The effect of oxygenated groups near the peroxy radical site remains uncertain but is very relevant to understanding the yield of alkyl nitrates derived from biogenic VOCs, such as isoprene.

Because the formation of organic nitrates proceeds through reaction sequences that are common to O₃ production, correlations of RONO₂ and O₃ in the atmosphere have been used previously to understand the sources of O₃. The ability to predict both RONO₂ and O₃ correctly represents an affirmation that the underlying chemistry is understood. The results derived from field observations to date, however, are mixed, indicating more needs to be investigated about the organic molecules that are important in atmospheric chemistry and their role in RONO₂ production, as summarized by Perring et al. in 2013 and discussed even more recently by Teng et al. in 2014.

Recently, efficient nighttime production of organic nitrates has been reported. The presence of excess O₃ converts NO to NO₂ and further reaction between O₃ and NO₂ generates the NO₃ radical. NO₃ is rapidly (~10 sec) photolyzed in full sunlight but lives long enough to be an important oxidant for alkenes at night and in the shade of forest canopies. These NO₃ oxidation pathways are effective NOₓ sinks and organic nitrate sources. Laboratory and field studies have also suggested the possibility of aerosol formation as a result of condensation from multi-functional oxidation products. Incorporation of organic nitrate compounds into the particulate phase may alter their atmospheric lifetime, extending it by encapsulation to prevent direct gas phase oxidation, or shortening it through condensed phase chemistry. These processes affect the atmospheric lifetime of RONO₂ and the spatial patterns of nitrogen deposition, as
demonstrated recently by Rollins et al.\textsuperscript{29} in 2012 who showed that RONO\textsubscript{2} species are a major component of organic aerosol. The role of RONO\textsubscript{2} in setting the optical properties of aerosol is also unknown.

1.2. New insights into RONO\textsubscript{2} chemistry

In this dissertation, I advance our understanding of atmospheric chemistry by investigating important unresolved issues in the chemistry of organic nitrates. Examples include (1) an understanding of the fate of specific compounds making up the most commonly occurring atmospheric RONO\textsubscript{2} species – i.e. those derived from isoprene oxidation in the presence of NO\textsubscript{x}, (2) the role of RONO\textsubscript{2} formation in the production of O\textsubscript{3} at low temperatures, and (3) the role of RONO\textsubscript{2} in organic aerosol production and oxidation.

In Chapter 2, I describe laboratory experiments to study the oxidation of isoprene-derived hydroxy nitrates. These hydroxy nitrates are ~10\% of the first generation oxidation products of isoprene, a C\textsubscript{5}-diene which is emitted to the atmosphere at a globally average rate of ~500 Tg (10\textsuperscript{12} g) C per year.\textsuperscript{30} The ~25 Tg C per year of isoprene hydroxy nitrates formed (note that some isoprene is oxidized in regions where NO\textsubscript{x} concentrations are zero and thus the global yield is less than 10\% of isoprene emissions) are a mix of 8 distinct isomers. To understand the chemistry of these RONO\textsubscript{2} species, I synthesized pure standards of 3 of the isoprene-derived hydroxy nitrates. I then collaborated on experiments to study the oxidation of these 3 isomers, measuring the rate of oxidation by OH and O\textsubscript{3} as well as the product yields during these reactions in an atmospheric chamber study incorporating cross-calibrated CF\textsubscript{3}O\textsuperscript{-} chemical ionization mass spectrometry and thermal dissociation laser induced fluorescence techniques. The results are within a factor of two of previous and less direct measurements for the OH reaction rates but 100 times slower for the O\textsubscript{3} reaction rates,\textsuperscript{31} which necessitate a revision in currently accepted chemical loss processes for these species. The major products of isoprene nitrate oxidation include hydroxy acetone, ethanal nitrate, methylvinylketone nitrate, methacrolein nitrate and di-hydroxy di-nitrates that can then participate in further atmospheric reactions and transport.

In Chapter 3, I examine the process of heterogeneous oxidation of organic aerosol by NO\textsubscript{3}. Heterogeneous or liquid phase reactions taking place on the surface or in the interior of organic aerosols are important to understanding and predicting the composition, the chemical lifetime and the optical properties of the aerosol. To study the effect of NO\textsubscript{3} radicals, I investigated experimentally a model system consisting of ~100 nm particles of pure squalane and pure squalene in a flow tube reactor coupled to a tunable vacuum UV photoionization aerosol mass spectrometer. Squalane and squalene are branched C\textsubscript{30} aliphatic compounds of the same carbon chain structure: squalane is fully saturated, while squalene has 6 non-conjugated double bonds. We exposed these organic aerosol particles to mixtures of NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} in dry N\textsubscript{2} and measured the reaction products. The measurements provide evidence for rapid radical chemistry occurring within the squalene liquid matrix and are suggestive of an accelerated photochemical aging applicable to the ambient aerosols.
In Chapter 4, I describe the low temperature chemistry of RONO$_2$ and its effects on O$_3$ and aerosol using observations from the Uintah Basin Winter Ozone Study (UBWOS) in Utah, USA, in 2012. The Uintah Basin has experienced high wintertime O$_3$ events in recent years due to the unique combination of emissions to the atmosphere from oil and gas extraction operations and extremely low and stable boundary layers. The high O$_3$ concentrations exceed regulatory standards, a situation which is highly unusual since winter O$_3$ concentrations are typically low. In *Part A*, I focus on gas phase RONO$_2$ chemistry. During the observational period, average daytime temperatures in the region were near 0°C, providing a contrast between these observations and more typical summertime atmospheric chemistry occurring at ~30°C. The alkane-rich organic composition of the air in the basin simplifies the oxidation chemistry. Our analysis indicates that alkyl nitrate formation represents a significant radical termination process, and that this formation suppresses O$_3$ production by an amount approaching 20% when compared to a model that includes RONO$_2$ formation but neglects its temperature dependence. In *Part B* of Chapter 4, the organic nitrate content in the aerosol phase as observed during UBWOS 2012 is examined. The observations show that organic nitrates are a significant fraction of the particulate organic matter in the region, and I attribute the source to nearly equal contributions of gas phase condensation and heterogeneous reactions.

In Chapter 5, I present a detailed description of a novel instrument combining gas-chromatography (GC) with thermal-dissociation laser-induced-fluorescence (TD-LIF) for the detection and quantification of speciated organic nitrates. This system is used most directly in the isoprene hydroxy nitrate work reported here in Chapter 2, both during the preparation of the nitrate sample and in the main chamber experiments (with modifications), but was originally conceived as a general alkyl nitrate analyzer providing isomer-specific quantification data. A prototype for a direct-sampling pre-concentrator inlet designed for atmospheric sampling is also described.

Finally, I conclude and summarize the advances to the field from each chapter with remarks about follow-up questions for the chemistry of RONO$_2$ and its role in aerosol and O$_3$ production in Chapter 6.
Figure 1.1
Reactions for the tropospheric O$_3$ null cycle. The arrows represent chemical reactions, pointing from reactants to products, such as NO + O$_3$ → NO$_2$, and NO$_2$ + hv → O + NO (for which O + O$_2$ → O$_3$ is implied).
Figure 1.2
Tropospheric net O₃ formation catalytic cycle in the presence of solar radiation and NOₓ, driven by the radical reactions of OH-initiated oxidation of volatile organic compounds (VOCs). VOC reacts with OH to form peroxy radical (RO₂) in the presence of O₂. The RO₂ reacts with NO to form NO₂ and an alkoxy radical (RO). The RO reacts with O₂ to give an oxygenate (typically a carbonyl) and HO₂ radical which subsequently reacts with NO to regenerate OH (hence the radical chain propagation).
Chapter 2

On rates and mechanisms of OH and O3 reactions with isoprene-derived hydroxy nitrates

Abstract

Eight distinct hydroxy nitrates are stable products of the first step in the atmospheric oxidation of isoprene by OH. The subsequent chemical fate of these molecules affects global and regional production of ozone and aerosol as well as the location of nitrogen deposition. We synthesized and purified 3 of the 8 isoprene hydroxy nitrate isomers: (E & Z)-2-methyl-4-nitrooxybut-2-ene-1-ol and 3-methyl-2-nitrooxybut-3-ene-1-ol. Oxidation of these molecules by OH and ozone was studied using both chemical ionization mass spectrometry and thermal-dissociation laser induced fluorescence. The OH reaction rate constants at 300K measured relative to propene at 745 Torr are $(1.1\pm0.2)\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for both the E and Z isomers and $(4.2\pm0.7)\times10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the third isomer. The ozone reaction rate constants for (E & Z)-2-methyl-4-nitrooxybut-2-ene-1-ol are $(2.7\pm0.5)\times10^{-17}$ and $(2.9\pm0.5)\times10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. 3-Methyl-2-nitrooxybut-3-ene-1-ol reacts with ozone very slowly, within the range of $(2.5\sim5)\times10^{-19}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Reaction pathways, product yields and implications for atmospheric chemistry are discussed. A condensed mechanism suitable for use in atmospheric chemistry models is presented.
2.1. Introduction

As a result of biological processes, more isoprene is emitted to the atmosphere than any other non-methane hydrocarbon.\textsuperscript{33} Isoprene is highly reactive and its oxidation affects concentrations of OH, O\textsubscript{3} and NO\textsubscript{3} with the largest effects in the near-field of the emission sources. The first generation oxidation products of isoprene are also reactive (they typically contain one double bond) but are usually longer lived and extend the influence of isoprene chemistry to larger scales\textsuperscript{15, 19, 34, 35}. Despite its importance, it is only recently that we have begun to have a quantitative understanding of the oxidation of isoprene — as methods capable of controlling oxidants at levels relevant to the atmosphere and observing key products including peroxydes, epoxides and nitrates have been developed. Significant advances in our understandings of isoprene oxidation are reflected in recent lab studies that achieved carbon balance in the 1st stage of oxidation\textsuperscript{26, 31, 36, 37}, in theoretical studies that provided insight into structural rearrangements of radical products\textsuperscript{38-40} and in detailed comparison of regional and global models to observations of isoprene and isoprene oxidation products\textsuperscript{34, 41-43}. Hydroxy nitrates are of particular interest due to their role as free radical chain terminators, their effect on secondary organic aerosols\textsuperscript{25, 29, 44} and their role as a reservoir for NO\textsubscript{x} (NO + NO\textsubscript{2})\textsuperscript{17} that can permit long range transport from source regions in the continental boundary layer to remote locations where subsequent release of the NO\textsubscript{x} can result in accelerated photochemistry and enhanced ozone\textsuperscript{34, 45, 46}. The time scale of NO\textsubscript{x} release from isoprene hydroxy nitrates depends on both the rate and mechanism of their oxidation. Previous studies have indicated that lifetimes for isoprene hydroxy nitrates are in the range of 3 to 28, 0.7 to 28 and 16 hours against respective oxidation by OH, O\textsubscript{3} and NO\textsubscript{3} (at typical atmospheric values)\textsuperscript{25, 31, 47, 48}. However, few of these experiments used authentic standards, and the methods for estimating the concentrations have not been subject to independent confirmation by multiple methods. As a result, uncertainties persist about the rates and mechanism of the oxidation of isoprene hydroxy nitrates. In addition to the difficulty in synthesis, purification and quantification of authentic standards, these compounds thermally dissociate under standard conditions used for separation in gas chromatography and are subject to hydrolysis reactions\textsuperscript{18, 49} that result in nonorganic-nitrate-containing products such as alcohols.

Here we present synthesis and identification of 3 isomers: (E & Z)-2-methyl-4-nitrooxybut-2-ene-1-ol and 3-methyl-2-nitrooxybut-3-ene-1-ol as shown in Table 2.1. For the ease of naming, we’ll refer to (E)-2-methyl-4-nitrooxybut-2-ene-1-ol as \textit{trans-δ}-1,4 hydroxy nitrate, (Z)-2-methyl-4-nitrooxybut-2-ene-1-ol as \textit{cis-δ}-1,4 hydroxy nitrate and 3-methyl-2-nitrooxybut-3-ene-1-ol as β-4,3 hydroxy nitrate in the following text. Carbon number designation is in accordance with IUPAC convention. We describe measurements of these molecules and observe their oxidation by OH and O\textsubscript{3}. Reaction rates and products are listed and mechanisms consistent with the observations are presented.

2.2. Experimental methods

Sample preparation
The synthesis of isoprene hydroxy nitrates followed the general procedure described by Cavdar and Saracoglu in 2008. Briefly, the hydroxy nitrates were formed by the ring-opening reaction of the corresponding epoxide precursor in the presence of Bi(NO$_3$)$_3$·5H$_2$O. 2-methyl-2-vinylloxirane (Sigma Aldrich, 95%) containing impurities of 2-(2-oxiranyl)-1-propene (~3%, verified with NMR) was used in the synthesis to yield a mixture of the target isomers. The procedure was as follows: 1.5 ml methylene chloride and 1 g Bi(NO$_3$)$_3$·5H$_2$O pre-ground in a mortar was added to a dry empty 10 ml glass flask. Then 0.17 g of the epoxide were diluted with 0.7 ml methylene chloride and the solution added drop-wise to the 10 ml flask while stirring. The mixture was stirred at room temperature for ~1 hour. The progress of the reaction was checked with silica gel thin-layer chromatography using an elution solvent of 1:1 mixture of ethyl acetate : hexane and visualized with either vanillin or KMnO$_4$ staining solution. The crude mixture of dissolved products was obtained after filtering out the solid and then concentrated under dry N$_2$.

Column chromatography (silica gel, ethyl acetate : hexane = 1:1) was used to separate the hydroxy nitrates from other impurities. The purified samples were concentrated, producing a colorless oil that was immediately redissolved in methylene chloride at a ratio of 1:1. Separation of the multiple isoprene hydroxy nitrate isomers from each other was achieved using high-performance liquid chromatography (HPLC). We used an XDB-CN column (Agilent, 4.6×100 mm 3.5 µm) and eluted with a triplet mixture of methylene chloride : isopropanol : hexane of 15:2:83 which resulted in good peak separation and solvent capacity. The nitrates were detected using a UV-Vis absorption diode array detector at two wavelengths (220 nm and 286 nm), and manually collected. The overall yield of purified hydroxy nitrates was approximately 10% with relative yields of 9%, 25% and 66% for β-4,3, cis-δ-1,4 and trans-δ-1,4 hydroxy nitrate isomers.

The purified hydroxy nitrates were stable for several weeks at concentrations below 0.01% mole fraction with no interconversion between isomers in an aprotic solvent at room temperature. At concentrations above 1% we observed signs of decomposition (pale yellow hue) after one week. Pure hydroxy nitrate samples were unstable and decomposed within 30 minutes at room temperature. Storage of concentrated samples (~1%) in a freezer prolonged the lifetime substantially with no change in composition observed over the span of one month. Prior to each experiment, the target sample was thawed to avoid water condensation during handling.

**Chamber and instruments**

Experiments were conducted at Caltech using a 1 m$^3$ FEP Teflon chamber at ambient pressure (745 torr) as described previously. H$_2$O$_2$ was used as the photolytic source of OH radicals in the presence of excess NO for most experiments. The chamber gas was sampled by pulling air through a 6.35 mm PFA tube at a flow rate of ~1.9 liter per minute, This flow was then sampled by a chemical-ionization mass spectrometer (CIMS), a gas chromatograph with
flame ionization detector (GC-FID, Agilent 5890 II), a thermal dissociation laser-induced fluorescence (TD-LIF) instrument, a chemiluminescence NO\textsubscript{x} detector (Teledyne 200EU) and an O\textsubscript{3} monitor (UV absorption, Teledyne 400E). Most instruments sampled the chamber continuously. The GC-FID system had a run cycle of approximately 15 minutes and was equipped with a megabore (0.53 µm) PLOT-Q column (JW Chemicals) for separating small organic molecules, such as propene. As described below, occasionally the CIMS and TD-LIF instruments were coupled to a GC column instead of continuously sampling the chamber.

CIMS

The Caltech CIMS instrument used in these experiments is similar to the version described in detail elsewhere\textsuperscript{37, 51, 52} with the exception that a time-of-flight mass analyzer (TOF, TofWerk/Aerodyne) was used instead of a quadrupole mass filter. The reagent ion (CF\textsubscript{3}O\textsuperscript{−}) was generated by passing 10 ppmv CF\textsubscript{3}OOCF\textsubscript{3} in N\textsubscript{2} through a radioactive source (Po-210, α decay) and then joined with the diluted sample flow of 1700 standard cubic centimeter per minute (sccm). The ions were accelerated toward a pinhole and then passed through an hexapole ion guide over a differentially pumped region into the TOF mass spectrometer. Generally, chemical species are detected in the form of ion clusters containing CF\textsubscript{3}O\textsuperscript{−} (at m/z = M+85) or as fluoride transfer products (at m/z = M+19). For example, nitric acid (m/z = 63) and acetic acid (m/z = 60) were detected as fluoride transfer products at m/z = 82 and 79, and hydroxy acetone (m/z = 74) was detected as a cluster at m/z = 159. The observed ion signals were normalized to the concentration of reagent ion to account for variation of the ion source strength. We use the summation of ion intensity at 3 masses: m/z = 86, 104 and 120 to represent the reagent ion concentration. m/z = 86 is primarily the \textsuperscript{13}C isotope of the unreacted reagent ion (CF\textsubscript{3}O\textsuperscript{−}). m/z = 104 is primarily the cluster of \textsuperscript{13}CF\textsubscript{3}O\textsuperscript{−} with water and m/z = 120 is the cluster of \textsuperscript{13}CF\textsubscript{3}O\textsuperscript{−} with H\textsubscript{2}O\textsubscript{2}. Calibration factors for various species were generated by either comparing the normalized signal to concentration measured by other techniques such as FT-IR (off-line) or TD-LIF (in-situ), or with theoretical calculation of ion-molecule collision rate based on the dipole moment, polarizability and fluoride affinity of the molecule.\textsuperscript{53}

TD-LIF

The UC Berkeley TD-LIF instrument used in these experiments is similar to versions described elsewhere.\textsuperscript{54, 55} This version was modified to have a minimum of plumbing volume to enable sampling under low flow conditions (~6 sccm) allowing direct coupling to a GC column. Organic nitrate groups (R-ONO\textsubscript{2}) were converted quantitatively to NO\textsubscript{2} (in 10 ms) by thermal decomposition at 400°C. The resulting NO\textsubscript{2} concentration was then measured by laser induced fluorescence with excitation from a 445 nm pulsed (12 kHz) diode laser. The fluorescence signal, in the near-IR region beyond 900 nm, was detected with filtered red-sensitive PMT (Hamamatsu H7421-50) and time-gated photon counting. The system was calibrated frequently with 5 ppmv NO\textsubscript{2} in N\textsubscript{2} (Praxair, certified master).

GC+CIMS/TD-LIF
To further distinguish hydroxy nitrate isomers including those that are products from chemical reactions in the chamber, a direct sampling Agilent GC system was set up using CIMS and TD-LIF as GC detectors by connecting both instruments to the tail of a HP 624 megabore column in parallel configuration via a glass splitter. In addition to the advantage of GC for separating structural isomers, mutual detection allowed direct transfer of TD-LIF calibration to all nitrates detected by CIMS. Briefly, the flow from the chamber was sampled into the GC column while the first column loop was manually immersed in isopropanol bath at ~ -20°C. This effectively cryo-focused the larger organics ($\geq C_3$) into a narrow band at the head of the column. After sufficient amount of sample had been collected, typically ~200 cm$^3$ gas by volume, a 3-way valve switched the column flow to the carrier gas (N$_2$) and the column loop was allowed to warm up under the GC temperature program. The GC temperature program was optimized as to allow separation without decomposition of the major organic nitrates, by limiting the oven temperature to less than 120°C.

**Experimental conditions**

The chamber was operated in batch mode meaning no replenishing zero air was introduced during experiments and the bag was allowed to freely collapse from gas drawn by the instruments. This typically provided a chamber life of ~8 hours. A nominal initial concentration of 500 ppbv NO was used for all but one OH experiments along with ~2 ppmv H$_2$O$_2$ (Table 2.2). This amount of NO was sufficiently high that alkyl peroxy radical self reactions (RO$_2$ + RO$_2$) and RO$_2$ + HO$_2$ reactions were suppressed. The initial concentrations of hydroxy nitrates varied, as briskness of handling took priority over preciseness in sample delivery in order to minimize the time that the liquid sample was exposed to ambient temperature and humid air. The experiments with cis and trans-$\delta$-1,4 isomers were initiated with concentrations of nitrate in the range of 28 to 54 ppbv. The $\beta$ isomer experiments were initiated at concentrations of 8 to 17 ppbv. Acetone, the solvent used for the hydroxy nitrate samples, was introduced into the chamber in all experiments at concentrations approximately 50 to 100 times the nitrate concentration. This added reagent did not interfere with rate measurements.

The OH reaction rates of isoprene nitrates were measured relative to the oxidation of propene (Sigma Aldrich). Isoprene nitrate samples in liquid form were first introduced into a small glass bulb using gravimetric (analytical balance) or volumetric (syringe) methods. The bulb was then connected to the chamber and the liquid evaporated and transferred with a volume of zero air corresponding to ~60% of the chamber capacity. Additional gases (e.g. propene, NO) were first loaded into another larger, air-tight glass bulb of known volume (500 cm$^3$). The concentration inside the bulb was measured with FT-IR for molecules where absorption cross section data are available, or calculated using the fill pressure by assuming ideal gas behavior. The filled bulb was then connected to the chamber and backed with zero air for complete transfer of the gas species. Concentrations were confirmed prior to adding H$_2$O$_2$ with both CIMS and TD-LIF instruments to ensure sufficient nitrate concentration was present as well as providing a cross-calibration point. Absolute measurements by TD-LIF were not available later during the
experiment without the use of the GC+CIMS/TD-LIF mode as elevated concentrations of H$_2$O$_2$ caused a negative interference to the TD-LIF signal at 400°C, possibly due to pyrolysis of H$_2$O$_2$ and formation of OH radicals in the TD oven. After filling the chamber with all reactants and to the target volume, several GC-FID measurements were collected to characterize the initial propene concentration and the CIMS and TD-LIF operating in GC mode gave isomeric-specific information of initial hydroxy nitrates. The UV lights were then switched on and the decay of starting materials observed with both CIMS and GC-FID. The reaction was allowed to proceed until the starting material had decayed beyond 2 e-folds (~10% of initial concentration). At this point the UV lights were switched off and the final chamber composition measured.

The effects of possible interferences and secondary reactions during OH experiments are expected to be small. A brief discussion is included in the Supporting Information A3.

O$_3$ oxidation experiments were carried out in a similar fashion to the OH experiments, with the exception that NO and H$_2$O$_2$ were omitted and phenol added as an OH scrubber (except during experiment 2). O$_3$ was generated prior to each experiment with a discharge type ozonizer from pure O$_2$ gas then trapped with a granular form of silica gel maintained at -70°C in an isopropanol bath. Adsorption of O$_3$ onto silica gel changed its color from translucent white to purple which served as a visual aid for the amount of O$_3$ trapped. After collection, the trap was flushed with N$_2$ and then slightly warmed (to ~ -50°C) allowing O$_3$ and N$_2$ to fill the 0.5 liter glass bulb. The O$_3$ concentration in the glass bulb was then checked directly with FT-IR before addition to the chamber gas. The initial concentrations for O$_3$ and phenol are listed in Table 2.3. For each experiment, the chamber was first brought to 90% of full capacity with introduction of hydroxy nitrates and phenol in zero air followed by confirmation of initial nitrate concentration with CIMS and TD-LIF before final addition of O$_3$ to initiate the reaction. Excess O$_3$ was used for all experiments so that the decay of isoprene nitrates can be treated as pseudo first order. The O$_3$ concentration during the experiments was continuously monitored by UV absorption. It is noted that ppmv levels of phenol may cause interference to the O$_3$ measured due to overlap in UV (254 nm) absorption spectrum. However, phenol breaks through the O$_3$ scrubber in the O$_3$ monitor on a time scale of ~30 min, making the excess O$_3$ signal decay in a near exponential fashion which can be corrected by calculating the decay of signal prior to O$_3$ addition. For most experiments the phenol had saturated the O$_3$ scrubber by the time we introduced O$_3$ into the chamber and the effect was negligible.

2.3. Results

**OH oxidation**

A total of 8 high-NO experiments were performed to measure the reaction rate of the 3 hydroxy nitrates with OH. For all experiments, CIMS was used to monitor the progress of reaction by observing the decay of normalized m/z = 232 signal (ion cluster of CF$_3$O$^-$ with hydroxy nitrate) while GC-FID was used to measure the decay of propene. Example decay curves for both species are shown in Figure 2.1 along with observed NO. As the UV lights were turned on, photolysis of H$_2$O$_2$ generated OH radicals which reacted with both the nitrate and
propene. At the same time NO was converted to NO$_2$ by reaction with HO$_2$ and RO$_2$, both were oxidation products from OH initiated reactions. O$_3$ was observed to increase and reached approximately 25 ppbv just prior to the switching off of lights. An additional low NO experiment was performed for comparison of reaction products.

The relative rate constant method requires an accurate measurement of the decay of both hydroxy nitrate and propene. As evident in Figure 2.1, significant scatter sometimes occurred from the GC-FID data and the precise sampling time of the GC sample loop can be difficult to define. We found m/z = 206 to be a good surrogate for the amount of propene reacted, as plotting normalized m/z = 206 signal versus GC-FID propene measurements gave a linear relationship. m/z = 206 is the cluster ion of hydroxy propyl nitrate, the nitrate product formed from the oxidation of propene by OH in the presence of O$_2$ and NO. Due to the much lower OH reactivity of hydroxy propyl nitrate compared to propene, we estimated that the subsequent reactions with OH had an effect of less than 5% on its final concentration, hence no further correction was applied. The estimated propene concentration is shown as the “Propene CIMS” trace in Figure 2.1.

To assess wall loss, we also performed blank experiments using only trans-$\delta$-1,4 hydroxy nitrate and H$_2$O$_2$ while keeping all the lights off. The result indicated that the wall loss time constant for the nitrate is over 20 hours and provided no evidence of dark reaction. Photooxidation reactions were completed within a time span of ~2 hours, a time scale over which wall loss of the initial reactant is negligible.

Figure 2.2 shows the log-log decays of each of the hydroxy nitrate isomers versus propene. The slopes of the linear fits represent the relative OH rate constant to propene, as reported in the last column of Table 2.2. The data exhibited linear behavior, with r$^2$ values of over 0.99 for ~1.5 e-folds of decay of the nitrate starting material. The chamber temperature during experiments was 27°C. The OH reaction rate constant for each isomer was calculated by multiplying last column value in Table 2.2 by the OH reaction rate constant of propene: 2.59$\times$10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ as recommended by Atkinson$^{56}$ at 760 Torr and 27°C. The resulting rates are summarized in Table 2.4 with pooled uncertainty from the reference reaction rate.

The relative rate technique may be applied to any pair of starting components measured in a chamber experiment. For example, the cis-$\delta$-1,4 hydroxy nitrate contained ~15% trans-$\delta$-1,4 isomer impurity which was difficult to completely remove due to the proximity in retention time during HPLC separation. Since the two isomers are readily separated by GC+CIMS/TD-LIF technique, we estimated their individual concentration at both the beginning and the end of OH experiments. A log-log plot similar to Figure 2.2 showed a relative OH rate constant of cis-versus trans-$\delta$-1,4 hydroxy nitrate of 1.15, indicating that the cis isomer reacts with OH 15% faster than the trans isomer.

The major products from hydroxy nitrate oxidation by OH were detected individually by CIMS and by GC+CIMS/TD-LIF. Given that TD-LIF detects compounds containing organic
nitrate group as NO\textsubscript{2} with unit sensitivity, a ratio of corresponding peak area from the chromatogram between the CIMS signal at the targeted mass and TD-LIF gives a direct estimation of CIMS sensitivity. A GC+CIMS/TD-LIF chromatogram taken at the end of one experiment is shown in Figure 2.3. Note the 4 major nitrogen containing compounds formed from OH oxidation of \textit{trans}-\delta-1,4 hydroxy nitrate, namely ethanol nitrate (m/z = 190), 3-hydroxy-4-nitrooxy-2-butanone (an isomeric form of methyl vinyl ketone nitrate, abbreviated as MVKN', m/z = 234) and 2 isomers of hydroxy propyl nitrate (m/z = 206) were well separated. The m/z = 232 peaks are the remaining \textit{cis}-\delta-1,4 and \textit{trans}-\delta-1,4 hydroxy nitrate, with the \textit{trans} isomer having a slightly longer retention time. The broad ethanol nitrate signal and the elevated TD-LIF baseline (due to chamber NO\textsubscript{2}) at the beginning of the chromatogram indicated that these species were not effectively cryo-focused at the trapping temperature of -10°C, so that a certain degree of sample break through occurred. To completely trap ethanol nitrate and further separate it from NO\textsubscript{2} signal we attempted sampling the compounds at a lower trapping temperature. However, signs of heterogeneous reactions affecting product quantification due to co-trapping of water and H\textsubscript{2}O\textsubscript{2} were observed. We therefore obtained calibration of ethanol nitrate by correlating the TD-LIF counts to m/z = 190 CIMS signal after initiation of the GC run (after 250 seconds in Figure 2.3) when the NO\textsubscript{2} interference to TD-LIF was absent. Calibration of all other nitrates was performed with peak area integration. The calculated relative CIMS sensitivity, normalized to the sensitivity of \textit{trans}-\delta-1,4 is shown in Table 2.5 with 1-σ uncertainty. Note that by using GC, products unique to the \delta isomers (MVKN') and the \beta isomer (4-hydroxy-3-nitrooxy-2-butanone, abbreviated as MVKN) were distinguished and calibrated individually.

Table 2.6 summarizes the molar yields of major products observed following OH oxidation. Note the similarity in product yields of \textit{cis}- and \textit{trans}-\delta-1,4 hydroxy nitrate, which is expected given that the structures become identical after initial addition of OH radical. Both \delta isomers produce ethanol nitrate and hydroxy acetone with high yields while the \beta isomer generated mostly MVKN with a minor yield of hydroxy acetone estimated by subtracting out the m/z = 159 contribution from propene oxidation (see discussion). For the low NO\textsubscript{x} oxidation of \textit{trans}-\delta-1,4 hydroxy nitrate we observed lower yields for both ethanol nitrate and hydroxy acetone, but a somewhat increased yield of MVKN'. Di-nitrate species formed from RO\textsubscript{2}+NO reaction were also observed, but only when the CIMS was sampling directly from the chamber, indicating the GC column transmission efficiency for di-nitrates was poor. As a result, no direct calibration for the di-nitrate species is available and we provide yields based on two separate assumptions. The first yield value is calculated from CIMS signals by assuming the same CIMS sensitivity as the \delta-hydroxy nitrates. The di-nitrate signal from the \beta isomer experiment was too weak to be quantified directly. The second value is obtained by achieving carbon balance on the observed products by assuming that the summed yield of hydroxy acetone, MVKN' and di-nitrate is unity for the \delta hydroxy nitrates and the sum of MVKN, hydroxy acetone and di-nitrates for the \beta nitrate. This estimate represents an upper limit for the nitrate yield.

\textbf{O\textsubscript{3} oxidation}
5 experiments observing reaction of O$_3$ with isoprene hydroxy nitrates were performed, of which 1 experiment was carried out without addition of OH scavenger and an additional experiment for the O$_3$ reaction with MBO (2-methylbut-3-ene-2-ol). The reactant was injected into the chamber first, followed by addition of phenol as an OH scavenger. The O$_3$ concentration and the decay of the m/z = 232 CIMS signal was used to calculate the reaction rate. An example time profile for the O$_3$ reaction with *trans*-δ-1,4 hydroxy nitrate is shown in Figure 2.4. Note the prompt formation of ethanal nitrate and hydroxy acetone, both of which are expected major products from ozonolysis.

We observed a decrease in CIMS sensitivity of the hydroxy nitrate (m/z = 232) when high concentrations of phenol were present. We believe the reduction in signal arises from ligand exchange between the m/z = 232 cluster and a neutral phenol molecule, giving a fluoride transfer ion consisting of a phenol and a hydroxy nitrate molecule at m/z = 260. By monitoring the normalized CIMS signal at m/z = 232 before and after addition of phenol, we derived a correction based on the 2-body rate formulation as Equation 1.

\[
\ln \left( \frac{[m_{232}]_{obs}}{[m_{232}]} \right) = -k[m_{114}] 
\]

([m$_{232}$]$_{obs}$ represents the observed normalized CIMS signal at m/z = 232 while [m$_{232}$] is the corrected signal. [m$_{114}$] is the normalized heavier isotopic signal from the fluoride transfer ion cluster with phenol. The extent of ion chemistry depended on the collision rate, reaction time and the nature of ion cluster considered and we represent it collectively with parameter $k$ determined experimentally from chamber dilution. Since the collision rate and reaction time for ion clusters were maintained constant by controlling the CIMS inlet pressure, $k$ is only a function of the organic nitrate being corrected. We used $k = 1.38$ for both δ-hydroxy nitrate isomers, and 0.878 for the β isomer. The typical correction was 1.2–1.5 as a multiplicative factor to the m/z = 232 signal.

We calculated the rate constant for both δ isomers by fitting the natural log of normalized m/z = 232 signal versus the time integration of O$_3$ concentration. The same procedure was repeated for MBO except that the GC-FID was used to monitor the decay of the reactant. For the β isomer, its slow reaction rate combined with uncertainty in wall loss prevents obtaining a direct measurement of the hydroxy nitrate reacted. Assuming no wall loss and full consumption of the β isomer by O$_3$ reaction alone gives an upper bound to the rate, calculated using the same method as for the δ isomers, of 5×10$^{-19}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Alternatively, using the formation of MVKN (m/z = 234), a unique product from ozonolysis reaction, to constrain the consumption of β-hydroxy nitrate, we derive a lower limit to the reaction rate. As the formation of one MVKN required the consumption of at least one β-hydroxy nitrate, this estimation represented the minimum necessary amount of hydroxy nitrate reacted. Using calibration factors for both MVKN and the β isomer, we obtained a value of 2.6×10$^{-19}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. A summary of the O$_3$ reaction rates is presented in Table 2.7.
The major products observed from the O₃ reactions were primary carbonyls (Table 2.8). The two primary carbonyls formed from ozonolysis of δ isomers are ethanal nitrate and hydroxy acetone. In spite of the similarity in structure, the cis-δ isomer gave almost twice the yield of hydroxy acetone as did the trans-δ isomer. The product yield of the β isomer includes an MVKN yield of 0.5 (assuming no wall loss) or a yield of 1 implying a wall loss time constant of 35 hours. This time constant is longer than the typical value measured for the δ isomers of ~20 hours and appears to be consistent with the fact that the β isomer is more volatile than the δ isomers. The other primary carbonyl expected from the β isomer is formaldehyde, for which CF₃O⁻ CIMS is not sensitive.

2.4. Discussion

OH reaction rates

We report the first reaction rate measurements of the isoprene-derived δ-1,4 and β-4,3 hydroxy nitrates with OH. Molecules of similar structure have been studied previously. For example, Treves and Rudich in 2003 obtained the OH reaction rates of 2 unsaturated hydroxy nitrate isomers on a 4 carbon backbone, namely 4-nitrooxy-1-butanol-2-ene and 1-nitrooxy-2-butanol-3-ene, with corresponding rate constants of 2.2×10⁻¹¹ and 3.6×10⁻¹¹ cm³ molecule⁻¹ s⁻¹. The first compound differs from our δ-1,4 isomers by the absence of a methyl group which represents a direct substituent to the double bond and, based on the structure-activity relationship (SAR) derived by Kwok and Atkinson, have an activating effect toward OH addition. Such an effect is indeed observed. Comparing the rate constants of the δ-1,4 isomer (1.1×10⁻¹⁰ cm³ molecule⁻¹ s⁻¹) and 4-nitrooxy-1-butanol-2-ene (2.2×10⁻¹¹ cm³ molecule⁻¹ s⁻¹), we find an approximate enhancement factor of 5. For the β isomer, a direct comparison is less straightforward as the order of the substitution groups are swapped but a weaker rate enhancement is still present (4.2×10⁻¹¹ versus 3.6×10⁻¹¹ cm³ molecule⁻¹ s⁻¹). We further compared our rate constants with SAR predictions using Kwok’s parameterization, resulting in k_SAR = 6.5×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for the δ-1,4 isomers and k_SAR = 2.4×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for the β isomer. The same low bias in the SAR rate (a factor of 1.7) for both δ and β isomers indicates that the nitrooxy group may not be as deactivating as previously suggested and we propose a revised group contribution factor for nitrooxy group of 0.8 within Kwok’s SAR framework for OH reaction with substituted alkenes. This number should be verified by additional modeling or experimental studies. Recently, indirect estimation of OH rate constants for isoprene-derived hydroxy nitrates was made by Paulot et al. from OH initiated isoprene oxidation in a chamber study. Using a box model to simulate the time profile of products observed, Paulot obtained a rate constant of 9.5×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for the δ-hydroxy nitrate isomers and is in good agreement with our measurements. For the β isomer Paulot’s assignment of 1.9×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ is slower than the 4.2×10⁻¹¹ cm³ molecule⁻¹ s⁻¹ that we observed.

OH oxidation products and mechanism
Figure 2.5 represents our summary of the reaction mechanism for reaction of trans-δ-1,4 hydroxy nitrate with OH at high NO$_3$. Due to excess NO in our system, the RO$_2$ and HO$_2$ lifetimes against reaction with NO were short, typically $<5\times10^{-2}$ seconds. Under such conditions the product channels were dominated by alkoxy radical chemistry, most importantly decomposition. The major products from both δ isomers were ethanal nitrate (m/z = 190), hydroxy acetone (m/z = 159) and MVKN$'$ (m/z = 234). Note the formation of hydroxy acetone is generally accompanied by the formation of ethanal nitrate by cleavage of the carbon bond between carbon 2 and 3 from the corresponding alkoxy radical. We expect similar product yields from both cis- and trans- isomer because the structure becomes identical after OH addition to the double bond.

Although ethanal nitrate and hydroxy acetone shared a similar formation channel, an imbalance in molar yield was observed with a deficit in ethanal nitrate yield of ~10%. This may be explained by an additional decomposition channel following reaction with NO, denoted as Λ in Figure 2.5. An alternative mechanism proposed by Paulot et al.$^{31}$, who observed a similar difference in the chamber study of isoprene oxidation, invokes a 6-electron mechanism involving nitrate and peroxy group in a 6-membered ring configuration to yield acetic acid, formaldehyde and NO$_3$ radical. Under our experimental conditions NO$_3$ is converted back to NO$_2$ in excess NO to give the same product distribution. We therefore cannot confirm or rule out the possibility of either mechanism with the current measurements. Formation of MVKN$'$ (m/z = 234) was possible only through initial OH addition to carbon 3 of the molecule (A channel) while a similar process in the α channel would yield a di-hydroxy ketone (m/z = 189) which was not observed (<1%).

The di-nitrate yield based on the direct CIMS measurements appears low (~3%) when compared with the currently accepted first generation isoprene nitrate yield of ~10%, as well as the estimation$^{20}$ derived for 5 carbon alkane molecules. Due to the high wall loss and the potential to form aerosol particles, we believe our gas phase measurements may significantly underestimate its concentration. A calculation of the vapor pressure using the group contribution method$^{59}$ gives a value of ~1 ppb at 298K. For this reason, we use carbon closure to constrain the formation yield of second generation isoprene di-nitrates. The corresponding upper limit yield of 0.29–0.39 from δ-1,4 hydroxy nitrate and 0.18 from β-4,3 hydroxy nitrate are reasonable estimates based on yields observed for other related compounds (~0.23)$^{60}$ and based on the argument that the the nitrate yield should increase with the total number of heavy atoms in the peroxy radical. This is an extension from the treatment of simple alkanes. As organic nitrates are formed from collision-stabilized ROONO* adduct of RO$_2$+NO reactions$^{61}$, increasing the number of heavy atoms (e.g. longer carbon chain length) enhances internal vibrational energy redistribution (IVR) and extends the lifetime of the adduct and thereby increases the nitrate yield. As a first approximation, our starting hydroxy nitrate should have a nitrate yield corresponding to that of decane (10 heavy atoms), with an estimated yield of ~40% for secondary RO$_2$ radicals at 298K$^{20}$. 

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For experiments where excess NO was used, it was not possible to constrain the formation of inorganic nitrogen species produced by the reactions directly. Assuming a di-nitrate yield using carbon balance, our observation of δ-1,4 isomers indicated a NOx recycling of -17% (trans) and -25% (cis) as a result of OH initiated oxidation through alkoxy radical reactions. Note the definition of NOx recycling we adopt here is the amount of NOx formed minus NO consumed through reaction. The negative values are driven by the high nitrate formation yields inferred, as the only NOx releasing channel (Δ in Figure 2.5) is constrained by the difference in hydroxy acetone and ethanal nitrate yields of 12–14%. Due to the possibility of di-nitrates condensing to form aerosol particles, the above estimated recycling may not be observable from measuring gas phase nitrates alone.

With the observed products, we now describe branching ratios in the mechanism shown (Figure 2.5). We begin by comparing pathway A and α. Along both pathways, the initial peroxy radical formed following OH and O2 addition has the peroxy moiety one carbon away from the nitrooxy group. The molecules then react with NO to form either a di-nitrate or an alkoxy radical. Both alkoxy radicals can decompose by cleavage of carbon bond C2-C3 to proceed down B and β pathways. Products from the alternative decomposition pathway (cleavage of C1-C2 or C3-C4 bond) was only observed for channel A, giving MVKN' (pathway Γ). Both B and β pathways lead to the formation of hydroxy acetone and ethanal nitrate. However, the additional reaction pathway (Δ) unique to pathway B reduces the ethanal nitrate yield relative to the hydroxy nitrate yield. We therefore assign, from the observed yield difference, a value of 12% to the Δ channel for the trans-δ isomer. The channel strength of Δ' can subsequently be estimated based on the HO2 elimination rate and NO reaction rate. We used the first order decomposition rate of 176 s⁻¹ from C1 α-hydroxyperoxy radical62 for Δ' and 70 s⁻¹ calculated with a representative NO concentration of 300 ppbv and rate constant from Miller et al.63 for Δ channel. The ratio indicated an ethanal nitrate yield of 31% from Δ' pathway. With observed MVKN' yield of 16% and di-nitrate formation branching ratio of 29%, the total yield for the A branch is calculated as the sum of B (43%), Γ (16%) and di-nitrate yield (24%) to be 83%. By conservation of mass the α branch is 17%, of which 5% proceeds to form the alternative di-nitrate molecule and the remaining portion (12%) forms equal amount of hydroxy acetone (β) and ethanal nitrate (δ).

The trans-δ-1,4 hydroxy nitrate experiment performed without added NO (Experiment 9) showed some product variation when compared with the high NO cases. The major cause is likely due to the decrease in importance of channels involving RO2+NO reaction such as channel B, β, Γ and γ in Figure 2.5. Products resulting from these pathways are therefore expected to decrease. Consistent with this, we observed 50% less ethanal nitrate and hydroxy acetone (Table 2.6). In fact, the observation is in broad agreement with the branching ratio proposed in Kwan’s recent study64 of alkoxy radical yield from RO2+RO2 reactions which are the alternative channel leading to ethanal nitrate and hydroxy acetone formation in the absence of NO. However, this does not explain the increased yield of MVKN’ (m/z = 234). This difference indicates the possibility of a separate formation pathway that generated MVKN' without proceeding through the corresponding alkoxy radical, possibly directly from RO2 reactions.
The OH initiated oxidation pathway for the β-4,3 hydroxy nitrate is summarized in Figure 2.6. The primary product from the β isomer is MVKN (m/z = 234, Γ + γ channel) with a molar yield of 72%. Formation of hydroxy acetone (m/z = 159) was also observed during oxidation, but a portion of this signal is attributed to the minor oxidation product from propene. Two isomers of m/z = 159, namely hydroxy acetone and 2-hydroxy propanal, were formed following O₂ reaction with the respective β-hydroxyalkoxy radicals after elimination of HO₂ radical. The absolute contribution is obtained by performing a follow-up OH oxidation experiment with propene only. The observed concentration ratio of hydroxy acetone to hydroxy propyl nitrate (m/z = 206) is 7%, giving a corrected hydroxy nitrate yield from β-4,3 isomer of 10% shown in Table 2.6. This value is consistent with the accompanying formation of glycoaldehyde (m/z = 145) with an estimated yield of 9%. We have also estimated the hydroxy acetone to hydroxy propyl nitrate ratio using rate constants proposed by Atkinson and obtained a value of 23%, which indicates a much higher contribution from propene oxidation to m/z = 159 signal and a correspondingly reduced yield (4%) from the β-4,3 isomer. Additional experiments are necessary to resolve this discrepancy but for consistency we use our experimental value for the ratio of hydroxy acetone to hydroxy propyl nitrate of 7% in the remainder of this discussion. By assuming carbon balance for di-nitrate formation, we obtain an NOₓ recycling of -8%.

We were unable to constrain the branching ratio of OH addition to the terminal carbon or to the secondary carbon due to the lack of channel-specific products as both channels appear to yield MVKN (Γ and γ channels, Figure 2.6).

O₃ reaction rates

O₃ was observed to react most rapidly with the δ isomers and the cis-δ reacts only 7% faster than the trans-δ, indicating the formation rate of the primary ozonide for both δ isomers is similar. In contrast, the β isomer reacts with O₃ approximately 2 orders of magnitude slower than the δ isomers. This difference is partially explained by the number of substitution groups on the double bond as has been previously observed for simple alkene analogs. For example, 2-methyl-2-butene (k_O₃ = 2.18×10⁻¹⁶ cm³ molecule⁻¹ s⁻¹) reacts with O₃ 10 times faster than 2-methyl-1-butene (k_O₃ = 1.42×10⁻¹⁷ cm³ molecule⁻¹ s⁻¹). Direct comparison with an existing SAR is not possible as the parameterization lacks training for nitrate functionality. However, as far as the general effect of the functional group on the O₃ reactivity of a double bond is concerned, our observation is in line with the parameterization proposed by Pfrang et al., 2008 for unsaturated alcohols, as rates of the δ hydroxy nitrates (2.7×10⁻¹⁷, 2.9×10⁻¹⁷ cm³ molecule⁻¹ s⁻¹) are an order of magnitude slower than the simple alkene analog of 2.18×10⁻¹⁶. We calculate SAR rates for 1,4-dihydroxy-2-methyl-2-butene (k_SAR = 9.3×10⁻¹⁸ cm³ molecule⁻¹ s⁻¹), an analog of δ hydroxy nitrate isomers by substituting the nitrate group with a hydroxy group, resulting in a rate that is 1/3 of our observation. The rate for 1-hydroxy-2-methyl-2-butene (k_SAR = 3.5×10⁻¹⁷ cm³ molecule⁻¹ s⁻¹) gives a closer prediction, suggesting that for the case of δ hydroxy nitrates the nitrate group has a near neutral effect within this SAR on the reactivity of the double bond toward O₃. It should be cautioned, however, that the O₃ reaction involves intermediates.
(ozonides) for which the effect of neighboring groups is complex. As a result, SAR predictions for \( \text{OH} + \text{alkene} \) reaction rates are generally more consistent with measurements than SAR predictions for \( \text{O}_3 + \text{alkene} \) reactions.

Lockwood et al.\(^{48}\) recently reported \( \text{O}_3 \) reaction rate measurements for the same \( \delta-1,4 \) hydroxy nitrates observed here. In their paper, the \( \text{cis} \)- and \( \text{trans} \)-isomers were not separated and the single reported reaction rate is \( 5.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), approximately a factor of 2 higher than our value. Also, of the two \( \beta \) isomers reported, specifically \( \beta-1,2 \) and \( \beta-2,1 \) hydroxy nitrates (\( k = 1.06 \times 10^{-16} \) and \( 3.42 \times 10^{-16} \) \( \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), respectively), their reaction rates with \( \text{O}_3 \) were both faster than the \( \delta \) isomer. This is interesting as more substituted alkenes tend to react faster and is different from our observation of the \( \beta-4,3 \) hydroxy nitrate. It is not clear why the \( \beta \) isomers in Lockwood’s work should react with \( \text{O}_3 \) at a rate more than 2 orders of magnitude faster than the \( \beta-4,3 \) hydroxy nitrate. We point out, however, that recent studies\(^{18, 49}\) have suggested that isolating the tertiary nitrate using conventional chromatographic technique may be difficult due to its short lifetime (minute time scale) against hydrolysis. Also, our MBO measurement performed under the same experimental condition is in good agreement with the recent work by Klawatsch et al.\(^{69}\)

**OH formation from ozonolysis**

\( \text{O}_3 \) reactions with alkenes are known to generate products that decompose to yield OH radicals. \( \text{O}_3 \) reactions with isoprene nitrates are no different. We estimate the OH yield using the product formed from the reaction of our OH scrubber, phenol. As suggested by Berndt and Boge\(^{70}\) under oxidation conditions similar to ours, formation of catechol (yield of 73–78%) was identified as a fluoride transfer ion at \( m/z = 129 \). However, direct quantification of catechol with a pure standard was difficult, due to strong interactions with our chamber wall and delivery systems which prevented quantitative introduction of standard at a relevant concentration. Instead, we first compared the \( \text{O}_3 \) reaction rate constants with and without phenol for \( \text{trans-}\delta-1,4 \) hydroxy nitrate to provide an estimate for OH yields. Consider a simplified reaction scheme consisting of reactions 1 and 2:

\[
\text{ISOPN} + \text{O}_3 \rightarrow P + \zeta OH \quad (1)
\]

\[
\text{ISOPN} + \text{OH} \rightarrow P' + 0.3 \text{HO}_2 \quad (2.1)
\]

\[
\text{Phenol} + \text{OH} \rightarrow 0.75 \text{Catechol} + 0.75 \text{HO}_2 \quad (2.2)
\]

We assume a single step reaction of isoprene hydroxy nitrate (ISOPN) with \( \text{O}_3 \) on average generated \( \zeta \) OH radicals, which can further react with another isoprene hydroxy nitrate or a phenol molecule (2.1 + 2.2). For experiments performed without an OH scrubber, the apparent loss rate of the hydroxy nitrate will generally be higher due to secondary reactions with OH. The exact relationship between \( \zeta \) and the enhancement of the apparent reaction rate depends on the
fate of the HO₂ radical formed. Under conditions where the majority of HO₂ did not reform OH radical, the ratio of the reaction rate measured without an OH scrubber to that with a scrubber will be enhanced by a factor of \((1+\zeta)\). The fates of HO₂ are listed as reactions 3.1 to 3.3:

\[
\begin{align*}
    \text{HO}_2 + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 + O_2 \\
    \text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + 2\text{O}_2 \\
    \text{HO}_2 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

Due to the very high reactivity of both our hydroxy nitrate and phenol, the OH concentration (in reaction 3.3) during O₃ reactions was too low to compete with reaction 3.1 and 3.2. Note that reaction 3.1 represents the radical termination step while 3.2 regenerates OH radical and leads to propagation. A radical propagation cycle consists of reaction 2.1, 2.2 and 3.2, initiated by reaction 1. In the case of high O₃ concentration, the OH cycling efficiency can be quite high (reaction 3.2 dominating over 3.1) and the amount of additional isoprene nitrate reacted may well exceed \(\zeta\). Further, in the presence of high concentrations of phenol, which is efficient in regenerating HO₂, the OH propagation efficiency can be as high as 0.75, corresponding to an overall chain length of 4. Correction is therefore necessary to account for the OH cycling as the loss of phenol will be up to 4 times the OH generated from reaction 1. We estimated the OH yield of trans-δ-1,4 hydroxy nitrate with correction for HO₂ and OH recycling, then used the relative ratio of catechol formed to reactant consumed to estimate OH recycling from cis-δ-1,4 hydroxy nitrate and MBO. The results are summarized in Table 2.9. Note the HO₂ yield of 0.3 from OH oxidation of δ hydroxy nitrates in the absence of NOₓ was assumed (reaction 2.1) based on arguments as follows: HO₂ is formed from α-hydroxy alkyl radicals generated from decomposition of the β-hydroxy alkoxy radical. Based on recent work of Kwan et al. on isoprene-derived peroxy radical reactions, the alkoxy radical formation yield from RO₂ reactions with HO₂ was suggested to be 38–58%. Assuming alkoxy radicals are formed with 50% efficiency via reaction with HO₂ (the dominant reaction in the absence of NO), the HO₂ formation yield will be effectively halved, from 59% (e.g. \(\Gamma^+\Delta^+\) channel in Figure 2.5) to 30% accounting for channels that lead to ethanal nitrate (m/z = 190) and MVKN’ (m/z = 234). We also assumed that the HO₂ yield from the phenol+OH reaction is the same as the cited yield of catechol.

Different OH yields are obtained for the cis- and trans- isomers of the δ hydroxy nitrates, indicating yield variation in proceeding through the peroxide channel from Criegee intermediates. Similar asymmetry in the OH yield has also been observed for 2-butene by Atkinson and Aschmann, with the trans-2-butene having a higher OH yield of 0.64 versus cis-2-butene of 0.41. It is possible that the nitrate and hydroxy groups actively participate in the formation of the primary ozonide which alters the syn/anti conformation ratio of the subsequent Criegee as well as its energetic distribution. Unfortunately we do not have sufficient product closure to elucidate the distribution among the possible channels. The OH yield from MBO oxidation is relatively low when compared with structures of similar carbon backbone, such as 1-butene (0.41) or isoprene (0.27). This is not surprising as the primary channel for Criegee

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formation is expected to be from the 4-carbon fragment accompanying the formation of formaldehyde. Since there is no hydrogen on the carbon next to the bi-radical group, the decomposition cannot proceed through peroxide channel and OH formation is likely suppressed. In fact, the MBO OH yield is much closer to that of 1,3-butadiene (8%)\(^7\) for which abstraction of vinyl hydrogen is less favorable.

**O\(_3\)** oxidation products and mechanism

We summarize the mechanism of isoprene nitrate oxidation by O\(_3\) in Figure 2.7. Note that certain pathways are suggestive as they have been observed for small alkenes. These pathways yield products that are not effectively detected with our instruments (e.g. the ester channel, see Atkinson et al.\(^6\) and references therein). The formation yield of primary carbonyls can serve as surrogates for the decomposition of the primary ozonide. In the case of \(\delta\) isomers the relative yield of ethanal nitrate to hydroxy acetone reflects the branching ratio of C\(_3\) Criegee to C\(_2\) Criegee formation in Figure 2.7 at points labeled \(\alpha\) and A. Generally Criegee radicals with more alkyl substitutions are preferred, as is the case for trans-\(\delta\)-1,4 hydroxy nitrate. However, the cis-isomer had almost equal yield of ethanal nitrate and hydroxy acetone, indicating possible contributions from the hydroxy and nitrate groups in closer proximity. Products other than the primary carbonyls have also been detected, including dihydroxy acetone (m/z = 175). Note the formation of dihydroxy acetone proceeds through the peroxide channel and is accompanied by the formation of OH radical. The cis-\(\delta\) isomer generated about 2 times the amount of OH relative to the trans-\(\delta\) isomer, a result consistent with the corresponding enhancement in the peroxy channel as reflected in the higher yield (1.7 times larger) of dihydroxy acetone observed for the cis-\(\delta\) isomer than the trans-\(\delta\) isomer. Overall, closure on primary carbonyls of 80% and 113% was obtained for cis and trans-\(\delta\) isomers, respectively. From the perspective of NO\(_x\) recycling, the mechanism illustrated in Figure 2.7 suggests that most of the nitrate group remained attached to an organic backbone, except for the pathway leading to the formation of glyoxal (pathway B) for which we have tentatively assigned a yield of 5% for trans- and 11% for cis-\(\delta\)-1,4 isomer. We have not detected appreciable HNO\(_3\) formation during O\(_3\) experiments. However, in the presence of excess O\(_3\), any NO\(_x\) released would have been converted to NO\(_3\) and N\(_2\)O\(_5\) which were expected to have high wall loss rates and potentially high reactivity toward the hydroxy nitrate reactant. Considering no NO\(_x\) was intentionally added to our system and the absence of di-nitrate ion masses observed from OH experiments (m/z = 311, 291 and 245), we believe the interference from NO\(_3\) reaction was small and suggest that NO\(_x\) released due to O\(_3\) reaction is low.

Product yield estimation from the O\(_3\) reaction with \(\beta\)-4,3 hydroxy nitrates was difficult, mostly due to the slow reaction rate and uncertainty regarding wall loss. The major carbonyl product is MVKN (m/z = 234) with at least 50% yield.

**Summary and recommendations**

Table 2.10 summarizes the OH and O\(_3\) reaction rates of first generation isoprene hydroxy nitrate isomers using values obtained in this study alongside those from literature and SAR
estimations with the nitrooxy group contribution factor derived previously (0.8 for OH reactions). It was necessary to make certain assumptions in assigning O$_3$ reaction rate constants among the isoprene hydroxy nitrate isomers for which we do not have direct measurements. First, the δ-4,1 hydroxy nitrate is assumed to have a similar reaction rate as the δ-1,4 isomers. For β isomers, the β-1,2 is assigned a rate constant by scaling the SAR prediction proposed by Pfang et al.\textsuperscript{68} based on the β-4,3 isomer as both isomers share the same relative positioning of nitrooxy and hydroxy group relative to the double bond. We then assume that the β-nitrooxyhydroxy functional group has the same effect as a whole and assign the same rate constant for β-2,1 as β-1,2 and β-3,4 as β-4,3.

With the revised reaction rates and products observed, we recommend a condensed reaction scheme for treating first generation isoprene hydroxy nitrate oxidation that is suitable for use in atmospheric chemistry models in Table 2.11. Reactions for low NO$_x$ conditions are explicitly included (reactions 5 and 6) as well as product distributions from O$_3$ oxidations (reactions 7 and 8). We found it necessary to lump δ and β isomers separately as they demonstrate very different reaction rates toward OH oxidation. Temperature dependence (B values) of the rate constants are taken from experimental data on compounds that best resemble the isomers. The pre-exponential factors (A values) are subsequently calculated to match the 298K values. For all presented reactions, oxidation pathways for 4 dominant structural isomers were explicitly traced using known reaction rates and product distributions as suggested by Paulot et al. and those inferred from this work. Characteristics of the δ isomer group (ISOPN$_\delta$) are represented by δ-1,4 (52%) and δ-4,1 (48%) isomers ignoring the difference in E/Z configurations. The β isomer group (ISOPN$_\beta$) is represented by β-1,2 (64%) and β-4,3 (36%) isomers. OH formation from RO$_2$ + HO$_2$ reactions are adapted from the work of Kwan et al.\textsuperscript{64} The major addition to the product distribution at high NO$_x$ is the inclusion of a di-hydroxy di-nitrate (DHDN) species with 29% and 21% molar yield for the lumped δ- and β- ISOPNOO species, respectively. RO$_2$ + RO$_2$ reactions are likely to have a minor role under typical atmospheric conditions and are included in Supporting Information A4. For O$_3$ oxidation, a relatively large uncertainty persists in the product distribution, specifically the channel branchings associated with Criegees. Also, RO$_2$ radicals formed following the elimination of the OH radical through the peroxide channel can yield different products depending on the oxidation environment. Considering that O$_3$ reactions are likely important only in the absence of sunlight, RO$_2$ + HO$_2$ should dominate. We therefore subjectively assign hydroperoxides as products from these channels (giving PROPNOOH in reaction 7 and MVKNOOH in reaction 8). Those wishing to treat them in a more exact manner may re-assign the PROPNOOH and MVKNOOH as primary RO$_2$ and propagate them accordingly. We intentionally retain some of the product distinctions such as ROOR (Supporting Information A4) and DHDN as they have the potential to partition into the aerosol phase with high yields\textsuperscript{25, 29, 44} and may be useful in prediction of aerosol formation in forested regions.

**Atmospheric implications**

Isoprene-derived hydroxy nitrate formation has been shown to represent an important NO$_x$ sink and to form a NO$_x$ reservoir species in regions of intense biogenic emissions. The fate of
these hydroxy nitrates can serve to modulate the O\textsubscript{3} concentration by acting as a NO\textsubscript{x} sink near isoprene source regions and as a NO\textsubscript{x} source upon oxidation downwind. Crucial to accurate prediction of this spatial re-distribution of NO\textsubscript{x} is knowledge of the chemical lifetime and NO\textsubscript{x} recycling characteristics of these hydroxy nitrates against common atmospheric oxidants: OH, O\textsubscript{3} and NO\textsubscript{3}. Observations of reaction products during this study confirm that a large portion of the NO\textsubscript{x} stored as nitrooxy groups remain attached to a carbon skeleton past at least the first step of OH or O\textsubscript{3} oxidation. Of these second-generation nitrogen-containing products, MVKN, MACRN and di-hydroxy di-nitrates are highly functionalized and therefore will be more susceptible to wet and dry deposition relative to the more volatile ethanal nitrate, or methyl nitrate from ozonolysis reactions. Due to the diversity of atmospheric lifetimes of these higher generation nitrogen-containing products and the retention of a significant portion of the original nitrogen moiety (e.g. ~88% for δ-1,4 and ~90% for β-4,3 hydroxy nitrates from OH oxidation), the ongoing fate of these other compounds must be considered in simulations attempting to represent the NO\textsubscript{x} budget.

Atmospheric lifetimes for the hydroxy nitrates under study have been calculated based on our experimental results for both OH and O\textsubscript{3} initiated oxidations at atmospherically relevant concentrations and summarized in Table 2.12. Also included are the expected relative contributions of each nitrate isomer to the summation of first generation isoprene-derived hydroxy nitrates. In addition, we have estimated the corresponding NO\textsubscript{3} reaction rates using SAR methods proposed by Pfrang et al., 2008 and Kerdouci et al., 2010\textsuperscript{68,73} Since neither SAR has explicit consideration of nitrooxy groups, we assume the contribution to be the same as a hydroxy group. For Pfrang’s parameterization, the reaction rates were further scaled by a factor obtained by taking the ratio of predicted and measured NO\textsubscript{3} reaction rate constant of 1-hydroxy-2-butene reported by Zhao et al. in 2011\textsuperscript{74} as this method tends to underestimate rates of small oxygenated alkenes by an order of magnitude. The resulting prediction for δ and β isomers are 1.8×10\textsuperscript{-13} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} and 2.8×10\textsuperscript{-13} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1}, respectively by Pfrang’s parameterization and 5.8×10\textsuperscript{-12} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} and 4.2×10\textsuperscript{-13} cm\textsuperscript{3} molecule\textsuperscript{-1} s\textsuperscript{-1} by Kerdouci’s method.

During daytime, the major chemical loss process for all 3 hydroxy nitrate isomers are oxidation by OH. The atmospheric lifetime appears to agree well with the result from total alkyl nitrate concentration measurements during Intercontinental Chemical Transport Experiment-North America (INTEX-NA) 2004 when high isoprene influences were observed. Specifically, Perring et al.\textsuperscript{15} suggested an atmospheric lifetime of alkyl nitrates derived from isoprene oxidation to be 2.5 hours constrained by correlation between total alkyl nitrate concentration and formaldehyde (a product of isoprene oxidation). The authors also inferred a NO\textsubscript{x} recycling of 21% (or nitrate recycling of 79%), a value higher than what we obtained (-8% to -25%) from the individual isomers assuming high di-nitrate yield, but lower than the value of 28% to 53% assuming all unaccounted channels recycle NO\textsubscript{x} with unit efficiency. Given that δ-1,4 and β-4,3 hydroxy nitrate together may amount to half of the first generation isoprene derived hydroxy nitrates, the nature of this discrepancy is uncertain at this point due to the lack of data from other hydroxy nitrates as well as the possible complication from aerosol processing if di-nitrates
condense efficiently (e.g. hydrolysis\textsuperscript{18, 49}). We also point out that upon oxidation, other major first-generation hydroxy nitrates may have very different \(\text{NO}_x\) recycling characteristics. For example, the \(\beta\)-1,2 hydroxy nitrate can potentially have a higher \(\text{NO}_x\) recycling value as a result of both its tertiary nitrate group being more readily hydrolyzed under atmospheric condition and also the likelihood of forming \(\alpha\)-nitrooxy alkyl radical after OH initiated oxidation. Further investigation is necessary to constrain the oxidative pathways of other important hydroxy nitrate isomers as well as aerosol yields from di-nitrate species.

For nighttime oxidation, the hydroxy nitrate oxidative lifetime against \(\text{O}_3\) can be comparable to \(\text{NO}_3\) oxidation. In addition to the daytime source of isoprene hydroxy nitrates, \(\text{NO}_3\) oxidation of isoprene has been shown to give high yields of organic nitrates including unsaturated hydroxy nitrates of the same structure as studied in this paper, resulting from \(\text{RO}_2 + \text{RO}_2\) reactions after initial \(\text{NO}_3\) addition. The recent work by Kwan et al.\textsuperscript{64} suggested the aldehyde and alcohol forming channel from isoprene-derived \(\text{RO}_2 + \text{RO}_2\) reactions to be 59\% to 77\%, indicating an hydroxy nitrate yield of 29\% to 38\% (with accompanying formation of equal amount of carbonyls) for an \(\text{RO}_2\) radical not reacting with \(\text{HO}_2\). Further, significant \(\text{OH}\) radical formation was also observed, hinting at the possibility of \(\text{OH}\) initiated oxidation of hydroxy nitrates in the absence of \(\text{NO}\) during the night.

We have constructed a box model to evaluate the importance of chemical loss processes of hydroxy nitrates by \(\text{OH}, \text{O}_3\) and \(\text{NO}_3\) with rates currently used in atmospheric models and those observed here. For simplicity, concentrations of \(\text{OH}, \text{O}_3\) and \(\text{NO}_3\) were prescribed at typical diurnal profiles with peak daytime \(\text{OH}\) concentration of \(5 \times 10^6\) molecule cm\(^{-3}\) and nighttime \(\text{NO}_3\) concentration of \(2.5 \times 10^8\) molecule cm\(^{-3}\). The \(\text{O}_3\) concentration was set to 40 ppbv constant. Isoprene emission profiles were constructed with the temperature and sunlight profiles following Guenther et al.\textsuperscript{30} then scaled so that the isoprene concentration reached 5 ppbv at noontime (~8 ppbv hour\(^{-1}\) maximum emission). We simulated the formation and loss of individual isoprene hydroxy nitrate isomers, with initial formation rate following the branching ratios of Paulot et al.\textsuperscript{31} from \(\text{OH}\) oxidation. Nighttime formation of hydroxy nitrates by reactions of \(\text{NO}_3\) with isoprene was not considered. To reach a steady-state profile, the same daily oxidant and emission profiles were used for a 4-day spin-up period. 2 sets of simulations which differ in \(\text{OH}\) and \(\text{O}_3\) reaction rates were performed. For the first set, individual isoprene hydroxy nitrate isomers were simulated with rates summarized in Table 2.10. The second set followed the parameterization from recent modeling\textsuperscript{19, 43}, using ensemble averaged \(k_{\text{OH}}\) and \(k_{\text{O}_3}\) values of \(6.2 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) and \(8.4 \times 10^{-17}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for all first generation isoprene hydroxy nitrates. The same set of \(\text{NO}_3\) rate constants estimated using Pfang’s parameterization was applied for both simulations. The grouped hydroxy nitrate concentration profile is depicted as stacked plots in Figure 2.8, with the blue sector representing the sum of \(\beta\) isomers and the golden sector representing sum of \(\delta\) isomers. The revised parameter set is shown in solid color while the other is shown as the hatched area. At an overall nitrate yield of 11.7\%, we observe an enhancement in maximum total hydroxy nitrate concentration, due to the reduction in \(\text{O}_3\) reaction rates. For the same reason, the concentration of \(\beta\) isomers dominates the hydroxy nitrate composition, with extended influences well into the night. The overall reduction in \(\delta\) isomer fraction during the day.
(from ~55% to 30%) is a result of both the increase in β isomer concentration and the accelerated loss due to higher OH rate constants. We did not consider hydrolysis of the isomers.

2.5. Conclusion

We have directly measured OH and O₃ reaction rates for 3 first-generation isoprene-derived hydroxy nitrates. Based on these measurements, both cis- and trans-δ-1,4 hydroxy nitrates are expected to react quickly and predominantly with OH during the day, while the loss of β-4,3 hydroxy nitrate will be determined by both OH reaction and dry deposition. Ozone reaction rates for all 3 isomers are too slow to compete with the dominant processes, but may become important in low light conditions for the δ isomers. Product channels have also been identified for both OH and O₃ oxidation reactions. The formation of various higher-generation organic nitrates with different atmospheric lifetime at substantial yield indicates accurate representation of these nitrogen-containing products are necessary to predict NOₓ both at the source region and downwind from biogenic emissions of isoprene. A revised reaction scheme for Isoprene hydroxy nitrate is provided based on the current work for incorporation into atmospheric chemical models.
Table 2.1 Molecular structures and abbreviations of all first generation isoprene hydroxy nitrate isomers

<table>
<thead>
<tr>
<th>Structure</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>β-1,2</td>
</tr>
<tr>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>β-2,1</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure 3" /></td>
<td>β-3,4</td>
</tr>
<tr>
<td><img src="image4.png" alt="Structure 4" /></td>
<td>β-4,3&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image5.png" alt="Structure 5" /></td>
<td>cis-δ-1,4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td><img src="image6.png" alt="Structure 6" /></td>
<td>trans-δ-1,4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td><img src="image7.png" alt="Structure 7" /></td>
<td>cis-δ-4,1</td>
</tr>
<tr>
<td><img src="image8.png" alt="Structure 8" /></td>
<td>trans-δ-4,1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isomers studied in this work.
Table 2.2 Summary of OH initiated oxidation experimental conditions

<table>
<thead>
<tr>
<th>experiment number</th>
<th>hydroxy nitrate name</th>
<th>hydroxy nitrate ppbv</th>
<th>H$_2$O$_2$ ppbv</th>
<th>NO ppbv</th>
<th>propene ppbv</th>
<th>$k/k_{propene}$ (300K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$trans$-$\delta$-1,4</td>
<td>50$^a$</td>
<td></td>
<td>30$^a$</td>
<td></td>
<td>4.16</td>
</tr>
<tr>
<td>2</td>
<td>$trans$-$\delta$-1,4</td>
<td>50$^a$</td>
<td></td>
<td></td>
<td></td>
<td>3.98</td>
</tr>
<tr>
<td>3</td>
<td>$cis$-$\delta$-1,4</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
<td>4.19</td>
</tr>
<tr>
<td>4</td>
<td>$\beta$-4,3</td>
<td>7.9</td>
<td></td>
<td></td>
<td></td>
<td>1.68</td>
</tr>
<tr>
<td>5</td>
<td>$trans$-$\delta$-1,4</td>
<td>47</td>
<td>2000$^a$</td>
<td>500$^a$</td>
<td>100$^a$</td>
<td>4.25</td>
</tr>
<tr>
<td>6</td>
<td>$trans$-$\delta$-1,4</td>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td>4.10</td>
</tr>
<tr>
<td>7</td>
<td>$cis$-$\delta$-1,4</td>
<td>54</td>
<td></td>
<td></td>
<td></td>
<td>4.31</td>
</tr>
<tr>
<td>8</td>
<td>$\beta$-4,3</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td>1.60</td>
</tr>
<tr>
<td>9</td>
<td>$trans$-$\delta$-1,4</td>
<td>31</td>
<td>2000$^a$</td>
<td>0</td>
<td>0</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*a.* Nominal value.
Table 2.3 Summary of O$_3$ initiated oxidation experimental conditions

<table>
<thead>
<tr>
<th>experiment number</th>
<th>hydroxy nitrate isomer</th>
<th>O$_3$ (ppbv)</th>
<th>phenol (ppm)</th>
<th>k$_{O_3}$ (300K) cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$trans$-$\delta$-1,4</td>
<td>23.7</td>
<td>350</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>$trans$-$\delta$-1,4</td>
<td>14.3</td>
<td>1600</td>
<td>NA$^a$</td>
</tr>
<tr>
<td>3</td>
<td>$\beta$-4,3</td>
<td>10.0</td>
<td>1000</td>
<td>2.6</td>
</tr>
<tr>
<td>4</td>
<td>cis-$\delta$-1,4</td>
<td>11.2</td>
<td>3300</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>$trans$-$\delta$-1,4</td>
<td>11.1</td>
<td>3000</td>
<td>0.9</td>
</tr>
<tr>
<td>6</td>
<td>MBO$^c$</td>
<td>36</td>
<td>900</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$^a$. No phenol added.
$^b$. Upper and lower limit, see discussion.
$^c$. 2-methylbut-3-ene-2-ol.
Table 2.4 OH reaction rate constants (300K, cm$^3$ molecule$^{-1}$ s$^{-1}$) at 95% confidence

<table>
<thead>
<tr>
<th>nitrate isomer</th>
<th>this work$^a$</th>
<th>Paulot et al.$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-$\delta$-1,4</td>
<td>$(1.06\pm0.16)\times10^{-10}$</td>
<td>$9.5\times10^{-11}$</td>
</tr>
<tr>
<td>cis-$\delta$-1,4</td>
<td>$(1.10\pm0.17)\times10^{-10}$</td>
<td>$9.5\times10^{-11}$</td>
</tr>
<tr>
<td>$\beta$-4,3</td>
<td>$(4.24\pm0.65)\times10^{-11}$</td>
<td>$1.9\times10^{-11}$</td>
</tr>
</tbody>
</table>

$^a$ Extra digit preserved to reduce rounding error.  
$^b$ Ref.$^{31}$
Table 2.5 Relative CF$_3$O$^-$ CIMS sensitivity

<table>
<thead>
<tr>
<th></th>
<th>β-4,3</th>
<th>cis-δ-1,4</th>
<th>trans-δ-1,4</th>
<th>ethanal propyl nitrate</th>
<th>hydroxy propyl nitrate$^a$</th>
<th>hydroxy propyl nitrate$^b$</th>
<th>MVKN$^c$</th>
<th>MVKN$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.09±0.12</td>
<td>1.00±0.06</td>
<td>1</td>
<td>1.05±0.13</td>
<td>1.50±0.04</td>
<td>1.50±0.11</td>
<td>0.90±0.09</td>
<td>0.82±0.10</td>
</tr>
</tbody>
</table>

$a$. 2-Nitrooxy-1-propanol.
$b$. 1-Nitrooxy-2-propanol.
$c$. 3-Hydroxy-4-nitrooxy-2-butanone.
$d$. 4-Hydroxy-3-nitrooxy-2-butanone.
Table 2.6 Molar yield of major OH oxidation products

<table>
<thead>
<tr>
<th>nitrate isomer</th>
<th>ethanal nitrate (m/z = 190)</th>
<th>hydroxy acetone (m/z = 159)</th>
<th>MVKN/ MVKN’ (m/z = 234)</th>
<th>di-nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-δ-1,4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>high NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>0.43±0.06</td>
<td>0.55±0.11</td>
<td>0.16±0.02</td>
<td>0.04&lt;sup&gt;a&lt;/sup&gt;/0.29&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>low NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>0.23±0.03</td>
<td>0.34±0.07</td>
<td>0.19±0.03</td>
<td></td>
</tr>
<tr>
<td>cis-δ-1,4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>high NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>0.36±0.05</td>
<td>0.50±0.10</td>
<td>0.11±0.02</td>
<td>0.03&lt;sup&gt;a&lt;/sup&gt;/0.39&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>β-4,3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>high NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>0.10&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.72±0.11</td>
<td>0.18&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> CIMS signal, including contributions from m/z=311, 291 and 245. Assuming same sensitivity as the starting hydroxy nitrate.

<sup>b</sup> Estimated using carbon balance, see text.

<sup>c</sup> No initial NO.

<sup>d</sup> Corrected for propene oxidation, see discussion.
Table 2.7 O₃ reaction Rate constants (300K, cm³ molecule⁻¹ s⁻¹), at 95% confidence except for β-4,3 isomer

<table>
<thead>
<tr>
<th>compound</th>
<th>this work</th>
<th>previous study</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-δ-1,4 nitrate</td>
<td>$(2.73\pm0.46)\times10^{-17}$</td>
<td>$5.3\times10^{-17}$ a</td>
</tr>
<tr>
<td>cis-δ-1,4 nitrate</td>
<td>$(2.94\pm0.50)\times10^{-17}$</td>
<td>$5.3\times10^{-17}$ a</td>
</tr>
<tr>
<td>β-4,3 nitrate</td>
<td>$(2.6-5)\times10^{-19}$ b</td>
<td></td>
</tr>
<tr>
<td>MBOc</td>
<td>$(7.46\pm1.48)\times10^{-18}$</td>
<td>$(8.3\pm1.0)\times10^{-18}$ d</td>
</tr>
</tbody>
</table>

a. Lockwood et al.48
b. Low limit assuming 100% molar yield of MVKN (m/z = 234), high limit assuming all m/z = 232 decay due to O₃ reaction.
c. 2-methylbut-3-ene-2-ol
d. Klawatsch et al.69
Table 2.8 Primary carbonyl yield from O₃ reaction with respective nitrate isomers

<table>
<thead>
<tr>
<th>nitrate isomer</th>
<th>ethanal nitrate (m/z = 190)</th>
<th>hydroxy acetone (m/z = 159)</th>
<th>MVKN (m/z = 234)</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-δ-1,4</td>
<td>0.50±0.08</td>
<td>0.30±0.06</td>
<td></td>
</tr>
<tr>
<td>cis-δ-1,4</td>
<td>0.55±0.08</td>
<td>0.58±0.12</td>
<td></td>
</tr>
<tr>
<td>β-4,3</td>
<td></td>
<td></td>
<td>0.50ᵃ/1.0ᵇ</td>
</tr>
</tbody>
</table>

ᵃ. Not corrected for wall loss.
ᵇ. Assuming 100% MVKN yield, giving wall loss time constant of 35 hours.
Table 2.9 OH yield from O₃ reaction

<table>
<thead>
<tr>
<th>exp. number</th>
<th>isomer (ppbv)</th>
<th>O₃ ppbv</th>
<th>phenol ppmv</th>
<th>( \frac{d\text{phenol}}{d\text{OH}}^a )</th>
<th>( \frac{d\text{nitrato}}{d\text{O}_3^b} )</th>
<th>OH yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>trans-δ (23.7)</td>
<td>350</td>
<td>2.5</td>
<td>1.83</td>
<td>1.06</td>
<td>0.23</td>
</tr>
<tr>
<td>2</td>
<td>trans-δ (14.3)</td>
<td>1600</td>
<td>N/A</td>
<td>N/A</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>cis-δ (11.2)</td>
<td>3300</td>
<td>1.5</td>
<td>2.76</td>
<td>1.08</td>
<td>0.48</td>
</tr>
<tr>
<td>5</td>
<td>trans-δ (11.1)</td>
<td>3000</td>
<td>0.9</td>
<td>3.00</td>
<td>1.13</td>
<td>0.17</td>
</tr>
<tr>
<td>6</td>
<td>MBO (36)</td>
<td>900</td>
<td>1.8</td>
<td>2.84</td>
<td>1.11</td>
<td>0.11</td>
</tr>
</tbody>
</table>

* a. Number of phenol reacted per OH formed.
* b. Total number of hydroxy nitrate consumed per O₃ reacted, including secondary reaction due to OH.
Table 2.10 Summary of revised rate constants (cm$^3$ molecule$^{-1}$ s$^{-1}$)

<table>
<thead>
<tr>
<th>nitrate isomer$^a$</th>
<th>$k_{OH}$</th>
<th>$k_{O3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$-1,4 (E &amp; Z)</td>
<td>$1.1\times10^{-10}$$^b$</td>
<td>$2.7\times10^{-17}$ (E)$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.9\times10^{-17}$ (Z)$^b$</td>
</tr>
<tr>
<td>$\delta$-4,1 (E &amp; Z)</td>
<td>$1.1\times10^{-10}$</td>
<td>$2.8\times10^{-17}$</td>
</tr>
<tr>
<td>$\beta$-1,2</td>
<td>$2.1\times10^{-11}$</td>
<td>$2.8\times10^{-19}$</td>
</tr>
<tr>
<td>$\beta$-2,1</td>
<td>$3.4\times10^{-11}$$^c$</td>
<td>$2.8\times10^{-19}$</td>
</tr>
<tr>
<td>$\beta$-3,4</td>
<td>$6.6\times10^{-11}$$^c$</td>
<td>$5\times10^{-19}$</td>
</tr>
<tr>
<td>$\beta$-4,3</td>
<td>$4.2\times10^{-11}$$^b$</td>
<td>$5\times10^{-19}$$^b$</td>
</tr>
<tr>
<td>$\langle k \rangle$</td>
<td>$7.9\times10^{-11}$</td>
<td>$1.7\times10^{-17}$</td>
</tr>
</tbody>
</table>

$a$. Naming consistent with Table 2.1.

$b$. This study

c. Paulot et al.$^{31}$
### Table 2.11 Condensed reaction recommendations

<table>
<thead>
<tr>
<th>Reactions</th>
<th>k (298K)</th>
<th>$A \times 10^{12}$</th>
<th>B (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ( \text{ISOPN}_5 + \text{OH} \rightarrow \text{ISOPNOO}_5 )</td>
<td>1.1 $\times 10^{-10}$</td>
<td>12</td>
<td>-652$^a$</td>
</tr>
<tr>
<td>2 ( \text{ISOPN}<em>\beta + \text{OH} \rightarrow \text{ISOPNOO}</em>\beta )</td>
<td>2.9 $\times 10^{-11}$</td>
<td>2.4</td>
<td>-745$^a$</td>
</tr>
<tr>
<td>3 ( \text{ISOPNOO}_5 + 1.06 \text{NO} \rightarrow 0.84 \text{NO}_2 + 0.65 \text{HO}_2 + 0.29 \text{DHDN} + 0.08 \text{MVKN} + 0.02 \text{MACRN} + 0.32 \text{PROPNN} + 0.22 \text{ETHLN} + 0.29 \text{HACET} + 0.32 \text{GLYC} + 0.06 \text{HCOOH} + 0.16 \text{HCHO} )</td>
<td>8.1 $\times 10^{-12}$</td>
<td>2.4</td>
<td>-360$^c$</td>
</tr>
<tr>
<td>4 ( \text{ISOPNOO}_\beta + \text{NO} \rightarrow 0.88 \text{NO}_2 + 0.69 \text{HO}_2 + 0.21 \text{DHDN} + 0.26 \text{MVKN} + 0.44 \text{MACRN} + 0.09 \text{HACET} + 0.09 \text{GLYC} + 0.69 \text{HCHO} )</td>
<td>8.1 $\times 10^{-12}$</td>
<td>2.4</td>
<td>-360$^c$</td>
</tr>
<tr>
<td>5 ( \text{ISOPNOO}_5 + \text{HO}_2 \rightarrow 0.5 \text{HO}_2 + 0.5 \text{OH} + 0.5 \text{ROOH} + 0.06 \text{MVKN} + 0.01 \text{MACRN} + 0.23 \text{PROPNN} + 0.2 \text{ETHLN} + 0.2 \text{HACET} + 0.23 \text{GLYC} + 0.07 \text{HCHO} )</td>
<td>2.2 $\times 10^{-11}$</td>
<td>0.087</td>
<td>-1650$^c$</td>
</tr>
<tr>
<td>6 ( \text{ISOPNOO}_\beta + \text{HO}_2 \rightarrow 0.06 \text{NO}_2 + 0.44 \text{HO}_2 + 0.5 \text{OH} + 0.5 \text{ROOH} + 0.16 \text{MVKN} + 0.28 \text{MACRN} + 0.06 \text{HACET} + 0.06 \text{GLYC} + 0.44 \text{HCHO} )</td>
<td>2.2 $\times 10^{-11}$</td>
<td>0.087</td>
<td>-1650$^c$</td>
</tr>
<tr>
<td>7 ( \text{ISOPN}_5 + \text{O}_3 \rightarrow 0.06 \text{NO}_2 + 0.37 \text{OH} + 0.24 \text{PROPNN} + 0.26 \text{ETHLN} + 0.26 \text{HACET} + 0.24 \text{GLYC} + 0.63 \text{CO}_2 + 0.24 \text{MEOH} + 0.09 \text{ETOH} + 0.2 \text{METHN} + 0.1 \text{ETHN} + 0.06 \text{GLYX} + 0.16 \text{OHACET} + 0.14 \text{PROPNNOOH} )</td>
<td>2.9 $\times 10^{-17}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 ( \text{ISOPN}_\beta + \text{O}_3 \rightarrow 0.05 \text{HO}_2 + 0.05 \text{OH} + 0.11 \text{MVKN} + 0.32 \text{MACRN} + 0.16 \text{HCOOH} + 0.62 \text{HCHO} + 0.36 \text{CO}_2 + 0.21 \text{CO} + 0.06 \text{C4NACID} + 0.36 \text{HPROPN} + 0.10 \text{MVKNOOH} )</td>
<td>3.7 $\times 10^{-19}$</td>
<td></td>
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</tbody>
</table>

**Notes:**
- $^a$ Cometto et al.\textsuperscript{170}
- $^b$ Paulot et al.\textsuperscript{31}
- $^c$ Orlando and Tyndall\textsuperscript{62}
- $^d$ Atkinson et al.\textsuperscript{56}

Abbreviations followed Paulot et al. (2009). Isomers of MVKN and MACRN are not distinguished. Additionally: DHDN = C5 di-hydroxy di-nitrate; ROOH = C5 hydroperoxide; R=O = C5 hydroxy di-nitrooxy ketone/aldehyde; METHN = methyl nitrate; ETHN = ethyl nitrate; OHACET = HACET with one additional oxygenated (-OH or =O) group; PROPNN OOH= PROPNN with one additional hydroperoxide group; C4NACID = C4 hydroxy nitrooxy carboxylic acid; HPROPNN = hydroxy propyl nitrate; MVKNOOH = MVKN with one additional hydroperoxide group.
Table 2.12 Important parameters under atmospheric oxidation

<table>
<thead>
<tr>
<th>nitrate isomer</th>
<th>relative importance&lt;sup&gt;a&lt;/sup&gt;</th>
<th>oxidation lifetime</th>
<th>dry dep. &lt;sup&gt;τ&lt;/sup&gt;</th>
<th>NO&lt;sub&gt;x&lt;/sub&gt; recycling</th>
<th>&lt;sup&gt;OH&lt;/sup&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>&lt;sup&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;/sup&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-δ-1,4</td>
<td>38.3%</td>
<td>2.8 hr</td>
<td>10.3 hr</td>
<td>12 min&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-17%</td>
<td>&lt;25%</td>
</tr>
<tr>
<td>cis-δ-1,4</td>
<td>24.4%</td>
<td>2.5 hr</td>
<td>9.6 hr</td>
<td>-6.3 hr&lt;sup&gt;e&lt;/sup&gt;</td>
<td>8 hr</td>
<td>-25%</td>
</tr>
<tr>
<td>β-4,3</td>
<td>19.7%</td>
<td>6.5 hr</td>
<td>1000 hr</td>
<td>2.7 hr&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-8%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4 hr&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Relative yield among all first generation isoprene hydroxy nitrates.
<sup>b</sup> Using di-nitrate yield of 18% to 39%. See discussion.
<sup>c</sup> High limit, by assuming unaccounted nitrates are released as NO<sub>x</sub>.  
<sup>d</sup> Kerdouci et al. 73
<sup>e</sup> Pfrang et al. 68
<sup>f</sup> Using V<sub>dep</sub> = 2.7 cm/s and boundary layer height of 800 m. 169
Figure 2.1
Typical OH oxidation experiment showing decay of organic nitrate and propene. The 2 vertical lines span the region when UV lights were on. The cause of the low point in GC-FID around 1500 seconds is unclear. Increase of O$_3$ concentration during this period is caused by photolysis of NO$_2$ formed from the oxidation reaction.
**Figure 2.2**
Concentration log-log plot for estimating the OH reaction rate of each hydroxy nitrate isomer relative to the rate of propene. The more reactive δ-hydroxy nitrate isomers have steeper slopes than the β isomer.
Figure 2.3
Direct comparison of parallel chromatograms obtained with TD-LIF and CIMS running under GC mode, after an OH oxidation experiment on cis-δ-1,4 hydroxy nitrate (m/z = 232). The nitrate containing products has matching peaks from both instruments, in this case the hydroxy propyl nitrate (m/z = 206) from oxidation of propene and 3-hydroxy-4-nitrooxy-2-butanone (abbreviated MVKN', m/z = 234) from the δ hydroxy nitrate.
Figure 2.4
Concentration profile of reactant and products from an O₃ oxidation experiment. Concurrent increase of hydroxy acetone (m/z = 159) and ethanal nitrate (m/z = 190) is consistent with them being the primary carbonyls of the ozonolysis reaction.
Figure 2.5
Proposed reaction pathways for OH + trans-δ-1,4 hydroxy nitrate reaction. The cis-δ-1,4 hydroxy nitrate is expected to follow the same pathway. Bracketed species are detected at the denoted m/z, using CF₃O⁻ CIMS.
Figure 2.6
Proposed reaction pathway for OH + β-4,3 hydroxy nitrate. Bracketed species are detected at the denoted m/z, using CF$_3$O$^-$ CIMS.
Figure 2.7
Proposed reaction mechanism for O₃ + trans-δ-1,4 hydroxy nitrate reaction. Bracketed species are detected at the denoted m/z, with CF₃O⁻ CIMS.
Figure 2.8
Stack plot of steady state δ-hydroxy nitrate (yellow region) and β-hydroxy nitrate (blue region) concentration from a box model simulation driven by a periodic 24-hour isoprene emission and photochemistry profile. Solid region represent results from OH and O₃ reaction rate constant derived from this and recent studies³¹. The vertically hatched area is the result of parameterizations used in recent model simulations¹⁹, with a much faster O₃ + isoprene nitrate reaction rate.
Chapter 3

Observation of rates and products in the reaction of NO$_3$ with submicron squalane and squalene aerosol

Abstract

The reactive uptake coefficient, $\gamma$, for nitrate radical, NO$_3$, on ~100 nm diameter squalane and squalene aerosol was measured (1 atm pressure of N$_2$ and 293K). For squalane, a branched alkane, $\gamma_{NO3}$ of $2.8\times10^{-3}$ was estimated. For squalene which contains 6 double bonds, $\gamma_{NO3}$ was found to be a function of degree of oxidation with an initial value of 0.18±0.03 on fresh particles increasing to 0.82±0.11 on average of over 3 NO$_3$ reactions per squalene molecule in the aerosol. Synchrotron VUV-ionization aerosol mass spectrometry was used to detect the particle phase oxidation products that include as many as 3 NO$_3$ subunits added to the squalene backbone. The fraction of squalene remaining in the aerosol follows first order kinetics under oxidation, even at very high oxidation equivalents, which suggests that the matrix remains a liquid upon oxidation. Our calculation indicates a much shorter chemical lifetime for squalene-like particle with respect to NO$_3$ than its atmospheric lifetime to deposition or wet removal.
3.1. Introduction

NO$_3$ is one of the major oxidants in the atmosphere and its reaction with gas phase alkenes has been shown to generate organic nitrate compounds$^{75}$ and aerosol$^{28, 44, 76, 77}$ with high yields. Recent studies also reveal that heterogeneous reactions of aerosol with NO$_3$ may be important to aerosol properties$^{78-80}$. Processes that might occur include C-C bond scission of aerosol-bound molecules resulting in loss of aerosol mass or the addition of oxidized functional groups to molecules within the aerosol causing a reduction in aerosol vapor pressure. For reactive semivolatile compounds, oxidation may lead to irreversible partitioning onto the aerosol surface hence aerosol growth$^{81}$. As a result of these processes, heterogeneous NO$_3$ reactions may have important effects on the aging of atmospheric organic aerosol. Relatively little is known about NO$_3$ reactions on aerosol surface, especially for particles with significant organic fraction. A field study by Bertram et al., 2009$^{82}$ indicated that for N$_2$O$_5$ reactive uptake on aqueous aerosol, the existence of organic matter has an effect on the N$_2$O$_5$ reactivity that depends on the aerosol hygroscopicity. The chemistry of NO$_3$ and N$_2$O$_5$ are quite different and the presence of hydrophobic organics could possibly favor the reaction of NO$_3$.

In contrast to NO$_3$, the oxidation of condensed-phase organics by hydroxyl radical (OH) has been studied extensively$^{6, 83-89}$. For example, reactive uptake coefficients have been measured on aliphatic and aromatic surfaces with values generally above 0.2, up to 2 for the case of bis(2-ethylhexyl) sebacate$^{86}$. Parallel detection of condensed and gas phase products suggests the formation of oxygenated organic compounds. Shrinking of aerosol particle size or decay of the organic layer on a substrate during the process of OH oxidation indicates the importance of C-C bond scission and the re-volatilization of organic matter due to photochemical aging and may be an important control over aerosol lifetimes. A recent chamber study on aging of α-pinene SOA by Tritscher et al.$^{89}$ demonstrated that OH oxidation subsequent to ozonolysis increases the SOA mass and also the SOA volatility as evidenced by mass loss measured with a thermodenuder at 70ºC. Wilson and coworkers$^{90, 91}$ measured oxidation of saturated organic aerosols due to oxidation with OH. They were able to describe the oxidation product distribution using a statistical model assuming constant reaction probability for hydrogen abstraction reactions and by applying an empirical fragmentation probability as a function of molecule oxygen to carbon (O/C) ratio. With this parameterization, fragmentation of organic materials leads to volatilization of aerosol constituents and aerosol shrinkage.

As NO$_3$ is an important oxidant at night, it is imperative to understand the similarities and differences between aerosol oxidation by NO$_3$ and OH. Here we describe an atmospheric pressure flow tube experiment observing oxidation of a multi-unsaturated hydrocarbon (squalene) and its saturated analog squalane by NO$_3$, shedding new light on the NO$_3$ initiated aerosol oxidation processes. We calculate uptake coefficients for NO$_3$, report aerosol phase products observed by thermal desorption VUV ionization mass spectrometry, discuss the diffusion rates within the aerosol and describe a molecular oxidation mechanism.

3.2. Experimental methods
A number of research groups have measured the heterogeneous uptake coefficient of $\text{NO}_3/\text{N}_2\text{O}_5$ to organic material using several different techniques\(^{74, 92-96}\). To estimate the extent to which gas phase oxidant crosses the phase boundary to initiate a reaction with condensed phase organics, one may choose to monitor the decay of condensed phase reactants or the loss of gas phase oxidant. Monitoring the gas phase oxidant decay is more straightforward in terms of the definition of reactive uptake coefficient, but requires correction due to wall effects and possibly diffusion\(^{74, 92}\). Condensed phase reactants (organics) are generally easier to measure, but for cases with highly reactive species, the measured loss can be larger than the number initiated by gas phase oxidants because of secondary reactions, leading to an overestimation of the uptake coefficient. Also, the achievable oxidant to reactant ratio may be important for investigation of multi-generation chemistry. For the coated wall flow tube technique, the fraction of oxidation is usually small during the course of experiments due to the relatively large amount of condensed phase material, hence the measured uptake coefficient corresponds mostly closely to fresh aerosol with a similar composition. To achieve a higher degree of oxidation, one may freeze the wall coating or use monolayers to limit the accessible amount of material. Alternatively, the aerosol flow tube method has inherently larger surface to volume ratio of the condensed phase and allows design of experiments with high ratios of oxidation to reactant.

Here we observe gas phase oxidant decay and condensed phase composition simultaneously. The experiment (Figure 3.1) was performed at the Chemical Dynamics Beam Line (9.0.2) at the Advanced Light Source, Lawrence Berkeley National Laboratory. Aerosol of pure squalene and squalane was generated using a nucleator, as described by Smith et al.\(^{90}\). Briefly, a pyrex tube containing either squalane or squalene was heated in a tube furnace at $135^\circ\text{C}$ with 350 sccm $\text{N}_2$ carrier flow. Vapors of the organic compound carried by $\text{N}_2$ become supersaturated upon leaving the heated region and nucleation occurs, yielding single or multimode, log-normal particle size distribution. Particle distributions were observed using a scanning mobility particle sizer (SMPS, 3080 Classifier, 3081 DMA; TSI Inc.) and condensation particle counter (CPC, 3025; TSI Inc.). The sheath flow of 3081 DMA was set to 3 liter per minute (lpm) and aerosol flow at 0.3 lpm with scanning direction from fine toward coarse particles spanning a range of 15 nm to 673 nm. The scan time and retrace time was 120 and 15 seconds, respectively. Care was taken acquiring data so that during an SMPS scan, the system was at a steady condition. The estimated error for derived properties (e.g. surface concentration) from repeated scans are around 7% (1σ). The aerosol stream was then diluted with a split-flow system that maintained the size distribution. All flow through the experimental apparatus were regulated using MKS mass flow controllers. After dilution, the particle flow was joined with a mixture of $\text{N}_2\text{O}_5/\text{NO}_2$ in $\text{N}_2$ before entering the flow tube. The quartz flow tube with $\sim7.5$ cm inner diameter was mounted vertically with its injection port at the lower end and the outlet at the top. All experiments were at 293K. $\text{NO}_3$ was generated by thermal decomposition of $\text{N}_2\text{O}_5$. The synthesis of $\text{N}_2\text{O}_5$ followed the general procedure of Davidson et al.\(^{97}\) but instead of reacting NO with $\text{O}_3$, which involves oxidizing NO to NO$_2$ as a first step, 1% NO$_2$ in N$_2$ was reacted directly with excess $\text{O}_3$ in O$_2$ in a small glass manifold providing sufficient residence time for reaction to proceed to completion. The reaction vessel was kept dry to prevent reaction between $\text{N}_2\text{O}_5$ and
water. The synthesized N₂O₅ was then separated from the gas stream in a glass trap immersed in a dry ice/acetone bath at −70°C. It is important not to use a liquid N₂ trap as residual O₃ is explosive as a liquid. Collected N₂O₅ was observed to be needle shaped white crystals. During experiments, 200 sccm dry N₂ carried ppm level of N₂O₅ from the trap into the flow tube. The trap temperature was maintained at −70°C where vapor pressure of N₂O₅ was about 2 ppm.

At the Chemical Dynamics Beamline, a soft-ionizing aerosol mass spectrometer (VUV-AMS) with tunable VUV photo ionization was used to characterize the particle composition. A detailed description of this AMS is presented in Mysak et al.⁹⁸. Briefly, a time-of-flight mass spectrometer was coupled to a particle-concentrating aerodynamic lens which focuses particles to a beam and reduces the gas phase molecular concentration by manipulating the fluid streamlines with pinhole plates described in Liu et al.⁹⁹.¹⁰⁰ The aerodynamic lens was optimized to transmit ~1μm particles and had a flow of ~10 sccm. The transmitted particles impinged on a heated copper block (T=140°C) where non-refractory materials became vaporized and ionized by VUV radiation from undulator U10. Ions generated were repelled by an underside electrode and focused onto an accumulation region between pulse plates and detected using time of flight mass spectrometry. Ion counting was collected on a multi-channel scalar with bin width of 4 ns. All mass spectra presented were collected with accumulation of 100,000 spectra.

To quantify the gas phase concentration of N₂O₅ and indirectly infer the NO₃ concentration in the flow tube, a 3-channel thermal dissociation laser induced fluorescence instrument was used to provide on-line detection of initial NO₂, final NO₂ and final N₂O₅ concentrations.⁵⁴,¹⁰¹ Briefly, NO₂ was detected using excitation at 408 nm from a diode laser and fluorescence detection beyond 700 nm using a red sensitive PMT. N₂O₅ was quantitatively converted to NO₂ with thermal dissociation followed by LIF. The thermal dissociation oven consists of a heated quartz tube maintained at 100°C to completely dissociate N₂O₅ into NO₂ and NO₃ within the residence time of ~0.1 second. Excess NO was added to convert NO₃ to NO₂ with the result that we observed 3 NO₂ for each N₂O₅ dissociated.

Reactive uptake was monitored by measuring the difference in N₂O₅ concentration before and after the flow tube section. Initial N₂O₅ concentration was periodically monitored and found to be stable. Since NO₃ and N₂O₅ interconvert rapidly compared with the residence time of the flow tube and the equilibrium ratio of NO₃ to N₂O₅ is approximately 3×10⁻³, loss of NO₃ is reflected in the loss of N₂O₅. For NO₃ oxidation experiments, wall loss of NO₃ is always significant. To keep the wall loss kinetics as stable as possible, we maintained the same flow rate for all lines containing NO₃, including the N₂O₅ trap flow and the flow through the tube reactor. The typical lifetime against wall loss for NO₃/N₂O₅ was 200 seconds. In the presence of aerosol surface, the wall loss fraction was in the range of 21% to 41% depending on aerosol loading conditions. Particle concentrations were varied by splitting and diluting the raw particle flow while maintaining a constant total flow before joint with the N₂O₅ flow, hence the residence time in the flow tube reactor was fixed at 167 sec in all experiments. Care was taken to ensure that the size distribution was preserved for all dilution conditions. NO₃ self-reaction was negligible.
compared with wall-loss and aerosol reactive loss. The reactive uptake coefficient was calculated from the N$_2$O$_5$ measurement using equation 1 and 2.

$$\frac{[N_2O_5]}{[N_2O_5]_0} = e^{-k\sigma \tau} \quad (1)$$

$$k = \frac{f \gamma \langle v \rangle}{4} \quad (2)$$

Equation 1 relates the effective second-order rate constant $k$ (cm/s) to the observed loss of N$_2$O$_5$ through the flow tube with $\sigma$ representing the aerosol surface concentration (unit: cm$^2$/cm$^3$), $\tau$ the reaction time and $[N_2O_5]_0$, $[N_2O_5]$ the concentration of N$_2$O$_5$ before and after the flow tube reactor, respectively. $\tau$ was fixed at 167 sec and $\sigma$ was calculated from the size distribution measured with the SMPS. A linear plot of the natural log of $([N_2O_5]/[N_2O_5]_0)$ versus $\sigma$ gives the product $(k \tau)$ as its slope. This assumes the wall loss kinetics remain first order and invariant under different aerosol loading condition. For slowly reacting oxidants such as NO$_2$, $\gamma$ can be a function of particle volume as the total reaction rate is dominated by sites within the interior of the aerosol, for OH or NO$_3$ oxidation, the high reactivity of the oxidants results almost exclusively in surface reactions. The second-order $k$ makes an implicit connection between the N$_2$O$_5$ concentration in free space and NO$_3$ concentration near the aerosol surface. We calculate NO$_3$ using the N$_2$O$_5$/NO$_3$ equilibrium and the reaction kinetics to give $\gamma$ value based on a 2-layer resistance model described in Appendix B1. The final result is shown as equation 2 where $f$ is the equilibrium ratio of NO$_3$ to N$_2$O$_5$ and $\langle v \rangle$ the mean molecular speed of N$_2$O$_5$.

### 3.3. Results

Two sets of experiments were performed: the heterogeneous reactions of NO$_3$(g) + squalane(p) and NO$_3$(g) + squalene(p), both in pure nitrogen. Note that the experiments were in the absence of oxygen, difference exists regarding extension to atmospheric oxidation, which will be discussed in a later section. Nevertheless, these measurements allow direct comparison of organic systems with similar structure but different reactivity and mechanism as a result of carbon double bonds. The OH(g) + squalane(p) reaction has been studied extensively by Wilson and coworkers$^{90, 102, 103}$, providing a useful point of comparison while NO$_3$ oxidation involving other similar saturated and unsaturated organics has been investigated by Gross et al.$^{92}$, Xiao et al.$^{93}$, Docherty and Ziemann$^{94}$, and Zhao et al.$^{74}$.

**Squalane + NO$_3$**

For squalane + NO$_3$, the particle size distribution was a single mode with average diameter of 103 nm. Figure 3.2 shows the natural log of the ratio of reacted to initial N$_2$O$_5$ versus squalane aerosol surface concentration. Using equation 2, we derive $\gamma$ for the combined reaction of N$_2$O$_5$ and NO$_3$ of $(7.8\pm0.2)\times10^{-3}$ if all the reaction flux is through direct reaction of NO$_3$ (NO$_3$ + aerosol) and $(6.2\pm0.9)\times10^{-5}$ if the reaction of N$_2$O$_5$ (N$_2$O$_5$ + aerosol) dominates. These values are upper limits since the reaction likely occurs in both pathways. We estimated $f$, the NO$_3$ to N$_2$O$_5$
ratio used in equation 2 using the recommended rates
c with an estimated relative uncertainty of 20% and our NO2 measurement. This additional uncertainty is reflected in the value shown above for the NO3 uptake coefficient. It is noted that for estimating the N2O5 uptake coefficient, we use \( f = 1 \) in equation 2 since N2O5 concentration is directly measured in our experiment. Differentiating oxidation by NO3 and N2O5 was not possible in our experiment. Mass spectra of the aerosol phase were collected but no product mass fragments were observed possibly due to the small fraction of squalane reacted.

**Squalene + NO3**

The reaction of squalene with NO3 was studied using the same procedures. The ratio of reacted to initial N2O5 vs. squalene aerosol surface concentration is shown in Figure 3.3 for aerosol loading ranging from 132 µg/m³ to 2504 µg/m³. Each series represents data from one single day’s experiment. The vertical offset between the two data sets at projected zero surface area is due to difference in wall conditioning. Tube oven temperature of 135ºC and 140ºC were used for low loading and high loading experiments, giving larger and smaller particle distributions, respectively (Figure 3.4). The cause of the multi-mode behavior is unclear.

We solve for the uptake coefficient \( \gamma \) using equation 2. As apparent from Figure 3.3, the N2O5 loss versus aerosol surface area cannot be explained by a single linear fit. Instead, there appears to be several distinct linear relations at different ranges of aerosol loading. The change of slope within the high loading range indicates that the result is not due to day-to-day variation in experimental conditions. We find it useful to define an “oxidation ratio” as the ratio of net NO3 reacted to the total squalene in aerosol phase. Net NO3 reacted is calculated from total loss of N2O5 in the flow tube reactor less the wall-loss contribution. Total aerosol-bound squalene is estimated using SMPS measurements and the density of squalene. The oxidation ratio describes the average number of reactions each squalene molecule has undergone with NO3. For a fixed N2O5 concentration, increasing the aerosol mass provides a larger quantity of squalene available to react with nitrate, resulting in a lower oxidation ratio. Conversely, reducing the aerosol loading increases the average number of NO3 attacks per squalene molecule, yielding higher oxidation ratio.

The oxidation ratio for the data shown in Figure 3.3 spans a range of 0.86 to 4.2. A single linear fit describes the low loading data set, corresponding to a \( \gamma \) of 0.82±0.11 assuming that the chemistry is due to NO3. At high loading, the data set was split into 2 segments at a surface concentration of 5.5×10⁻⁴ cm²/cm³ (oxidation ratio of ~1.4) with one linear fit applied to each. The resulting \( \gamma \) for an oxidation ratio from 0.86 to 1.4 is 0.18±0.03 and for an oxidation ratio from 1.4 to 2.5 is 0.48±0.06 (Table 3.1). Due to the much larger uptake coefficient of NO3 onto unsaturated hydrocarbons, the direct contribution of N2O5 reaction is considered minor (less than 10%).

We propose a mechanism for condensed phase reaction of NO3 and squalene in the absence of O2 (Figure 3.5) based on reaction products observed from the aerosol mass spectrum in which
boxed species are directly observed as marked in Figure 3.6 and 3.5b. Multiple isomers are expected for each illustrated pathway and thick arrows indicate the dominant reactions. In general the initial reaction involves addition of NO$_3$ radical to one of 6 double bonds followed by condensed phase alkyl radical reactions. The alkyl radical may lose or gain a hydrogen atom from its surrounding neighbors, or decompose to an epoxide and NO$_2$. The mechanism shown includes steps through the second NO$_3$ reaction. Note the possibility of reforming double bonds (species III), suggesting more than 6 addition reactions may occur if the reaction was allowed to proceed to completion. The aerosol mass spectrum of squalene shown in Figure 3.6 and 3.5b were obtained at 10.3 eV photon energy. We observed that higher photon energy yields larger ion signal, but also more fragmentation from parent ions. Energy scans were performed (7.4eV up to 10.8eV photon energy) and a compromise between overall signal strength and product fragmentation was made. The product peaks (also boxed species in Figure 3.5) reported here are based on the observation of parent ions. Major peaks with mass above the squalene parent ion (m/z = 410.4) are product series with m/z corresponding to addition of 1 to 3 NO$_3$ units as illustrated by the guide lines. The $^{13}$C isotopes for squalene and its oxidation products are marked with * and † for singly and doubly $^{13}$C substituted molecules ($^2$H contributions are minor). The relative intensities of isotopic peaks are consistent with the carbon chain length given the instrumental uncertainty. We also observe fragment ions generated by dissociative photoionization from each organic nitrate product arising from loss of NO$_2$ in the ionization process. For example, the m/z = 534 peak is identified as squalene with 2 nitrate groups attached (species IV and VII). Two major fragment ions can be identified centering at m/z = 488 and m/z = 442 corresponding to loss of one or two NO$_2$ subunits. Another interesting feature of the product mass spectrum is that the groupings of peaks appear to be structured. For the first nitrate product centered at m/z = 472 (squalene + NO$_3$) we see two peaks of roughly equal magnitude with relative mass of +1 and −1. Since direct addition of NO$_3$ to a double bond yields a radical species, it’s likely that hydrogen abstraction takes place soon after with the radical acting as either a donor or an acceptor of hydrogen from its neighbor (species I and III in Figure 3.5). Similar reasoning can be applied to the group centering at m/z = 534 using the structures at m/z = 472 as a starting point. NO$_3$ attack on the first generation products (species I + III) followed by hydrogen abstraction would give a triplet with intensity of 1:2:1 as is observed (Figure 3.6 species IV to VII). Higher oxidation products are also observed including squalene with 3 nitrate groups attached (squalene + 3NO$_3$ + H, m/z = 597.1) as well as fragments indicative of higher products (squalene + 3NO$_3$ + O + H, m/z = 613.7). For mass region beyond m/z = 650 (Figure 3.7), the assignment becomes more difficult due to reduction of sensitivity and the increase in mass uncertainty (±0.5 amu). However, we have tentatively assigned mass peaks corresponding to products that involve dimerization after initial NO$_3$ addition to the first squalene molecule, illustrated in Figure 3.5 as the pathway leading to species VIII. Since the dimer is initiated by NO$_3$ addition, we expect NO$_3$ group or its fragment to be present on the squalene dimer ion detected. Indeed, dominant peaks around m/z = 884 (unresolved) likely correspond to squalene dimer with one NO$_3$ group attached. Quantification of dimer formation channel is challenging due to fragmentation and low sensitivity.
Epoxide formation may also be inferred by noting that the pattern observed near m/z = 426 does not resemble that near m/z = 472. If peaks near m/z = 426 are fragmentation products of m/z = 472 the fragmentation patterns should be similar for all 3 peaks and the relative intensity of m/z = 425 to 428 should be similar to that of the 3 parent species. Excess ion intensity is observed at m/z = 426 which could be explained with direct formation of an epoxide (species II). Considering that the epoxide still has high degrees of unsaturation like the adducts and assuming similar NO3 reactivity and photoionization efficiency of epoxide as first generation organic nitrate products, the ratio between signals corresponding to the epoxide and the first squalene adduct (species I & III) is a measure for the branching ratio of epoxide formation from NO3 initiated squalene oxidation. We estimate the branching ratio for epoxide formation to be 8%. Skov et al.105 measured a similar, but slightly higher branching ratio (17.4%) for the gas phase reaction of NO3 with 2,3-dimethyl-2-butene (740 Torr air).

Concentration profiles of squalene, its first generation and second generation products as a function of oxidation ratios are shown in Figure 3.8 and 3.9. Quantification for aerosol-bound molecules is absolute only for squalene molecules due to the lack of pure standards for reaction products. However, the ionization conditions (i.e. photon energy and flux) remained constant throughout the experimental period and we assume the unknown calibration factor is constant. From oxidation ratios of 0.8 to 2.3, we observe a decrease in both squalene (Figure 3.8) and its first oxidation products at mass 471 & 473 (squalene + NO3, Figure 3.9). The second generation oxidation product at mass 534 (squalene + 2NO3) increases up to the oxidation ratio of 1.6 and then decreases. This transition in the squalene + 2NO3 product occurs at a similar oxidation ratio as the transition in γ from 0.18 to 0.48.

3.4. Discussion

Squalane

The measured total uptake on squalane aerosol was (6.2±0.9)×10⁻⁵ at 293K interpreted as pure N2O5 reaction. This value compares well with measurement performed on diethyl sebacate (DES) by Gross et al92. Using the reported values of NO3 and N2O5 specific γ’s, we calculate the apparent overall uptake by both processes interpreted as pure N2O5 reaction to be (7.1±0.7)×10⁻⁵ (298K), similar to our value of (6.2±0.9)×10⁻⁵ on squalane. Recently, Xiao and Bertram93 measured the NO3 specific reactive uptake coefficient on squalane and reported a value of γNO3 = 5.2×10⁻³. This is similar to our upper limit of 7.8×10⁻³. Using the value of 5.2×10⁻³ we calculate γN2O5 = 3.5×10⁻⁵, a value indicating about 50% of the reaction we observe as due to NO3 and 50% to N2O5 and similar to the N2O5 specific reactive uptake coefficient of 5.1×10⁻⁵ measured on DES92. No uptake was observed for NO2 on squalane aerosol giving an upper limit for γNO2 of 4.6×10⁻⁷.

Our main insight into possible reaction mechanism is from analysis of the NOx signal. Considering loss processes of NO3 in our flow tube, either formation of organic nitrate via addition or formation of HNO3 via hydrogen abstraction as typical with saturated hydrocarbons...
leads to a net loss of observable NO signal in the gas phase by our LIF instrument. If those are the major reaction pathways then since each NO$_3$ has N$_2$O$_5$ as its source, we will observe an increase in NO$_2$ equal to the N$_2$O$_5$ lost. However, a ratio ($\Delta$NO$_2$/\Delta$N$_2$O$_5$) of 2.4±0.7 was observed. We interpret this as observing a yield of 2 NO$_2$ per N$_2$O$_5$ removed with the implication that essentially every NO$_3$ is converted to NO$_2$ in the reaction and not to HNO$_3$. One possible mechanism explaining this result is a catalytic chain converting NO$_3$ to NO$_2$ as shown in equation 3 based on the mechanism of Biggs et al.$^{106}$ and Ray et al.$^{107}$.

\[
N_2O_5 \rightleftharpoons NO_2 + NO_3 \quad (3.1)
\]

\[
NO_3 + RH \rightarrow HNO_3 + R^\cdot \quad (3.2)
\]

\[
NO_3 + R^\cdot \rightarrow NO_2 + RO^\cdot \quad (3.3)
\]

\[
NO_3 + RO^\cdot \rightarrow NO_2 + RO_2^\cdot \quad (3.4a)
\]

\[
\rightarrow HNO_3 + R'CHO \quad (3.4b)
\]

\[
\rightarrow ROONO_2 \quad (3.4c)
\]

\[
NO_3 + RO_2^\cdot \rightarrow NO_2 + RO \cdot + O_2 \quad (3.5a)
\]

\[
\rightarrow CH_3CHO + HONO + O_2 \quad (3.5b)
\]

\[
\rightarrow CH_3CHO + NO_2 + HO_2^\cdot \quad (3.5c)
\]

Reaction 3.4a and 3.5a form a catalytic cycle for NO$_3$ conversion to NO$_2$ while 3.2 and 3.3 represent the initiation reactions. With the estimated specific branching ratio for reaction 3.5a of over 80%$^{106}$, the recycling efficiency is largely determined by the ratio of chain propagation (3.4a) to chain termination (3.4b + 3.4c, 3.5b + 3.5c) reactions. Reaction rates measured by Ray et al. and estimated by Biggs et al. suggest the branching for chain propagation to be more than 50% and may approach unity. For the squalane aerosol + NO$_3$ reaction, we estimate a branching ratio to chain propagation of 64% using a numeric model (Appendix B2) of the rates with parameters adjusted to fit the observed NO$_2$ concentration from experiments.

**Squalene**

The reactive uptake coefficient for squalene was measured to be a function of reaction extent ranging from 0.18±0.03 on fresh squalene aerosol to 0.82±0.11 for aerosols with an average of over 3 NO$_3$ reactions per squalene molecule. High reactivity of NO$_3$ toward double bonds dominates the NO$_3$/N$_2$O$_5$ loss onto aerosol surface and direct N$_2$O$_5$ reactions are estimated to be less than 10%. However, we have observed ions in the mass spectrum that correspond to direct N$_2$O$_5$ addition to double bond on the squalene backbone (m/z = 518, specie IX). This mass corresponds to the formation of an α-β-nitro-nitrate as suggested by Stevens and Emmons in 1957$^{108}$. This peak has the same temporal profile as the dominant first generation product at m/z = 471 (the first adduct, species III). Since we expect both species to have very similar subsequent reactivity toward NO$_3$ due to the number of remaining double bonds, the similarity in
concentration profile suggests similar source profile. Its low intensity (1.2%) compared with m/z = 471 indicates that formation of species IX is a minor product channel in initial NO₃ addition reactions.

Our measurement of \( \gamma \) for NO₃ + squalene is similar (\( \gamma = 0.18 \)) at a low oxidation ratio (<1.4) to measurements on related systems. For example, Gross et al.⁹² reported \( \gamma = 0.29 \) for NO₃ + linoleic acid at 298K. Zhao et al.⁷⁴ showed \( \gamma = 0.53 \) for linoleic acid with similar mean particle diameter conducted in pure N₂. Linoleic acid was chosen for comparison because of the presence of 2 non-conjugated double bonds, similar to squalene. The larger uptake coefficient in the other two measurements may be due to an additional contribution to the reactivity from unsaturated organic acids, or from secondary reactions. The degree of contribution from the extra carboxylic acid functional group on linoleic acid is unclear at the moment, although enhancement in ion signal giving deprotonated linoleic acid was observed by Zhao et al.⁷⁴. We estimate the degree of secondary reaction, such as pathways that lead to species VIII where a second squalene molecule is involved, by computing the NO₃ lost to aerosol phase versus the corresponding amount of squalene loss (Figure 3.10). Where there is incomplete consumption of squalene (low oxidation ratio), we find a slope of 1.5, indicating 1.5 squalene molecules are consumed per NO₃ attack. This suggests a chain propagation mechanism is active when squalene is in excess. Such secondary reaction will affect \( \gamma \) estimated from experiments measuring the time dependence of organic starting material concentrations. If the linoleic acid measurement by Zhao has similar chain propagation as we infer from our data, the reported \( \gamma \) of 0.53 would be approximately 1.5 times smaller, giving \( \gamma = 0.35 \). This value is closer to the one we measured (0.18) and to the 0.29 measured by Gross et al. Similar effects of radical chain propagation has also been observed in a recent flow tube study by Renbaum-Woff and Smith, 2012⁹⁶ when enhanced oleic acid loss was observed in an organic mixture aerosol (olive oil) containing squalene. The oleic acid loss in olive oil aerosol was ~2 time faster than in pure oleic acid aerosol of the same size (100 nm). The authors suggested that chain propagation may be more efficient in olive oil environment. We calculated the equivalent second-order loss rate (\( k_{eff} \), as defined in the paper by Renebaum-Woff and Smith) based on 126 nm particle size and obtained \( k_{eff} = 5.8 \times 10^{-13} \) cm³/s for pure and fresh squalene aerosol, larger than the reported value for oleic acid but smaller than the value of squalene component in the olive oil aerosol (\( k_{eff} = 4.0 \times 10^{-12} \) cm³/s).

The increase in uptake coefficient for NO₃ oxidation of multi-unsaturated molecules (NO₃ + squalene) has not been previously reported and is in contrast to some previous results where uptake rates decreased as reactions progress. For example, Xiao and Bertram⁹³ reported surface reactive uptake coefficients for solid-liquid binary mixture of methyl oleate in diethyl sebacate. Under room temperature as a homogeneous liquid, the uptake coefficient of the mixture was constant. At lower temperature (-5°C) when phase segregation occurs, they observed a \( \gamma \) of ~0.04 initially and less than 0.01 after 40 minutes of exposure to 1 to 6 ppb NO₃. The results were interpreted as implying that at room temperature the mobility of methyl oleate from the bulk was sufficient to replenish the surface reactivity while at low temperature less reactive products were trapped at the surface. Another surface aging example was reported by Knopf et al.¹⁰⁹ for O₃ oxidation of oleic acid (mono-unsaturated organic acid) mixed with either lauric acid or myristic
acid (both saturated organic acids). An increase in the uptake coefficient of O$_3$ was observed for solid-liquid condensed phase mixture of 65 wt% oleic acid in oleic acid/myristic acid solution at 298K prepared by either quenching the homogeneous solution to liquid N$_2$ temperature followed by thawing or cooling slowly to room temperature. The authors suggested that the change in uptake coefficient may be related to the natural relaxation of domains in the solid-liquid mixture or the relaxation from a non-equilibrium state to normal phase segregation. For squalene aerosol particles, there has been no clear indication of formation of solid phase during our reaction condition (discussed in section 4.3) and we attribute the increase of $\gamma$ to increased reactivity of higher-generation products.

**Fluidity of Squalene Aerosol**

Observations of squalene and its oxidation products in the aerosol phase provide information on the mobility of the condensed phase material in the absence of O$_2$. Figure 3.8 shows the decrease of squalene in the aerosol phase as a function of oxidation ratio. The linear behavior of ln([squalene]/[squalene]$_0$) indicates that the loss rate of squalene molecules to NO$_3$ only depends on the instantaneous concentration of squalene in the aerosol phase. As there is more than sufficient NO$_3$ to deplete squalene at the surface, it is required that the reactivity of squalene in the core of the particle or near the surface be similar on the time scale of the experiment. To satisfy such kinetic constraint, free radial movement of either reactant within the aerosol phase is necessary. Given the condensed phase self diffusion constant of squalene to be $\sim 6 \times 10^{-7}$ cm$^2$/s, for a droplet of 100 nm diameter the characteristic time of diffusional mixing between core and surface is in the order of 0.1 ms which is much shorter than our N$_2$O$_5$ decay time scale of $\sim 10$ sec. We would thus expect that all squalene molecules in the aerosol phase to have an equal probability of reacting with NO$_3$ by diffusion to the surface implying squalene matrix remained mobile throughout the reaction with a terminal diffusion constant larger than $10^{-12}$ cm$^2$/s at 293K.

The first order decay of squalene component in the aerosol phase appears to be consistent with the limiting case of a surface reaction and is similar to the conclusions of Hearn et al.$^{110}$ who invoked this mechanism as an explanation for the behavior of oleic acid reaction with O$_3$. It is implied in the functional form (Equation 3.7 in Hearn et al., 2005) that diffusion of oleic acid (or squalene) to the particle surface does not become rate limiting, an idea that is consistent with our conclusion that the aerosol remains a liquid. Perraud et al.$^{81}$ recently performed NO$_3$ aging experiments on $\alpha$-pinene derived SOA and suggested the SOA was so viscous that gas phase-condensed phase equilibrium could not be achieved at $\sim 1$ hour time scale. The contrast among these results suggests additional experiments are needed to assess the viscosity of ambient aerosol.

**3.5. Atmospheric implication**

Neglecting for the moment that our experiment does not include oxygen, we estimate the lifetime of organic particles of 126 nm diameter with matrix properties similar to squalene under a fixed ambient concentration of NO$_3$. The detailed equations used for numerical integration are
included in Appendix B3. Under 10 ppt NO$_3$ concentration the oxidation ratio as a function of exposure time is plotted in Figure 3.11. For the first hour of reaction, the oxidation ratio increases by approximately 0.7, while for the following hour the steeper slope (due to the increase of uptake coefficient) brings it to around 2.4, indicating that the particle would have reacted with more than twice as much of NO$_3$ as the number of molecules that makes up the condensed phase in 2 hours. The size-dependent lifetimes for particles with diameter of 10 nm, 126 nm and 1 µm to reach oxidation ratio of unity are 9.2 minutes, 1.2 hour and 10.4 hours, respectively. It is noted that we assume the curvature of the particle surface has minimal effect on NO$_3$ uptake so that $\gamma$ only depends on the internal variable of average oxidation ratio of the particulate matter. In other words, for squalene particles of different sizes, the initial uptake coefficient will always start from the same value ($\gamma=0.18$) for all particles. However, $\gamma$ will change at different rate due to the difference in surface to volume ratio under the same NO$_3$ exposure concentration. As a comparison, the lifetime of 126 nm squalene particle subjected to heterogeneous oxidation by $10^6$ 1/cm$^3$ OH and 20 ppb O$_3$ are calculated to be 5 days and 656 seconds, respectively. We used $\gamma_{\text{OH}} = 0.39$ reported by Waring et al., 2011$^{111}$ and assuming the same $\gamma_{\text{O}_3} = 8.8 \times 10^{-4}$ as oleic acid$^{110}$. The lifetime estimation indicates that NO$_3$ oxidation will be competitive with O$_3$ oxidation for squalene-like particles. The chemical lifetime of squalene-like multi-unsaturated organic compound in the aerosol phase is thus small compared with tropospheric lifetime (estimated to be ~20 days)$^{112}$ of aerosol.

In the presence of oxygen, the chemistry of organic oxidation is more complex. In the gas phase nitrooxyalkylperoxy radical formation would follow the initial NO$_3$ addition reaction and then be followed by RO$_2$ + RO$_2$ reactions to form alcohols and ketones and/or alkoxy radicals. However, it is uncertain whether alkyperoxy and alkoxy radicals in the condensed phase follow similar reaction pathways as in the gas phase. Docherty and Ziemann$^{94}$ reported the absence of decomposition products via alkoxy radical from NO$_3$ initiated oxidation of oleic acid aerosol particles while similar OH-initiated condensed phase oxidation has shown significant fragmentation. Knopf et al., 2006$^{113}$ performed NO$_3$ oxidation on saturated hydrocarbon monolayer (C$_{18}$H$_{38}$S) and reported less than 10% volatilization of organic mass at accumulated oxidation that we calculated to be $2.6 \times 10^{-8}$ atm.sec.$\gamma$ (\gamma-weighted) whereas Molina et al., 2004$^6$ observed complete depletion of organic monolayer under OH-initiated oxidation at $4.9 \times 10^{-10}$ atm.sec.$\gamma$. More recently, Gross and Bertram, 2009$^{95}$ observed NO$_3$ oxidation of an alkene monolayer and reported the formation of organonitrates without appreciable volatilization. If fragmentation of alkoxy radical proceeds very slowly in the condensed phase following NO$_3$-initiated oxidation, one may expect the oxidation products to remain aerosol-bound that radical reactions as indicated in Figure 3.5 will occur, with the modification that the majority of radical carriers will be alkoxy and alkylperoxy radicals. The reaction then propagates in the similar fashion with hydrogen abstractions to form an alcohol or ketone at each generation.

3.6. Conclusion

Squalane and squalene aerosol in pure N$_2$ were studied as models for aerosol aging by reaction with NO$_3$. The surface uptake coefficient measured for squalene is about 2 orders of
magnitude larger than its saturated analog and increases with the degree of oxidation from an initial value of 0.18 to 0.82 for oxidation ratio up to ~3.5. Simultaneous detection of reactive nitrogen loss with TD-LIF and squalene consumption with VUV ionization aerosol mass spectrometer gives better constraint on the extent of secondary reactions. We describe evidence suggesting that aerosol remains mobile up to at least an average of 2.3 units of NO\(_3\) attached to each squalene molecule. Direct detection of squalene dimer indicates the importance of alkyl radical chemistry in the condensed phase.
Table 3.1 Reactive uptake coefficients measured in this experiment under various oxidation conditions

<table>
<thead>
<tr>
<th>oxidation ratio</th>
<th>ln([N₂O₅]/[N₂O₅]₀) v.s. surface density, slope (cm)</th>
<th>γ&lt;sub&gt;NO₃&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1.4</td>
<td>-(1.3±0.1)×10³</td>
<td>0.18±0.03</td>
</tr>
<tr>
<td>1.4 ~ 2.5</td>
<td>-(3.40±0.06)×10³</td>
<td>0.48±0.06</td>
</tr>
<tr>
<td>&gt;2.5</td>
<td>-(6.5±0.2)×10³</td>
<td>0.82±0.11</td>
</tr>
</tbody>
</table>
Figure 3.1
Experimental setup at beamline (9.0.2) of the Advanced Light Source.
Figure 3.2
N$_2$O$_5$ attenuation versus squalane aerosol surface concentration.
Figure 3.3
N$_2$O$_5$ loss versus squalene aerosol surface area. Two aerosol loading conditions were used with different size distributions.
Figure 3.4
Particle size distribution of squalene aerosol generated under 2 different nucleator settings.
Figure 3.5
Proposed mechanism for squalene + NO\textsubscript{3} oxidation in the condensed phase. Boxes indicate products observed in this study. Crossed double bonds indicate both cis- and trans-configurations possible.
Figure 3.6.
Aerosol mass spectrum obtained from squalene heterogeneous reaction with NO$_3$ under 10.3 eV VUV ionization. Labels refer to the mechanism shown in Figure 3.5 and are described more fully in the text. Single (*) and double (†) $^{13}$C isotope peaks are also shown.
Figure 3.7.
10.3 eV AMS spectrum. m/z corresponding to squalene dimers (m/z = 883.8) and an adduct with 3 NO₃ (m/z = 596.3) are labelled. Other peaks are unassigned. The inset shows expected isotopic distribution of 2Sq + NO₃ + H ion (shaded curve).
Figure 3.8.

$\ln([\text{squalene}]/[\text{squalene}_0])$ vs. oxidation ratio. A linear fit has a slope of $-2.26$ and an intercept of $0.69$ ($r^2 = 0.96$).
Figure 3.9
The ratio of squalene + NO$_3$ + H, m/z = 473.3 (♦) and squalene + 2NO$_3$, m/z = 534.3 (□) oxidation products (species III and V, including isomers) to the initial squalene concentration in the aerosol phase vs. oxidation ratio. The Y-axis shows a relative scale for III and V.
Figure 3.10
Squalene versus NO$_3$ consumption derived from TD-LIF and AMS data. Dashed line indicates initial squalene concentration entering the flow tube while filled dots represent squalene consumed by chemical reaction estimated from AMS at the exit of flow tube.
Figure 3.11
Oxidation ratio as a function of exposure time to 10 ppt NO$_3$ modeled on aerosol particle of 126 nm diameter. Accelerated aging is a direct result of enhanced uptake coefficient with oxidation.
Chapter 4

Part A

Low Temperatures Enhance Organic Nitrate Formation: Evidence from Observations in the 2012 Uintah Basin Winter Ozone Study

Abstract

Nitrogen dioxide (NO$_2$) and total alkyl nitrates (ΣANs) were measured using thermal dissociation-laser induced fluorescence during the 2012 Uintah Basin Winter Ozone Study (UBWOS) in Utah, USA. The observed NO$_2$ concentration demonstrated a diurnal profile highest before sunrise and lowest in the late afternoon, suggestive of a persistent local source of NO$_2$ coupled with turbulent mixing out of the boundary layer. In contrast, ΣANs co-varied with solar radiation with a noontime maximum, indicating that local photochemical production combined with rapid mixing and/or deposition was the dominant factor in determining the ΣANs concentrations. We calculate that ΣANs were a large fraction (~60%) of the HO$_x$ free radical chain termination and show that the temperature dependence of the alkyl nitrate yields enhances the role of ΣAN formation in local chemistry during winter by comparison to what would occur at warmer temperatures of summer.
4a.1. Introduction

The Uintah Basin in Utah is a region of concentrated fossil fuel extraction operations using hydraulic fracturing to extract natural gas and oil from shale formations. The basin has experienced high wintertime ozone as has the nearby Upper Green River Basin in Wyoming. The observed ~200 ppb peak ozone in the basin during the winter of 2011 was associated with elevated concentrations of volatile organic compounds (VOCs) coincident with a shallow boundary layer stabilized by snow cover, which doubled as a solar reflector leading to more rapid photochemistry.

Organic nitrates (RONO$_2$) are products of atmospheric VOC oxidation in the presence of NO$_x$ (NO + NO$_2$). During daytime, their formation involves the association reaction of alkyl peroxy radicals with NO. This reaction terminates ozone formation and suppresses OH recycling. The importance of RONO$_2$ formation as a NO$_x$ sink and chain terminator of ozone production depends on the mixture of VOCs present as a result of variations in OH reactivity and organic nitrate yield, $\alpha$, among different organic molecules. Laboratory studies have shown that the nitrate yield follows standard expectations for 3-body reactions: $\alpha$ increases with carbon number of the organic peroxy radical and atmospheric pressure, but decreases with temperature. Field observations have found RONO$_2$ compounds to account for 25% or more of total reactive nitrogen (NO$_y$, defined as NO$_x$ + higher nitrogen oxides). However, none of these prior field experiments covered a temperature range wide enough to examine the role of the temperature dependence of $\alpha$ on nitrate formation rates, O$_3$, or OH concentrations.

In this chapter we present observations of organic nitrates obtained during the UBWOS 2012 experiment (1/15–2/29). We further describe the role of organic nitrates in wintertime ozone production and the associated temperature effect by comparing the $\alpha$ values either constrained by observed $\Sigma$ANs concentration or derived from temperature-dependent yields from VOC composition data. The findings show organic nitrate formation to be one of the primary radical sinks at this site and confirm that the temperature-dependent kinetics are important. However, temperature dependence of organic nitrate yields are not presented in any of the standard photochemical mechanisms used in chemical transport models. Accounting for the temperature dependent yields at 0°C (the typical daytime temperature during this field campaign) results in a 30% faster organic nitrate formation rate than what would occur at room temperature (300K). As a result, we estimate a suppression in OH concentrations by 15% and ozone formation by 20% relative to the calculations that do not include the temperature dependence of the RONO$_2$ yields.

4a.2. Instrumentation

The 2012 Uintah Basin Winter Ozone Study occurred from January 15th to the end of February at Horse Pool, Utah, a site approximately 30 miles south of the city of Vernal, Utah. This site sits amid intensive oil and gas extraction operations near the center of Uintah basin, with dense gas production wells to the south and oil production wells to the south-west (refer to
Figure 1 of Edwards et al., 2013). A 19 meter high tower was on-site for setting up measurements at various heights.

Our instrument inlet was mounted on the southern face of the tower, 16 m above the ground. Other measurements made from similar heights include NO and NO$_2$, speciated VOCs, O$_3$ and photolysis rates for O$_3$ (O$^1$D), NO$_2$ and NO$_3$. These measurements are described elsewhere (see description and supplemental information S1 in Edwards et al., 2013). Temperature, pressure, relative humidity, wind direction and wind speeds were measured from the top of the tower. 3D wind data were measured using the High Resolution Doppler Lidar nearby.

Thermal Dissociation-Laser Induced Fluorescence (TD-LIF) was used to measure NO$_2$, total peroxy nitrates ($\Sigma$PNs) and total alkyl nitrates ($\Sigma$ANs) using methods described previously. Briefly, laser induced fluorescence was used for detection of gas phase NO$_2$ using a CW solid-state tunable fiber laser (~80 mW, NovaWave) at 530 nm for excitation with detection of photons at wavelengths longer than 900 nm using a red-sensitive PMT (Hamamatsu H7421) preceded by a dielectric long-pass filter. Quartz tubes with external heating elements were maintained at 180°C for conversion of $\Sigma$PNs ($\Sigma$ROONO$_2$) and 380°C for $\Sigma$ANs ($\Sigma$RONO$_2$) to NO$_2$ under a residence time of ~20 ms. Simultaneous measurements of NO$_2$, $\Sigma$PNs and $\Sigma$ANs were achieved by operating 3 LIF cells, each measuring the cumulative concentration of NO$_2$-yielding compounds.

Corrections are necessary for the TD channel signals. As a negative interference, O$_3$ pyrolysis and subsequent O atom-initiated chemistry in the TD oven reduces the amount of NO$_2$ observed for a temperature in excess of 270°C. This effect is prominent when the contribution of $\Sigma$ANs is small compared to ambient NO$_2$. The correction is an empirical relationship developed in the laboratory by directly observing the loss of the 380°C signal as a function of both O$_3$ and NO$_2$ concentrations in the presence of an organic nitrate surrogate (2-ethylhexyl nitrate, Sigma Aldrich). Details of this correction are included in Appendix C1. The factors applied during the daytime hours that are the focus of this study were typically 6–17% of the total 380°C signal, of which $\Sigma$ANs account for approximately 25%. This amounts to a correction of 24–68% of the final $\Sigma$ANs concentration. Larger corrections were required at night due to higher NO$_2$ concentration. There are also additional contributions from inorganic species including N$_2$O$_5$ (which decomposes to NO$_2$ and NO$_3$ at ~90°C) in the 180°C channel and ClNO$_2$ (which decomposes to a chlorine atom and NO$_2$) in the 380°C channel. However, accounting for the inorganic signal was straightforward since direct measurements of both species were available at the site. Overall, the ClNO$_2$ contribution to the difference signal between 380°C and 180°C was only significant during the night and early morning since, for example, the noontime photolysis lifetime of ClNO$_2$ is only 1 hour. We note that N$_2$O$_5$, present only during nighttime, did not affect daytime $\Sigma$PNs measurements.

In subsequent analyses, $\Sigma$PNs is calculated as the difference in concentrations of the ambient and 180°C channel minus the N$_2$O$_5$ contribution, while $\Sigma$ANs is the concentration difference between the 180°C channel and the O$_3$-corrected 380°C channel minus the ClNO$_2$ contribution.
The TD-LIF instrument was calibrated hourly with a 5 ppm NO\textsubscript{2} gas standard diluted with zero air to generate 5 different concentration levels at the inlet manifold. In addition, the instrument zero (baseline) was monitored every half-hour by overflowing the inlet with NO\textsubscript{x}-free zero air. The NO\textsubscript{2} concentration measured by LIF and nearby chemiluminescence instrument were within 7% of each other on average, giving a linear slope (LIF vs. chemiluminescence) of 0.94, an intercept of 0.02 ppb, and an \( r^2 \) value of 0.97.

4a.3. Results

4a.3.1. Observations

Figure 4a.1 shows the time series (as hourly average) of NO\textsubscript{2}, \( \Sigma \)ANs, O\textsubscript{3} and windspeed through the observational period. The time-of-day median values of NO\textsubscript{2}, \( \Sigma \)ANs and O\textsubscript{3} are plotted in Figure 4a.2. During periods with wind speed lower than 5 m/s, the chemical species directly associated with human activity, such as large volatile organic compounds (VOCs) and NO\textsubscript{x}, accumulate, leading to an increase in concentrations until high wind episodes occur that flush the basin with clean air. The onset of high wind episodes were therefore coincident with a rapid decrease in VOC and NO\textsubscript{x} concentration. During the UBWOS campaign in the year before (2011), up to 200 ppb ozone was observed at the end of accumulation periods with snow cover on the ground. However, during similar period in the 2012 campaign, there was little snow and the ozone concentration did not exceed 51 ppb.

NO\textsubscript{2}

NO\textsubscript{2} showed a clear diurnal variation (Figure 4a.2). Concentrations were highest in the early morning when increased vehicle traffic became coincident with a stable nocturnal boundary layer. Turbulent mixing in the afternoon diluted the concentration, giving a minimum at 4 pm local time. We also observed early morning (~4 am) and late afternoon (~6 pm) spikes when changes of work shifts and scheduled maintenance runs took place. The multi-day effect of high/low wind episodes on NO\textsubscript{2} concentration is visible for which high windspeed always corresponds to low NO\textsubscript{2} levels (Figure 4a.1).

\( \Sigma \)ANs

The daily variation in \( \Sigma \)ANs concentration is less pronounced than for NO\textsubscript{2} but follows a similar multi-day trend controlled by meteorology. As shown in Figure 4a.2, the total RONO\textsubscript{2} concentration increases in the morning to a noon time peak of 1.5 ppb. The contributions from C\textsubscript{1}–C\textsubscript{3} alkyl nitrates measured by GC-MS are small and nearly constant at ~50 ppt and did not contribute to the diurnal profile observed.

O\textsubscript{3}
The observed O$_3$ concentration ranged from 4 to 50 ppb and was negatively correlated with NO$_2$. The diurnal profile has a maximum concentration in the late afternoon, corresponding to a delay of roughly 4 hours from the peak of organic nitrates. The increase in O$_3$ concentration is most rapid (~140 ppt hour$^{-1}$) at noon.

**VOCs**

The VOC composition is influenced heavily by the fossil fuel extraction operations. Alkane oxidation dominates the chemistry in the basin (Table 4a.1), accounting for 67% of total measured VOC reactivity (7.5 s$^{-1}$) at noon. The diurnal profile of VOCs follows NO$_2$, reaching a minimum in the late afternoon.

### 4a.3.2. The average branching ratio for nitrate formation

The average noontime temperature during the UBWOS experiment was 0ºC. These cold temperatures provide a unique opportunity to examine the role of temperature on the formation of organic nitrates and the associated radical chain termination compared with other field campaigns taking places in summer.

Organic nitrate compounds are formed via OH-initiated oxidation. For the specific mixture of VOCs observed, the dominant reaction starts with hydrogen abstraction from alkanes by OH. The resulting alkyl radical rapidly reacts with O$_2$ to give alkyl peroxo radical RO$_2$, which subsequently reacts with NO to form an energy-rich adduct of the structure ROONO$^*$.

Under typical atmospheric conditions, a fraction of ROONO$^*$ is collisionally stabilized to form the nitrooxy group, RONO$_2$, while the unstabilized portion dissociates to yield an alkoxy radical and NO$_2$. The fate of the alkoxy radical varies depending on the carbon backbone but, in general, returns a HO$_2$ radical.

For a particular rate constant of VOC reaction with OH, the key factor regulating RONO$_2$ production is the nitrate branching ratio, $\alpha$, defined as the overall fraction of the RO$_2$ + NO reaction that gives an organic nitrate product rather than an alkoxy radical and NO$_2$ product. The association reaction to form RONO$_2$ is compound-specific and temperature- and pressure-dependent.$^{61}$ In the subsequent sections, we present 2 independent methods for estimating ensemble-averaged $\alpha$ values (or $\langle \alpha \rangle$) for the specific environment of UBWOS campaign, and demonstrate they agree to within the uncertainty of our observations.

#### 4a.3.2.1. VOC-ensemble method for calculating $\langle \alpha \rangle$

The first method for calculating the average branching ratio for nitrate formation $\langle \alpha \rangle$ is based on parameterizations derived from laboratory experiments and using only the observed VOC composition data, while the second method (given in 4a.3.2.2. below) uses the $\Sigma$ANs concentration, photolysis rate and VOC reactivity calculated during the campaign period.
The ⟨\( \alpha \rangle \) is defined as the summation of compound-specific \( \alpha \) values weighted by their relative importance in atmospheric oxidation calculated as the product of OH reaction rate constant and compound concentration (namely, the OH reactivity).

\[
\langle \alpha \rangle = \frac{\sum_i k_i [x_i] \alpha_i}{\sum_j k_j [x_j]}
\] (1)

Here \( \alpha_i \) denotes the compound-specific nitrate branching ratio, \( k_i \) the OH reaction rate and \([x_i]\) the concentration of species \( i \). The VOC OH reactivity, \( k_i [x_i] \), in the Uintah basin was dominated by alkanes (see Table 4a.1). The net effect of temperature on the OH reaction rate constants was generally small, giving typically a 5% reduction in total OH reactivity compared with 298K values.\(^65\)

We use temperature- and pressure-dependent, compound-specific \( \alpha_i \) values\(^20\) and include contributions of secondary organic nitrate formation after alkoxy radical isomerization reactions which can become increasingly important for alkanes larger than butane. The isomerization pathways increase the individual organic nitrate yield by up to 30%, which is generally proportional to the size of the molecule. The compound-specific \( \alpha \) values are summarized in Table 4a.2 and examples for their calculations are given in Appendix C2.

Aldehydes were treated as having the same nitrate yield as the RO\(_2\) containing one less carbon, since the major reaction with OH involves aldehydic hydrogen abstraction and decomposition following reaction with NO to give a CO\(_2\) and a C\(_{n-1}\) alkyl radical. \( \alpha \) for ketones were estimated using the same method as detailed for alkanes. Methanol and ethanol are presumed to have a nitrate yield of zero, since their reactions with O\(_2\) after hydrogen abstraction to form carbonyls and HO\(_2\) are much more important. Finally, the nitrate yields for aromatics were set to 1% in this analysis, following the yield of benzyl nitrate from toluene oxidation\(^{65, 123, 124}\). The alkyl nitrate yields from aromatics are likely related to the ring-opening products and are still poorly constrained.

The average nitrate formation yield, \( \langle \alpha \rangle \), as calculated above including all VOC and CO throughout the campaign period is plotted in Figure 4a.3 as instantaneous values (yellow) and as a daytime (8am–6pm) average (red filled symbol). The organic nitrate yield ranged from 3% to 15% with low values corresponding to periods of high winds (e.g. 2/03). Variation in VOC concentration and composition is the dominant factor controlling the day to day variation as well as the variation over each day. Daytime averaged values of \( \langle \alpha \rangle \) calculated at a temperature of 300K are shown in blue. (Even at 300K, the \( \langle \alpha \rangle \) is significant, often around 10%, but is always lower than that at 0°C)

**4a.3.2.2. Oxidation-production method for calculating \( \langle \alpha \rangle \)**
Our second approach to estimating $\alpha$ is based primarily on the $\Sigma$AN measurements. In this case $\langle \alpha \rangle$ can be expressed as the ratio of the $\Sigma$AN production rate over the total VOC consumption rate (Equation 2). The individual terms in Equation 2 can be derived from observations, as indicated in Equation 2a and 2b.

\[
\langle \alpha \rangle = \frac{p(\Sigma ANs)}{[OH] \cdot \sum_j k_j [x_j]}
\]

\[
p(\Sigma ANs) = \frac{d(\Sigma ANs)}{dt} + k_{mix} \cdot \Sigma ANs
\] (2a)

\[
[OH] = f \left( \sum_j k_j [x_j], J, \langle \alpha' \rangle \right)
\] (2b)

First we derive the $\Sigma$AN formation rate using mass balance (Equation 2a). The total production rate is the time derivative of observed $\Sigma$ANs minus the loss rate. Chemical losses are negligibly slow, so the only relevant loss term is mixing out of the boundary layer. We employ a tracer method to derive the apparent loss rate constant “$k_{mix}$” by solving Equation 2a using a compound for which the production rate is well known and the same negligible chemical loss approximation applies. Note that the OH concentration is also needed in this step to calculate the production term of the tracer from its corresponding precursors. The OH concentration is a function of VOC reactivity and photolysis rates (J values) as well as the $\alpha$ value for the recycling efficiency. Due to the dependence of the OH concentration on the nitrate yield, it is not possible to represent $\alpha$ in a closed functional form using all other variables. Therefore, the set of equations must be solved iteratively until a self-consistent $\alpha$ and OH concentration are obtained ($\langle \alpha \rangle = \langle \alpha' \rangle$).

The calculations proceed by calculating the following: (1) OH concentration and VOC consumption rate; (2) mixing rate estimates; (3) $\Sigma$AN formation rate and $\langle \alpha \rangle$.

(1) *OH concentration and VOC consumption rate:* We used photolysis rates for O$_3$, NO$_2$, NO$_3$, HONO, ClNO$_2$, acetaldehyde, acetone, formaldehyde and HNO$_3$ to calculate OH and HO$_2$ production rates. OH formation from alkene ozonolysis reactions was negligible. Data for NO, NO$_2$ and VOCs coupled with literature values of OH reaction rate constants corrected for campaign measured temperature and pressure dependence$^{56,125}$ were then used for OH and HO$_2$ calculations including radical recycling. The resulting VOC consumption rate is shown in Figure 4a.4. Note the VOC consumption rate profile conforms more to the shape of the radical source strength (OH and HO$_2$ formation rate derived from photolysis, same shape as solar irradiation) than to the OH concentration, consistent with the notion that VOCs are the major reaction partner with OH.
(2) Mixing rate estimation: We estimate the dilution loss ($k_{\text{mix}}$) for $\Sigma$AN concentration by substituting [$\Sigma$AN] with n-propyl nitrate concentration in Equation 2a. The time derivative of n-propyl nitrate concentration was calculated using a finite difference method, followed by application of a 2-hour running mean to smooth hourly data. Kinetic studies dictate that ~24% of the OH reaction with propane at 273K yielded a primary alkyl radical, which promptly reacted with O$_2$ to form the corresponding peroxy radical. Larger alkane molecules can also yield n-propyl alkyl radical as a result of alkoxy radical decomposition from the appropriate structure, and we accounted for all such minor formation channels up to undecane to give a total additional contribution of 14% from sources other than propane. The total formation rate of n-propyl nitrate is presented in Figure 4a.5 as the red trace spanned by the 25 and 75 percentiles in the shaded area. Plotted in blue is the median value of time derivative of n-propyl nitrate concentration showing a diurnal pattern for which peak concentration was reached at noon time when the time derivative crosses the zero line. The initial concentration increase roughly coincided with the start of photochemical reaction, as is also marked by the onset of n-propyl nitrate formation rate. The negative portion of the blue trace in the afternoon then corresponds to faster dilution due both to turbulence and to the elevated concentration. These values are sufficient to solve for the time-varying dilution rate constant, $k_{\text{mix}}$, shown in Figure 4a.5 as green line with dashed traces bounding the interquartile range. Note the slight delay (~1 hour) in the daily maximum of the dilution rate constant when compared with the peak of n-propyl nitrate formation rate. As vertical turbulence was promoted by surface heating, this delay is a reasonable consequence of the expected lag in the mixing rate. The median daily maximum mixing rate shows a time constant of 6 hours, much more rapid than other loss processes such as the OH oxidative lifetime of n-propyl nitrate of over 150 hours under the OH concentration of $2\times10^6$ cm$^{-3}$ (Figure 4a.4) and a photolysis lifetime of over 200 hours, consistent with our initial assumption that chemical losses of n-propyl nitrate is not important.

(3) $\Sigma$ANs formation rate and $\alpha$: Using the $k_{\text{mix}}$ calculated above, the $\Sigma$AN formation rate was estimated using Equation 2a. We then inserted this $\Sigma$AN formation rate and VOC consumption rate back into Equation 2 to obtain the implied $\langle \alpha \rangle$ value based on the field observations and also the initial guess of $\langle \alpha' \rangle$. For time periods when $\langle \alpha \rangle$ mismatches $\langle \alpha' \rangle$, $\langle \alpha' \rangle$ is adjusted toward $\langle \alpha \rangle$ and the calculation repeated to achieve consistency. To reduce the number of points needed for calculation, we only estimated one self-consistent $\langle \alpha \rangle$ value for each day by averaging from 8am to 6pm, the same as the averaging window used for our first method.

Direct comparison of the estimate here from 4a.3.2.2 with the one derived from just the VOC composition from the previous section (section 4a.3.2.1) is shown in Figure 4a.6. There were 27 days to compare, and the two methods are nearly identical, yielding a slope of 1.06 and $r^2 = 0.61$. The similarity of the two methods lends support to the estimates of $\alpha$ and confirms the importance of a significant temperature dependence to the value of $\alpha$ affecting the UBWOS chemistry.

4a.4. Discussion
The relatively high value observed for the average nitrate yield, \( \langle \alpha \rangle \), of \(~15\%\) is a direct consequence of low temperatures and the presence of large alkanes, a special condition created by gas and oil extraction operations in the basin. In the following sections, we discuss how this elevated nitrate yield affects the fate of \( \text{NO}_x \) emitted into the basin and the rate of local \( \text{O}_3 \) production.

### 4a.4.1. Fate of \( \text{NO}_x \)

Organic nitrate formation was a significant chemical loss for \( \text{NO}_x \) in the Uintah Basin. We calculated that alkyl nitrate formation is 50% faster than \( \text{HNO}_3 \) formation during the low wind periods, of 0.23 ppb hour\(^{-1}\) vs. 0.16 ppb hour\(^{-1}\) using the estimated noontime \( \text{OH} \) concentration. Together, this amounts to a \( \text{NO}_x \) chemical lifetime of 17 hours, with relative branching of 59% to alkyl nitrate formation and 41% to \( \text{HNO}_3 \) formation. PAN and other peroxyacyl nitrate compounds were not observed to have high production rates based on measured \( \Sigma \text{PNs} \) and PAN concentration and direct calculation of their formation rate from VOC composition including aldehydes. We estimate a noontime median net production of 0.01 ppb PAN hour\(^{-1}\) which is negligible when compared with other chemical sinks mentioned. Alkyl nitrate formation is therefore the single most important chemical loss pathway for \( \text{NO}_x \) as well as the most important terminator for \( \text{OH} \) chain propagation. Note that, although \( \Sigma \text{AN} \) formation is the largest chemical sink, mixing out of the basin is the dominant overall loss of emitted \( \text{NO}_x \). We estimate 68% of \( \text{NO}_x \) is transported into the over-basin flow and carried downwind.

### 4a.4.2. \( \text{O}_3 \) formation

\( \text{O}_3 \) formation is closely related to the formation of organic nitrates, since the reaction channels lead from a branching point in a common pathway. Similar to our treatment of VOC-specific \( \alpha \) values, we calculated, for each measured VOC molecule, the average number of \( \text{O}_3 \) molecules generated in a single event of \( \text{OH} \) initiated oxidation, denoted as \( \gamma \) in Table 4a.2. Note that our definition and estimate for \( \gamma \) includes the contribution from multi-generation alkyl nitrate formation, making it slightly different from previous calculations\(^{13, 23, 115}\) (see Appendix C3). The \( \text{O}_3 \) production rate is then a product of the ensemble-averaged \( \gamma \) and the VOC consumption rate calculated above, as plotted in Figure 4a.7. The difference between the \( \text{O}_3 \) production rate and the rate of change in \( \text{O}_3 \) concentration signifies the contribution of mixing into the background air. When compared with the production characteristics of n-propyl nitrate in Figure 4a.5, it is apparent that dilution loss is much more important for the case of n-propyl nitrate (>80% of the formation rate) than for \( \text{O}_3 \) (~30% of formation rate). Using the \( k_{\text{mix}} \) derived from n-propyl nitrate formation, the local \( \text{O}_3 \) budget of the whole campaign period can be closed with a background \( \text{O}_3 \) concentration in the range of 20–35 ppb, consistent with observations during high wind periods. This also reinforces the notion that our estimate for turbulent mixing is representative of local condition. To reproduce the short-term variations in \( \text{O}_3 \) production over a 72-hour period with a fixed background \( \text{O}_3 \) level of 30 ppb, we estimate the expected change in \( \text{O}_x \) (= \( \text{O}_3 + \text{NO}_2 \))
concentration using the mass balance equation (Equation 2a) to find reasonable agreement with the observations (Figure 4a.8).

The average $p_O_3/p_{\Sigma AN}$ calculated as $\gamma/\alpha$ for UBWOS is 15. For comparison a value of 6.2 to 7.5 was reported for Deep Water Horizon (DWH) plume study\textsuperscript{128}. While both plumes were dominated by alkanes, the VOC suite for the DWH study was further enriched in heavier molecules. By comparison, a typical industrial city plume\textsuperscript{13} measured around Houston during Texas Air Quality Study 2000 has a value of 29 to 41, a direct result from low $\alpha$ value (6.5% to 4.7%) caused by high temperature ($\sim$ 40°C) and relatively low contribution from large alkanes.

### 4a.4.3. Temperature

Currently, none of the chemical mechanisms commonly employed in chemical transport models for regional $O_3$ predictions have incorporated the temperature dependence of alkyl nitrate yields. Since alkyl nitrate formation is a radical termination reaction, reduction in temperature decreases the OH recycling probability and shortens the OH radical chain length. For the UBWOS 2012 campaign, the effect is to reduce the chain length from a noontime median of 3.2 (300K) to 2.6 (273K). Since the chain length is directly proportional to the $O_3$ production rate, this corresponds to a 20% decrease in the $O_3$ formation rate. Table 4a.3 shows the estimated maximum $O_x$ concentration in a multi-day low wind accumulation event in the Uintah Basin based on the observed alkyl nitrate yield. We compare a calculation at 300K to one at 273K. Note that for a snowless winter condition, such as encountered in UBWOS 2012, the prediction matches well with the observed maximum hourly $O_x$ concentration of 51 ppb in the afternoon of 2/18/2012. While estimating the $\alpha$ value at 300K always yields a higher predicted $O_3$ concentration, the over prediction is greatest for the simulated snow condition (right most column) when persistent snow cover increases the photolysis rate and stabilizes the boundary layer impeding mixing.

### 4a.5. Conclusion

We presented an analysis of field observations obtained in the Uintah Basin in Utah, USA, during winter 2012. We find that the field data can be used to derive the temperature dependence of the ensemble average nitrate yield, $\langle \alpha \rangle$, and that this value is consistent with a parameterization derived from laboratory experiments. Including the proper temperature dependence based on the dominating VOC species should be considered for models aimed at estimating local $O_3$ concentrations in order to avoid substantial errors (15% at 0°C).
Table 4a.1 Median OH reactivity and associated formation rates at local noon

<table>
<thead>
<tr>
<th>compound class</th>
<th>OH reactivity (s(^{-1}))</th>
<th>p((\Sigma\Delta Ns))(^\dagger) (ppt(\cdot)hr(^{-1}))</th>
<th>p(O(_3))(^\ddagger) (ppt(\cdot)hr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkane C(<em>1)−C(</em>{11})</td>
<td>5.02</td>
<td>172</td>
<td>1760</td>
</tr>
<tr>
<td>Alkene C(_2)−C(_3)</td>
<td>0.15</td>
<td>0.71</td>
<td>44</td>
</tr>
<tr>
<td>Alkyne C(_2)</td>
<td>0.013</td>
<td>0</td>
<td>2.4</td>
</tr>
<tr>
<td>Aromatic C(_6)−C(_9)</td>
<td>0.58</td>
<td>0.90</td>
<td>120</td>
</tr>
<tr>
<td>Alcohol C(_1)−C(_2)</td>
<td>0.31</td>
<td>0</td>
<td>48</td>
</tr>
<tr>
<td>Ketone C(_3)−C(_4)</td>
<td>0.0084</td>
<td>~0</td>
<td>0.37</td>
</tr>
<tr>
<td>Aldehyde C(_1)−C(_4)</td>
<td>0.44</td>
<td>0</td>
<td>130</td>
</tr>
<tr>
<td>CO</td>
<td>0.95</td>
<td>0</td>
<td>150</td>
</tr>
<tr>
<td>NO</td>
<td>0.61</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>0.82</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>8.90</td>
<td>174</td>
<td>2250</td>
</tr>
</tbody>
</table>

\(\dagger\) Median noon time [OH] = 1\(\times\)10\(^6\) molecule cm\(^{-3}\)
Table 4a.2 Summary of specific organic nitrate and ozone yield calculated at 0°C

<table>
<thead>
<tr>
<th>compound class</th>
<th>α</th>
<th>γ</th>
<th>compound class</th>
<th>α</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkane</strong></td>
<td></td>
<td></td>
<td><strong>Alkene</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>methane</td>
<td>~0</td>
<td>2</td>
<td>ethene</td>
<td>0.025</td>
<td>1.95</td>
</tr>
<tr>
<td>ethane</td>
<td>0.019</td>
<td>1.96</td>
<td>propene</td>
<td>0.05</td>
<td>1.9</td>
</tr>
<tr>
<td>propane</td>
<td>0.045</td>
<td>1.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iso-butane</td>
<td>0.11</td>
<td>2.6</td>
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<td></td>
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</tr>
<tr>
<td>n-butane</td>
<td>0.114</td>
<td>2.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iso-pentane</td>
<td>0.21</td>
<td>2.46</td>
<td>ethyne</td>
<td>~0</td>
<td>1.2</td>
</tr>
<tr>
<td>n-pentane</td>
<td>0.2</td>
<td>2.19</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2,2-dimethylpropane</td>
<td>0.25</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.42</td>
<td>2.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>0.36</td>
<td>2.7</td>
<td>methanol</td>
<td>~0</td>
<td>1</td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>0.29</td>
<td>2.2</td>
<td>ethanol</td>
<td>~0</td>
<td>1.05</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>0.33</td>
<td>2.34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>methyl-cyclopentane</td>
<td>0.29</td>
<td>2.9</td>
<td>acetone</td>
<td>0.021</td>
<td>4</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.33</td>
<td>2</td>
<td>methylethylketone</td>
<td>0.11</td>
<td>3.56</td>
</tr>
<tr>
<td>methyl-cyclohexane</td>
<td>0.58</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethyl-cyclohexane</td>
<td>0.5</td>
<td>2.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dimethyl-cyclohexane</td>
<td>0.67</td>
<td>1.8</td>
<td>formaldehyde</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>heptane</td>
<td>0.6</td>
<td>2.2</td>
<td>acetaldehyde</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>octane</td>
<td>0.6</td>
<td>1.86</td>
<td>propanal</td>
<td>0.019</td>
<td>3</td>
</tr>
<tr>
<td>nonane</td>
<td>0.62</td>
<td>1.52</td>
<td>butanal</td>
<td>0.045</td>
<td>2.91</td>
</tr>
<tr>
<td>decane</td>
<td>0.74</td>
<td>1.43</td>
<td>methacrolein</td>
<td>0.05</td>
<td>2.45</td>
</tr>
<tr>
<td>undecane</td>
<td>0.81</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

†Previously assumed value of 0.1 is due to contribution of nitrobenzene which we do not detect in ΣANs channel.
‡Assumption based on toluene data.
Table 4a.3 Expected maximum O<sub>x</sub> concentration under UBWOS condition

<table>
<thead>
<tr>
<th>condition‡</th>
<th>UBWOS 2012 base condition</th>
<th>photolysis × 2 &amp; mixing ÷ 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>α calculated at 273K‡</td>
<td>57 ppb</td>
<td>140 ppb</td>
</tr>
<tr>
<td>α calculated at 300K‡</td>
<td>64 ppb</td>
<td>165 ppb</td>
</tr>
<tr>
<td>error</td>
<td>7 ppb</td>
<td>25 ppb</td>
</tr>
</tbody>
</table>

‡ Assuming background O<sub>3</sub> concentration of 30 ppb.
Figure 4a.1
Hourly-averaged time series of NO$_2$, total alkyl nitrates ($\Sigma$ANs), O$_3$ and windspeed data measured during UBWOS 2012. The concentrations are measured at height of 16 meters from a 19-meter scaffolding tower on site. The windspeed is measured at the tower top. Ticks on the x-axis mark local midnight.
Figure 4a.2
Time-of-day statistics calculated from the respective full time series. Lines represent median values while the shaded area of $\Sigma$ANs represents the interquartile (25–75%) coverage. The $\Sigma$AN data have been corrected for O$_3$ and ClNO$_2$ interferences (see text).
Figure 4a.3
Ensemble-averaged nitrate formation yield ($\langle \alpha \rangle$) calculated based on the method presented in section 4a.3.2.1. Red symbols represent daytime average of the hourly $\langle \alpha \rangle$ (in orange) estimated at 273K, representative of the campaign period. The blue symbols are the daytime averaged $\langle \alpha \rangle$ estimated at 300K routinely used by global models.
Figure 4a.4
Calculated daytime profiles of the VOC consumption rate and the OH concentration. The VOC consumption rate is controlled by the photolysis rate leading to OH and HO\textsubscript{2} radical formation, while OH concentration is regulated by the OH reactivity dominated by the NO\textsubscript{x} and VOC concentrations.
Figure 4a.5
The production rate and concentration change of n-propyl nitrate calculated from field observations. The difference between the red and blue traces represent the mixing loss promoted by solar surface heating. The green trace is the calculated effective first order mixing rate, $k_{mix}$.
Figure 4a.6
Correlation between daytime averaged $\alpha$ estimated using the VOC-ensemble method (VOC, section 4a.3.2.1) and oxidation-production method ($\Sigma$ANs, section 4a.3.2.2). The shaded area corresponds to the 95% confidence interval for the regression slope passing through origin. The 1:1 line is within this interval.
Figure 4a.7
Calculated daytime O₃ formation rate and the rate of change of Oₓ (= O₃ + NO₂) observed. The difference between traces can be attributed to mixing using the same mixing rate estimated from n-propyl nitrate. The existence of non-negligible background O₃ concentration (30 ppb) suppresses the net dilution.
Figure 4a.8
Correlation of the estimated daytime hourly \( \text{O}_3 \) production rate corrected for dilution loss to what was observed from \( \text{O}_3 \) and \( \text{NO}_2 \) data. A background \( \text{O}_3 \) concentration of 30 ppb was assumed.
Part B

Particulate organic nitrates observed during UBWOS 2012

Abstract

Organic nitrates in both the gas and condensed (aerosol) phases were measured during the Uintah Basin Winter Ozone Study in Utah, USA, from January to February in 2012. A high degree of correlation between total aerosol volume at diameters less than 500 nm and the particulate organic nitrate concentration along with much lower degrees of correlations of particulate organic nitrates with larger aerosol sizes indicates that organic nitrates are a constant fraction of the fine aerosol mass. The C:N atomic ratio inferred from the measurements is ~40:1. Calculations constrained by the observations indicate that both condensation of gas phase nitrates and heterogeneous reactions of NO$_3$/N$_2$O$_5$ with aerosol are responsible for introducing organic nitrate functionality into the aerosol.
Sub-micron sized aerosol affect the global radiative balance directly as a result of variation in their optical properties and indirectly via their effect on clouds. They also affect atmospheric composition via their role in scavenging gas phase material including oxidants. When found at the Earth’s surface these aerosol also affect visibility and public health. Observations have shown that micron sized aerosol typically contain ~50% organic material by mass. The source of organic aerosol has been the subject of considerable debate. Evidence suggests that most of the organic aerosol is secondary, by which we mean formed in the atmosphere through chemical reactions of gaseous precursors (e.g. Goldstein and Galbally, 2007 and Hallquist et al., 2009), and also that much of the aerosol is associated with anthropogenic influence but contains carbon that is “modern”. As nitrogen oxides are primarily anthropogenic, an aerosol formation pathway mediated by NO\(_x\) might explain this seemingly counter intuitive phenomenon in terms of \(^{14}\)C age. One possibility is the production of organic nitrate aerosol.

Recently, methods to identify organic nitrate in aerosol have become available. Observations in chamber studies of the NO\(^+\)/NO\(_2\)^+ peaks in aerosol mass spectrometer measurements, by FTIR of ambient aerosol and by TD-LIF of ambient aerosol indicate that aerosol organic nitrates are observable, that there are mechanisms that produce them in significant yields from common organic precursors and that they are present in significant quantities in some locations. For example, in Bakersfield, CA during summer, Rollins et al. (2012) found that aerosol organic nitrate production is as much as 30% of the aerosol growth rate at night with nitrooxy group representing 8.4% of the growth mass.

Recent studies of ambient organic aerosol precursors have focused on gasoline, diesel and motor oil as precursors. For long chain aliphatics, laboratory experiments and simulations have demonstrated substantial contribution of organic nitrates in the resulting particulate matter, but there exist few field observations capable of assessing whether these mechanisms are representative of the ambient processes. Here we describe observations of organic nitrate aerosol observed in the Uintah Basin, Utah during winter 2012. The site is heavily influenced by oil and gas drilling operations and has negligible input of biogenic emissions providing an excellent opportunity to explore the role of organic nitrates formed from aliphatic compounds in the production of ambient aerosol.

Observations of NO\(_2\), total organic nitrates and particulate organic nitrates (p\(\Sigma\)AN) were made as part of the Uintah Basin Winter Ozone Study (UBWOS) in January and February 2012. The instruments at the site were installed on a 19 m tower located on an operational oil and gas drilling pad containing a wellhead for water injection, with an existing overhead electrical power line and a nearby unpaved access road. The site (40.14370° N, -109.46718° W) is approximately
30 miles south of Vernal, the nearest town in Utah. The aerosol measurements that are the focus of this manuscript were from inlets 9 m above the ground.

NO$_2$, total organic nitrates and $p\Sigma$AN were measured by thermal-dissociation laser-induced fluorescence (TD-LIF) with coupling to a denuder as described in Rollins et al., 2010. TD-LIF is described in detail elsewhere$^{55,150}$. Briefly, in these experiments a CW 408nm solid state diode laser (Power Technology Inc., LDCU12/7639) was used to excite NO$_2$. The laser light was directed sequentially into 3 multi-pass white cells and total fluorescence at wavelengths longer than 700 nm was detected using a red-sensitive photomultiplier tube (Hamamatsu H7421-50) behind dielectric filters that set the transmission window. The cell pressure was maintained at 3 Torr.

Simultaneous detection of organic nitrate species was effected by quantitative conversion of alkyl nitrate (-ONO$_2$) and peroxy nitrate (-OONO$_2$) groups to NO$_2$ through thermal decomposition at 20 ms residence time and 380°C in a 0.25 inch OD quartz tube. The sample air passing through the oven contains both gas phase and aerosol phase organic nitrates which are both converted into an excess NO$_2$ signal compared to the ambient NO$_2$ concentration monitored in an unheated channel. To separate the particulate phase component, an activated charcoal multi-channel denuder of 10 cm length (MAST Carbon Inc.) was placed ahead of another 380°C TD oven. The denuder removes the gas phase organics$^{76}$. The particle transmission efficiency was calculated to be 60% for 20 nm diameter particles and over 90% for particle larger than 70 nm diameter, ensuring detection of the vast majority of aerosol mass. To reduce intake of dust, a 2.5 µm cyclone was placed on the main inlet with a bypass pump maintaining the necessary total flow rate of 5 liter per minute. In addition to these TD-LIF measurements, N$_2$O$_5$$^{121}$, peroxy acetyl nitrate$^{151}$ and ClNO$_2$$^{122}$ were measured. Effects of O$_3$ thermal dissociation on the RONO$_2$ signal are accounted for as described in Chapter 4a. Total RONO$_2$ ($\Sigma$AN) is defined as the measured TD-LIF signal at 380 °C, corrected for ozone effects and with N$_2$O$_5$, peroxy acetyl nitrate (PAN) and ClNO$_2$ subtracted. The particle organic nitrate observations require no correction as gas phase molecules are scrubbed by the denuder. We expect alkyl nitrates to be the dominant component of the particulate organic nitrate signal observed, as peroxy nitrate concentration as well as the concentration of their precursors are much lower than the corresponding alkyl nitrates and there have been no direct evidence that peroxy nitrate should dominate the organic aerosol composition.

The TD-LIF instrument was calibrated hourly using locally generated zero air mixed with an NO$_2$ standard to give a 5-point calibration, spanning a range from 0 to 20 ppb. The instrument zero was monitored twice an hour. Concentration data were reported to the NOAA archive (http://esrl.noaa.gov/csd/groups/csd7/measurements/2012ubwos/) on a time base of 1 minute, averaged from 1 Hz raw data. The detection limit for the instrument at 1-minute averaging time was 24 ppt for NO$_2$ and particulate nitrate and 34 ppt for total organic nitrate, defined as the 1-σ value of the noise. The denuder was occasionally checked for saturation by introducing the calibration NO$_2$ gas mixture before, rather than after, the denuder section in a calibration routine, and no NO$_2$ break-through was observed.
Co-located aerosol measurements include the particle size distribution from 10 nm to 500 nm covered by scanning mobility particle sizer (SMPS, TSI Inc.) and from 0.7 µm to 10 µm by aerodynamic particle sizer (APS, TSI Inc.) and aerosol mass spectrometer (AMS, Aerodyne Inc.). Filter samples for aerosol below 2.5 µm were collected twice daily, one during daytime and one during nighttime. Properties derived from these filter samples include total aerosol mass, total organic carbon (OC), total elemental carbon (EC) and cation concentrations using ion chromatography. Meteorological conditions were recorded at the top of the 19 m tower including wind direction, wind speed, temperature, pressure and relative humidity. Gas phase measurements used in this analysis include gas chromatography with mass selective detector (GC-MS) and proton transfer mass spectrometry (PTR-MS) for VOC speciation, cavity ring-down spectroscopy (CRDS) for N₂O₅ and NO₃, chemical ionization mass spectrometry (CIMS) for ClNO₂, and GC electron capture detector (GC-ECD) for PAN.

4b.3. Results

The observations of total alkyl nitrates (ΣAN) and particulate nitrates (pΣAN) are shown in Figure 4b.1. ΣANs account for a peak of 40% NOₓ and exhibit a strong diurnal pattern, reaching a median value of 2.2 ppb at local noon as shown in Figure 4b.2. At night there were high concentrations of N₂O₅ and ClNO₂ (~0.6 ppb combined) and ΣANs decreased to about 300 ppt. PAN was about 250 ppt at night increasing to 400 ppt in the late afternoon.

A median value of 45 ppt particulate nitrates were observed with peak value at ~150 ppt (Figure 4b.1). pΣAN varied more slowly than ΣANs, except at times of pristine air intrusion during which the concentrations decreased promptly. From a multi-day perspective, the particulate nitrates were observed to accumulate during stagnant periods as did other long-lived trace gases including VOCs, NO₂ and ΣAN.

pΣAN was correlated with other aerosol measurements, the strongest of which (r² = 0.72) was with aerosol volume at diameters below 500 nm as calculated from the SMPS observations (Figure 4b.3). The correlation with total aerosol volume of particles up to 2.5 µm diameter is weaker (r² = 0.23). We believe this is due to the presence of mineral dust in the larger size fraction.

4b.4. Discussion

4b.4.1. Aerosol composition inferred from observations

The inorganic components observed in the aerosol at UBWOS consist of mineral dust, salts and elemental carbon. The pΣAN data represent condensed phase organic compounds containing nitrooxy groups. Thus the strong correlation of pΣAN with PM0.5 volume suggests that aerosols in this size range are predominantly organic with a consistent organic nitrate component. Complementary evidence for this idea is obtained by correlating the concentration of Ca²⁺,
typically found in minerals, with the total aerosol volume at diameters between 500 nm and 2.5 \( \mu \)m. The resulting high correlation \((r^2 = 0.78)\) is in contrast to the one obtained for \( \text{Ca}^{2+} \) with the PM0.5 volume \((r^2 = 0.03)\), lending support to the idea that the organic particles dominate the particle size range smaller than 500 nm while inorganic components dominate the size range from 500 nm to 2.5\( \mu \)m.

To obtain a quantitative estimate of organic/inorganic mass in PM2.5, we used linear decomposition of aerosol specific volume (Appendix C4). The specific volume was calculated as the ratio of PM2.5 aerosol volume measured by SMPS and APS over PM2.5 aerosol mass from impacter filter samples. The use of filter data limits the number of estimations to 2 values per day, one during the day and one during the night. This method assumes that inorganic and organic components have distinctive density, and they form external mixture in the aerosol phase. The resulting equation relating the observed PM2.5 specific volume \((\bar{v})\) to aerosol organic nitrate group mass fraction \((\bar{v}_{\text{HNO}_3})\) is shown in Equation 1.

\[
\bar{v} = \bar{v}_{\text{dust}} + (\bar{v}_{\text{org}} - \bar{v}_{\text{dust}}) \cdot (1 + \gamma) \bar{v}_{\text{HNO}_3} \quad (1)
\]

\[
\bar{v}_{\text{HNO}_3} = \frac{[p\Sigma\text{AN}] \cdot N_{\text{ppb}} \cdot M_{\text{HNO}_3} \cdot 10^{12}}{N_A \cdot m_{\text{aerosol}}} \quad (2)
\]

\(\bar{v}_{\text{org}}\) and \(\bar{v}_{\text{dust}}\) represent the specific volume of aerosol organic and inorganic components, respectively, while \(\gamma\) is the mass ratio of the non-nitrate-containing organic mass to the organic nitrate group. Equation 1 predicts a linear relationship between the aerosol specific volume and organic nitrate mass fraction given that organic nitrates represent a constant fraction in the organic mass, a condition satisfied as demonstrated in Figure 4b.4. The \(\bar{v}_{\text{HNO}_3}\) is calculated directly from \(p\Sigma\text{AN}\) measurement according to Equation 2.

The y-intercept of a plot of aerosol specific volume versus organic nitrate mass fraction gives the specific volume of the inorganic component directly. From Figure 4b.4 we derive a value of 0.168 \(\text{cm}^3/\text{g}\) corresponding to a nominal density of 5.95 \(\text{g/cm}^3\), a value similar to iron(III) oxide \((d = 5.24 \text{ g cm}^{-3})\). With the assumption that the majority of organic molecules with moderate oxygenation have a density \((\bar{v}_{\text{org}})\) of around 0.85 \(\text{g/cm}^3\) (for example: 1-butyl nitrate \((d = 0.882)\), tert-butyl nitrate \((d = 0.867)\), nonanol \((d = 0.827)\) and butanol \((d = 0.81)\)), we obtain a \(\gamma\) value of 11. This constrains the organic mass associated with organic nitrate group in aerosol to approximately 680 amu. Aerosol mass spectrometer observations during high aerosol loading periods suggest an O:C value of 0.2 (Shane Murphy, private communication). A generic chemical formula containing carbon, oxygen, hydrogen and organic nitrate (-ONO_2) is of the form \((\text{CH}_2)_n\text{O}_m(\text{HONO}_2)\) for a fully saturated molecule. Note that a single hydrogen is grouped with nitrooxy for valence balance. The constraints \((680 \text{ amu and O:C of 0.2})\) combine to give a chemical formula for the organic aerosol of \((\text{CH}_2)_{40}\text{O}_8(\text{HONO}_2)\). One example of a set of compounds that would give this formula is an equal-molar mixture of \(\text{C}_{20}\text{H}_{40}\text{O}_8\) and \(\text{C}_{20}\text{H}_{41}\text{ONO}_2\).
4b.4.2. Daytime production

In the following section we demonstrate that a simple gas phase oxidation of aliphatic molecules and standard partitioning theory explain the source strength of the particulate nitrate observed.

pΣAN is thought to be exclusively secondary. The implication is that they are formed through partitioning of gas phase nitrates or heterogeneous oxidation. Consider daytime processes in the alkane-rich environment observed during UBWOS: the oxidation of an organic molecule R starts with a reaction with OH radical. For a simplified schematic (Reactions 1 and 2) of a single oxidation step, two generic products are formed with relative yield governed by the organic nitrate yield $\alpha$.

\[
R + OH \xrightarrow{NO,O_2} \alpha R(ONO_2) \quad (\text{Reaction 1})
\]

\[
\xrightarrow{NO,O_2} (1 - \alpha) RO. \quad (\text{Reaction 2})
\]

The simple alkyl nitrate $R(ONO_2)$ and subsequent products formed from the alkoxy radical RO are assumed to partition into the aerosol phase as a function of their respective vapor pressure. If the partitioning follows ideal solution behavior within the existing aerosol organics, the fraction of the organic products expected to end up in the condensed phase is represented as $K_p$ in Equation 3, where $P^*$ represents the saturation vapor pressure of the organic molecule, $N_{org}$ the amount of organic molecules in the condensed phase in mol/m$^3$ and $k_B$ as Boltzmann’s constant.

\[
K_p = \frac{1}{1 + \frac{P^*}{N_{org}k_BT}} \quad (3)
\]

The largest alkane reported was undecane (C$_{11}$H$_{24}$). To account for contributions of larger alkanes, we extrapolate the OH reactivity of alkanes using a power law, by fitting a linear relationship ($r^2 = 0.99$) to the observed C$_9$ ~ C$_{11}$ reactivity in the log space. This approximates the decay in gas phase concentration due to reduction in vapor pressure with alkane size. Using a simplified oxidation scheme with 3 species for each carbon number group: an alkyl nitrate, a hydroxy nitrate and a hydroxy carbonyl, with branching ratio of $\alpha$, $(1-\alpha)\alpha$ and $(1-\alpha)^2$, respectively. The absolute contribution to aerosol formation is the production rate weighted by $K_p$. The total contribution is obtained by summing over all carbon numbers (Appendix C5). We used $\alpha$ values estimated with the method by Carter and Atkinson$^{20}$ updated by Arey et al.$^{21}$ at the appropriate temperature and pressure. The saturation vapor pressure $P^*$ of the reaction products follows the parameterization of SIMPOL.$^{1}$

Using this framework, we calculate the particulate nitrate formation during the accumulation event beginning on 1/29/2012. The aerosol loading during this period reached 2 µg/m$^3$ as estimated from the specific volume method consistent with OC filter measurements. The formation rate of aerosol organic nitrates as a function of the source molecule carbon number for
a daytime OH concentration of $2 \times 10^6$ cm$^{-3}$ is shown in Figure 4b.5. The total contribution of nitrooxy groups to the aerosol phase calculated by integrating over all carbon compounds above C$_6$ is 5.5 ppt/hour. Figure 4b.5 shows the prediction that the dominant organic nitrate molecules in the aerosol phase have a carbon chain lengths in the range between C$_{10}$ to C$_{17}$. The contribution from nitrate molecules with carbon number less than 6 is negligible. Note that the carbonyls are predicted to have longer carbon chains, due to the relatively lower reduction in vapor pressure compared with hydroxy or nitrooxy group.

The representative chemical formula of aerosol organics given by the above bottom-up estimate is (CH$_2$)$_{19}$O$_2$(HONO$_2$), or a non-nitrate to nitrate mass ratio of 4.8:1. This is about 44% of the value inferred from observation (the $\gamma$ value of 11:1 derived from Equation 4). One possible explanation is that approximately half of the the non-nitrate carbonaceous component results from primary sources. Other possibilities include the error of aerosol partitioning due to the uncertainty in saturation vapor pressure predictions and further heterogeneous or condensed phase chemistry. Regarding the uncertainty in vapor pressure, Pankow and Asher stated an uncertainty factor for organic nitrate compounds of $10^{\pm0.3}$, or a factor of 2. This gives a range of $\gamma$ between 4.1:1 to 5.4:1.

$$p(p\Sigma AN) = \frac{d(p\Sigma AN)}{dt} + k_{mix} \cdot p\Sigma AN \quad (4)$$

To compare with observations, we calculated the p\Sigma AN production rate according to the mass balance equation (Equation 4) with the observed concentration. $p(p\Sigma AN)$ represents the net formation rate of p\Sigma AN. The loss term is represented as a first order loss rate $k_{mix}$ (1/s) estimated using the production and loss of n-propyl nitrate as detailed in Chapter 4a. Turbulent mixing out of the basin is the dominant driver of $k_{mix}$. The inferred production rate of the same period is 5.6 ppt/hour, nearly identical to our estimate using VOC composition. Considering aerosol may be subjected also to deposition loss, the p\Sigma AN formation rate re-calculated using the loss characteristic of HNO$_3$ gives an inferred production of 6.1 ppt/hour, a value ~10% higher and should be considered as an upper limit.

4b.4.3. NO$_3$/N$_2$O$_5$ chemistry

In addition to daytime source of p\Sigma ANs, nighttime oxidations may also be important. The dominant reactions are those initiated by NO$_3$/N$_2$O$_5$ radicals, either indirectly through gas phase oxidations followed by condensation, or directly through heterogeneous reactions on the surface of existing organic aerosol. From the VOC composition observed, the indirect pathway is likely unimportant due to the lack of alkenes as precursors. Multiple lab studies on both environmental and synthesized aerosol particles have demonstrated that the reactive uptake of NO$_3$ or N$_2$O$_5$ can be significant, and for certain class of organics molecules (e.g. alkenes and alcohols) can give high yield of organic nitrates as condensed phase products. It is difficult to obtain direct evidence from the variation of p\Sigma AN concentration observed during the night as substantial concentration from daytime production remains and no clear increase in concentration was
observed. However, we found that inclusion of heterogeneous production is necessary to explain the nighttime concentration of $p\Sigma AN$ and we characterize the heterogeneous reactions in the following modeling section.

4b.4.4. Modeling aerosol concentration

A box model incorporating the two mechanism above was used to simulate the organic nitrate content in the aerosol phase. The aerosol properties in our simulation are prescribed with the observed size distributions.

For the daytime mechanism, rather than tracing the production of individual organic nitrate molecules from various VOC precursors, a simplified scheme is used which only simulates the partitioning of organic nitrates into the aerosol matrix. The observed $\Sigma AN$ is used to represent the total concentration of organic nitrates produced due to photochemical productions as demonstrated in the Chapter 4a, with an effective saturation vapor pressure assigned as a tuning parameter to determine the effective partitioning based on Equation 3. The bi-directional exchange is calculated using gas kinetic theory and detailed balance derived from the saturation vapor pressure accounting for Kelvin effect.

For the nighttime mechanism, we introduce a parameter, the retaining coefficient ($\zeta$), defined as the probability of reactive uptake yielding condensed phase organic nitrates given a gas molecule-surface collision. This differs from the reactive uptake coefficient by excluding non-nitrate forming channels because the constraining factor, $p\Sigma AN$, is only sensitive to the fraction of heterogeneous reactions that ultimately yield organic nitrates. The $p\Sigma AN$ production is calculated using a 2-shell model for gas molecule-surface collision weighted by $\zeta$ in place of the reactive uptake coefficient as used in Chapter 3. The organic nitrates formed through this pathway is assumed to stay in the condensed phase without re-volatilization which is a reasonable assumption considering NO$_3$ heterogeneous reactions are not associated with high degrees of fragmentation as opposed to heterogeneous reactions initiated by OH$^6,113$. The $\zeta$ is the second tuning parameter.

Loss of $p\Sigma AN$s is assumed to follow the loss of aerosols. The most important process is turbulent mixing with a lifetime of ~8 hours during daytime periods. The full time series of first order loss rate is calculated using tracer methods (Chapter 4a) and applied to the simulation. We used HNO$_3$ to estimate the loss rate.

The resulting time series of predictions are shown in Figure 4b.6, where the top panel describes the 2 consecutive accumulation periods and the lower panel extends the simulation to all observations. Both panels use the same value of the adjustable parameters. This result corresponds to an effective saturation vapor pressure of 26 ppb for the ensemble of total organic nitrate species measured and an effective $\zeta_{NO_3}$ value of 0.1 for NO$_3$ surface reaction as they best describe the variation of the observed particulate organic nitrate concentration, giving a correlation slope of 0.98 and $r^2$ value of 0.72 over the 2-week period shown in the top panel of
Figure 4b.6. A reduced correlation with a slope of 0.72 and $r^2$ of 0.66 is observed for the full data set shown in the bottom panel of Figure 4b.6. We point out that this effective saturation vapor pressure fitted is consistent with one calculated from the VOC speciation which indicates a gas/aerosol partitioning corresponding to a $P^*$ of 28 ppb. The largest differences between our model result and the observations are model underestimations when organic mass becomes more abundant in the super-0.5µm size range (up to 36% of total pΣANs). Possible explanations include enhancement in surface area of organic matters when present as an external coating on the inorganic minerals, making heterogeneous oxidation more efficient, or additional chemistry due to active participation of inorganics in the reactions.

The obtained $\zeta_{NO_3}$ value of 0.1 should be considered as a projection of the overall reactivity onto the NO$_3$ metric. Since NO$_3$ and N$_2$O$_5$ are always in near equilibrium, both species can contribute to heterogeneous reactions. Given an observed median NO$_3$/N$_2$O$_5$ ratio of 0.007, the heterogeneous chemistry may be equally satisfied with an N$_2$O$_5$-based $\zeta_{N_2O_5}$ of $8 \times 10^{-4}$, or any linear combination of the two channels. These values are consistent with some of the more reactive organic aerosol reported from laboratory studies, such as for solidified oleic acid ($\gamma_{NO_3}=0.076$) and conjugated linoleic acid ($\gamma_{NO_3}=0.08$) for NO$_3$ uptake and glycerol ($\gamma_{N_2O_5}=8.14 \times 10^{-4}$) for N$_2$O$_5$ reactions. We point out that, in view of the absence of alkenes detected in the gas phase, the N$_2$O$_5$ heterogeneous reaction with hydroxy groups (e.g. glycerol or alcohols) to yield alkyl nitrate is probably a more likely pathway.

4b.5. Implications

Our particulate organic nitrate measurements during wintertime in the Uintah valley, Utah represent a unique opportunity to characterize the chemistry of alkane-derived SOA under ambient (albeit cold) conditions. This is relevant to environments when anthropogenic activities heavily influence the VOC composition. According to the study of Gentner et al., both gasoline and diesel fuel sampled at various locations in California contains dominantly alkanes, with longer chain length in the diesel fuel. In fact, tailpipe emissions of unburnt diesel fuel as well as motor oil may represent the predominant source for large alkanes observed in cities. For example, VOC enhancement ratios observed in Los Angeles shows a non-decreasing trend from n-nonane to undecane, the largest alkane reported. Similar results in mixing ratios have also been shown for Sacramento. This is different from the decreasing trend observed in Utah where the VOC sources are evaporative, but rather consistent with the liquid diesel composition for which the distribution of C$_{10}$ to C$_{20}$ alkanes are relatively flat.

We calculated the potential organic nitrate aerosol formation from alkanes using the liquid fuel composition tabulated in the supporting information of Gentner et al. and the partitioning method detailed in section 4.2 for OH initiated oxidation. OH reaction rates for alkanes larger than dodecane are parameterized. For an organic aerosol loading of 2 µg/m$^3$, the organic nitrate aerosol yield is 14 wt% for diesel fuel and 0.004 wt% for gasoline, both calculated at 298K. We did not include nitrate yields from aromatic compounds as they remain uncertain at this point. This indicates that emissions from diesel traffic may represent the major source of...
organic nitrate content in ambient aerosols at urban locations. Taking the observation at Bakersfield during CalNex-2010 campaign as an example, Rollins et al.\textsuperscript{29} reported local $\Sigma$AN concentration of $\sim$60 ppt during daytime periods. It was estimated in the work of Gentner that both gasoline and diesel vehicles emit similar amount of VOC by weight in the Bakersfield region (Kern county), of the ratio 44\% (gasoline) to 56\% (diesel). At this ratio the diesel emission dominates in term of the source strength of particulate organic nitrates. We further estimate the potential $\Sigma$AN concentrations according to the mass yield calculated above and tailpipe VOC emission of 7 $\mu$g/m$^3$ from diesel vehicles, a number we derived based on the SOA production estimation in Gentner et al. The result is 46 ppt $\Sigma$AN due to diesel traffic emissions in the Bakersfield region, a value accounting for 77\% of the observed concentration by Rollins et al., 2012. Contributions from local biogenic precursors may account for the remaining particulate nitrates. However, we point out that photochemical aging is required to achieve the yield from our estimation and the above value should be perceived as an upper limit.

4b.6. Conclusion

We present PM2.5 particulate organic nitrate concentration measurements obtained in wintertime Utah using TD-LIF technique. Of the median 1 $\mu$g/m$^3$ organic aerosol estimated, we found organic nitrate to be a consistent portion of the organic mass occupying predominately in the sub-0.5 $\mu$m particle size range of an average formula $C_{40}H_{81}O_8$(ONO$_2$) likely as a mixture of $C_{10}$ to $C_{17}$ organic nitrates and oxygenates. Source estimation using observed and extrapolated alkane composition suggested a nearly 1:1 ratio of primary and secondary contributions to the total carbonaceous component. With the help of a box model, we demonstrate that the particulate organic nitrate concentration observed can be reproduced by gas phase condensation and heterogeneous chemistry of NO$_3$ and/or N$_2$O$_5$. Both channels contribute almost equally, consistent with the lack of day/night change observed in condensed phase organic nitrate content. By applying our analysis to the California central valley region, we show that diesel tailpipe emissions are likely responsible for the majority of ambient particulate organic nitrates observed.
Figure 4b.1
Hourly time series measurements of total alkyl nitrates ($\Sigma$AN), particulate organic nitrates (p$\Sigma$AN), total aerosol volume measured by SMPS and APS, and local wind speed. The 2 traces in the first panel illustrate the relative contributions of ClNO$_2$, N$_2$O$_5$, and peroxy acetyl nitrate (PAN) to the $\Sigma$AN signal.
Figure 4b.2
Hourly time-of-day statistics for ΣAN (upper panel) and pΣAN (lower panel) throughout the campaign period. Note that the ΣAN daily maximum concentration occurs at noon when photochemical production is fastest. Contribution from a peroxy nitrate compound class is likely small based on local peroxy acetyl nitrate (PAN) measurements.
Figure 4b.3
Correlation of PM0.5 volume measured by SMPS with particulate organic nitrate concentration ($r^2 = 0.72$).
Figure 4b.4
Correlation of inverse density (specific volume) with the mass fraction of aerosol organic nitrate group for the PM2.5 size range ($r^2 = 0.6$). The linear correlation is suggestive of an external mixture of 2 essential components having very different densities. The organic nitrate functional group resides in the light component.
Figure 4b.5.
Source strengths of various functional groups on molecules contributing to aerosol formation as a function of carbon number for the accumulation event starting on 1/29/2012.
Figure 4b.6
Time series of predicted particulate organic nitrate concentrations from box model simulations for 2 accumulation events (top panel) and for the campaign period overall (bottom panel). Data are given as stacked areas showing the contributions from each of the 2 mechanisms responsible. The observations are plotted as golden linked dots.
Chapter 5

GC-TD-LIF system for specific organic nitrate detection and quantification

Abstract

The development of gas chromatography using thermal dissociation coupled to laser induced fluorescence of NO₂ (GC-TD-LIF) with application to organic nitrate detection is described. Optimization of the GC temperature program allows detection of semi-volatile organic nitrates (vapor pressure as low as 10⁻⁴ Pa) with a limit of quantification of ~100 fmol (1×10⁻¹³ mol) and limit of detection of 12 fmol (95% confidence interval). The inlet system I designed allows direct sampling of ambient air and includes a cold trap to collect molecules and subsequent thermal desorption and injection onto a GC column. The inlet system and instrument have a combined limit of quantification of 10 ppt per minute of sampling time under a typical sample flow rate of 180 cm³/min standard condition.
5.1. Introduction

Multifunctional organic nitrates are important products in the oxidation sequence of volatile organic compounds in the atmosphere affecting yields of O₃ and aerosol. The inherent difficulty in efficient detection of this class of compounds is tied to the fact that they are thermal labile so that methods utilizing high temperatures (in excess of ~180°C) inevitably lose the nitrogen moiety, leading to reduced sensitivity and difficulty in data interpretation as the molecules may appear in the background or be converted to more stable species and subsequently reported as a different molecule. Simple alkyl nitrates are stable in canisters and easily detected using GC methods. However, the most abundant organic nitrates are thought to be multifunctional compounds containing peroxide or hydroxyl groups. While total organic nitrates are routinely observed by TD-LIF, few analytical methods exist for reliable detection of multifunctional organic nitrates, making a more quantitative understanding of the role of specific nitrates challenging. A major recent advance has been the development of chemical ionization mass spectrometry for detection of specific organic nitrates. Using CF₃O⁻ as the reagent ion, Wennberg and coworkers have observed a variety of multifunctional organic nitrates. Other ionization schemes have also recently been developed that seems promising. Analysis of organic nitrates by GC-ECD or HPLC-ESI (e.g. Surratt et al., 2006, Werner et al., 1999) has received some attention, but has been less quantitative as standards are not available for most molecules of interest. A more general strategy would be to use a GC for separation and then convert the nitrates to NO₂. In this scheme, standards are not necessary—except as needed to characterize transmission through the instrument. Hao et al. were the first to develop an instrument along these lines. They direct the effluent of a GC to column into a thermal dissociation region and then onto a luminol detector and showed they could separate and detect multifunctional RONO₂ with 50 fmol sensitivity. In this chapter, we describe an improvement upon this method: coupling laser induced fluorescence of NO₂ to the effluent of GC column with thermal dissociation. We also describe an inert pre-concentrator designed for collection of ambient nitrates and delivery of them onto GC column.

5.2. Instrument design

A schematic of the instrument is shown in Figure 5.1. A Hewlett-Packard 5890 GC II Plus with electronic inlet pressure control was used for organic nitrate separation. We use a non-polar DB-5 column (30 m × 0.25 mm ID × 25 μm,) which results in retention sequence based on volatility. Immediately after elution, a small amount of O₂ is mixed with the helium carrier gas flow prior to entering the thermal dissociation oven where -ONO₂ group in organic nitrates are quantitatively converted to NO₂ and specifically detected by laser induced fluorescence. A MKS Baratron pressure gauge with 10 Torr full scale is used to monitor the pressure in LIF cell.

TD-LIF

The thermal-dissociation laser induced fluorescence technique has been described in detail previously. A brief description highlighting the modifications for this application are
described here. This design differs from prior direct-atmospheric-sampling instruments by reducing the gas transfer line volume to a minimum with the use of deactivated fused silica capillary joining the tail of GC column through the TD oven to the LIF cell. The capillary has the same inner bore diameter as the GC column itself, reducing perturbations to the flow streamline and further suppressing peak broadening. The TD oven was also redesigned to utilize the fused silica capillary as the heated contact surface, but can withstand repeated thermal stress resulting from heating the oven from ambient temperature to 400°C. The thermal dissociation oven converts alkyl nitrate or peroxy nitrate functional group quantitatively to NO$_2$ molecules and the corresponding radicals by heating the gas stream to 400°C. Under pure helium bath gas condition NO$_2$ yield of less than 100% has been observed and we attribute this to secondary reactions between the organic radicals and NO$_2$ as suggested by Griffiths, Gilligan and Gray in 1975. By introducing O$_2$ to the helium flow prior to TD oven, we recover 100% of the nitrates as NO$_2$. We used an n-propyl nitrate gas standard calibrated gravimetrically to evaluate the transmission and conversion (Figure 5.2).

The effluent of the TD region is directed into a multi-pass cell utilizing a white cell configuration (40 passes) to enhance the effective excitation photon flux from a gated blue diode laser with emission centered at 445 nm. The red-shifted fluorescence in the infrared region emitted by excited NO$_2$ molecule is detected by a red-sensitive photomultiplier tube (Hamamatsu H7421-50) behind a dielectric filter to block the excitation photons. The typical operating pressure in the cell is 32 mTorr, much lower than is typical in TD-LIF instruments due to the low flow from the GC column (~5 sccm helium). Under such conditions, the fluorescent photon counting rate is proportional to the number density of NO$_2$ molecule in the cell, rather than the mixing ratio. We keep the cell pressure constant through temperature ramping of GC oven, the electronic pressure control system is set for “constant flow” mode where automatic compensation of helium conductance change during temperature ramping is performed to maintain a constant volumetric flow under ambient pressure at the tail of GC column.

At low pressure in the detection cell, the fluorescence lifetime of NO$_2$ in helium is ~30 µs, favoring the use of gated excitation and fluorescence detection for optimized S/N ratio. A DG535 (Stanford Research System) is used as pulse generator to control the delay and width of laser gate (10 µs) and PMT gate (50 µs), at a repetition rate of 12 kHz. Photon counts are collected at 10 Hz interval to accurately capture peak shape in the chromatogram. Typical GC peak widths (FWHM) are ~3 sec.

To improve long-term laser stability, a photodiode with bias at 0 V is used to provide a voltage feedback signal on the laser current controller. Since the laser output is pulsed, a peak detector with slow output time constant of 0.1 sec is used to condition the signal from photodiode to avoid oscillations in laser control loop.
A pre-concentrator type sampler was designed to work with the GC system to achieve direct gas phase sampling capability (Figure 5.3). During the sampling stage, organic nitrates are introduced through the 8-port valve to the adsorption media positioned within the cold block for a prescribed collection time under a sample flow of 180 sccm. The injection mode is initiated by switching the 8-port valve to the alternative position along with pushing the adsorption media to the desorption position at a temperature of 200ºC. Multiple adsorption media were tested including TENAX resin commonly used for ambient VOC sampling. While TENAX resin has high affinity toward organic nitrates, eliminating the need to cool the media during sampling, it was not possible to release organic nitrates at a reasonably low temperature to allow quantitative desorption onto the GC column. We found glass wool to be an effective trapping material. The glass wool is cooled with a closed circulation system using hexane as coolant and isopropanol-dry ice bath as the heat sink, at approximately -50ºC. Glass wool is inert and provides surface area for adsorption with a minimum of retention of organic nitrates during desorption. To eliminate the possibility of overheating our sample during desorption while achieving a rapid transfer to the GC inlet, the glass wool was embedded in a thin-walled glass tube designed to slide alternately between a cold block for trapping and hot region for desorption. Compared to flash heating the sampler tube with programmed heater pulses, this configuration ensures that the maximum set temperature is never exceeded. The end of the sampler is designed to accept GC column directly by a press-fit connector with minimum dead volume to reduce peak broadening and providing an all-glass surface to the sample flow.

Dual column configuration

A helium ionization detector (HID, Valco Instrument Co. Inc. model D-2) is added to the system as a general detector for direct comparison with TD-LIF detector. Briefly, the HID is a window-less photoionization detector using pulsed discharge of helium gas to generate VUV in the range of 13.5 to 17.7 eV. The VUV light photo-ionizes most organic molecules and the change of ion current measured with collector electrode is converted to voltage as output. To allow direct comparison with chromatogram obtained with TD-LIF, two identical columns are used with flow splitting after the pre-column (3 m, deactivated fused silica). The alternative method for parallel detection where both detectors connect to the end of a single column was not possible due to the difference in operating pressure of the two detectors. The dual column configuration buffers the flow difference through the TD-LIF operating at vacuum and the HID at atmospheric pressure to give similar retention behavior with a temporal offset of ~3.7 sec.

Data System

The data system consists of a home-built data acquisition module which is hardware-clocked for consistent timing of PMT count accumulation with zero dead time between counting windows (100% duty cycle). A schematic of the system is shown in Figure 5.4. The idea behind this system is to transfer most of the timing-critical operation from software (Lab view programs loops) to hardware (crystal oscillators) so that the stability of the data system is essentially
independent of the computer. A single National Instrument NI USB-608 is used only as a digital interface between the computer and the data module.

The data module consists of a digital counting channel and an analog channel both triggered by the same 10 Hz time base pulse generated by a 1.0 MHz crystal oscillator. The counting depth of the digital channel is 24 bit (16777216) per 0.1 sec, equivalent to a maximum count rate of 167 MHz which is not limiting compared with the 14 MHz maximum rate from the PMT. Sufficient channel depth is important for dynamic range in GC applications due to the large variation in count rates in a chromatogram, especially in concentrated samples. The analog channel is used for converting the analog output from HID (2 column configuration) to digital signal at the same 10Hz interval as the photon counts. A 24-bit \( \Sigma-\Delta \) ADC (analog to digital converter, Analog Devices, AD7710AN) controlled by a micro controller (Atmel Co., AT89S51) is used for this purpose and is sufficient to resolve small signals from HID output while maintaining the full scale swing.

The necessary data throughput of this system is modest, at 60 bytes per second. To further improve the immunity against data loss, an output buffer is implemented with another micro controller (AT89S51) to handle asynchronous data transfer between the data module and computer. The internal RAM of the micro controller is used as a first-in-first-out (FIFO) buffer to temporary store data when the computer is busy. The assembly program for both micro controllers and the general wiring scheme is included in Appendix D.

5.3. Performance

\textbf{GC-TD-LIF}

\[ N_{NO_2} = \sum_i S x_i v \rho \]  

The sensitivity of LIF system used in this instrument is 20 counts per ppb NO\(_2\) per second with a baseline level of ~100 counts per second of which 75% can be attributed to PMT dark count. Calibration of the LIF sensitivity is carried out by injecting a NIST traceable NO\(_2\) standard at the same flow rate as the GC effluent before the O\(_2\) addition point so that the dilution may be accounted for automatically. Organic nitrate quantification is achieved by peak area integration of TD-LIF generated chromatogram. In essence, the PMT counts observed in each 0.1 second counting bin \((x_i)\) represents the instantaneous NO\(_2\) concentration in the eluted gas. The total number of molecules for a specific organic nitrate \((N_{NO_2})\) is the integrated peak area scaled by sensitivity of the detector \((S, \text{ ppb per PMT count per bin})\), total volume eluted in each bin \((v, \text{ cm}^3 \text{ per bin})\) and a conversion factor relating mixing ratio to molecular number density \((\rho)\) as in Equation 1. It is noted here that \(v, S\) and \(\rho\) are constants throughout the temperature program and the relative intensity of organic nitrate peaks relates directly to relative concentration within a chromatogram.
Due to the improved laser stability from photodiode feedback control, the absolute baseline level does not contribute to the determination of detection limit. Instead, the baseline counting statistic places the limit on peak detectability. The baseline counting noise follows Poisson distribution with a standard deviation of 3.3 counts in a 10 Hz counting window. For a typical peak width of 3 seconds, the baseline noise contribution to the integrated counts is ±35 counts at 95% confidence interval. A peak with such minimum integrated intensity corresponds to 12 fmol (1.2×10^{-14} mol) which represents the detection limit for species with known retention time in the absence of interference from neighboring peaks. For finding previous unidentified peaks as well as limit of quantification, we suggest a peak height 3σ of baseline noise which corresponds to 106 fmol (1.06×10^{-13} mol) with ±10% quantification uncertainty (95% confidence) at this level due to integrated baseline noise.

Nitrate transmission has been confirmed using an organic nitrate injection with standards of known concentration. n-propyl nitrate and 2-ethylhexyl nitrate (Sigma-Aldrich, 97%) were used without further purification to make standard solutions containing each compound at around 2×10^{-11} mol/µl in dichloromethane. The repeated syringe injections with on-column inlet show method precision of 3% (1σ) and accuracy of 10% while the transmission efficiency is at 100% within the rated uncertainty. The GC temperature program was optimized to ensure separation of organic nitrates while keeping the residence time short to avoid in-column decomposition. Current temperature program is as follows: 30°C hold for 2 minutes, 30°C to 80°C at 60°C per minute, 80°C hold for 3 minutes, 80°C to 180°C at 30°C per minute, 180°C hold. We also employed the system to detect the isoprene hydroxy nitrates used in the experiments described in Chapter 2 (Figure 5.5).

**Sampler**

The sampler performance including adsorption efficiency, desorption efficiency and peak sharpness was characterized and optimized using diluted 2-ethylhexyl nitrate vapor in N\textsubscript{2} gas. The concentration inferred from peak area integration by operating the sampler with a well defined sample flow rate and sampling time matches well with direct gas phase measurement using TD-LIF, as shown in Figure 5.6, indicating no appreciable loss or decomposition during both the adsorption and desorption stage. Generally, the sample flow is set between 100 to 200 sccm regulated with a mass flow controller. The cooling of the adsorption media places upper limit on sampling flow because the heat carried by the sample flow must not overwhelm the cooling power transferred onto the sampling media. Higher adsorption temperatures correspond to lower adsorption efficiency hence reduce the overall transfer efficiency of the sampler. The peak width is ~3 sec FWHM for species with retention time longer than 300 sec. Volatile (low molecular weight) compounds are more difficult to focus at the column head. Minor peak tailing is observed as shown in Figure 5.5 due to retention by the sampler. Overall, with a sample flow rate of 180 sccm without adsorption/desorption loss during sampling the quantification limit is 10 ppt organic nitrate per minute of sampling time.
5.4. Limitations

Thermal decomposition is the general problem associated with efficient detection of large or multi-functional organic nitrates. For example, 2-ethylhexyl nitrate is more thermally robust than β-4,3 hydroxy nitrates used in Chapter 2 in spite of the fact that both compounds elute at a similar GC retention time. To estimate general nitrate transmission efficiency using known thermal decomposition kinetics of n-propyl nitrate\textsuperscript{160}, we calculated the probability of decomposition at each time step with corresponding oven temperature to show the total fraction of nitrate remaining if being eluted at indicated retention time in Figure 5.7.

\begin{equation}
\ln x(\tau) = \int_{0}^{T} A e^{-E_a/k_b T(t)} dt \quad (2)
\end{equation}

Equation 2 is used for this calculation with $(E_a/k_b) = 20129$ K and $A = 3.16 \times 10^{16}$ s\(^{-1}\) from n-propyl nitrate data, $x$ representing the fraction of organic nitrate remaining at retention time $\tau$ and $T(t)$ representing the oven temperature as a function of time. The decrease of nitrate transmission at late elution time reflects in-column decomposition and puts an lower limit on volatility for compounds that can be analyzed with this method. So far, the least volatile organic nitrate we’ve tested is 2,3-dihydroxy-4-(nitrooxy)butyl nitrate with 2 hydroxy and 2 nitrate groups on a butane backbone synthesized in our lab and verified with NMR spectrometry. As a white crystalline solid under room temperature, the di-nitrate has a retention time of ~600 sec. For comparison, β-caryophyllene with boiling point of 264ºC shows up at retention time of 545 sec. This suggests that hydroxy nitrates with nominal boiling point exceeding 264ºC and ~1 ppb vapor pressure\textsuperscript{59} can be observed with this instrument.

It is noted that the calculation behind Figure 5.7 did not take total pressure change in the course of elution into consideration. However, pressure changes are not important inside the column since it is always above ambient pressure (TD oven acting as a flow restrictor) and the rate constants will be at the high pressure limit.

5.5 Comparison

Our sensitivity (12 fmol, 95%) compares well with the GC-TD-Luminol detector by Hao et al.\textsuperscript{158}, who reported a detection limit regarding a known nitrate compound to be 50 fmol at 99% confidence interval. Further, TD-LIF appears to be immune to excessive solvent concentration which was observed to generate negative peaks for the luminol detector. Also, the operation of TD-LIF is generally simpler compared to luminol detector which requires handling of consumable solutions. Similar advantage applies over HPLC methods which typically require chemical modification of the nitrooxy groups for effective transmission. With respect to mass spectrometry, the time resolution of GC-TD-LIF system is limited by the run cycle of the temperature program of ~30 min and therefore not suitable for measurements requiring fast time response. However, a significant advantage of our system is the capability to distinguish structural isomers, as demonstrated in Chapter 2 where all first-generation isoprene hydroxy
nitrates have the same molecular mass and therefore indistinguishable using single stage mass spectrometry. Recent evidence from cross-calibrations between GC-TD-LIF and two types of CIMS (CF$_3$O$^-$ and I$^-$) indicates that the relative ion yield of different isoprene hydroxy nitrate isomers vary depending on the specific reagent ion used. For example, with CF$_3$O$^-$ the relative sensitivity among hydroxy nitrate isomers are all within a factor of 2 of each other, while for I$^-$ the sensitivity between cis- and trans- δ isomers can differ by an order of magnitude. This suggests a single calibration factor may not be applicable for estimating the total concentration of isoprene hydroxy nitrates using mass spectrometry in all locations and GC-TD-LIF can provide important isomeric distribution data under such circumstances.

5.6. Summary

A prototype GC-TD-LIF system which compares favorably in performance with previous designs was described. The use of the modified GC-TD-LIF system in Chapter 2 alongside CF$_3$O$^-$ CIMS demonstrates the potential of quantification and identification of isomeric organic nitrates without the need for separate calibration with purified authentic standards. Multi-functional organic nitrates such as those found in biogenically influenced environments can be routinely and specifically detected with this instrument.
Figure 5.1
Simplified schematic of the GC-TD-LIF system operating under dual column configuration with a pre-concentration sampler. An 8-port valve is used to switch between sampling and GC mode by changing the direction of helium carrier gas and the air sample flow.
Figure 5.2
NO$_2$ formation yield from thermal-decomposition of n-propyl nitrate as a function of temperature. Note that in a pure helium environment, ~40% of NO$_2$ is lost to radical chemistry. Addition of O$_2$ at a volume ratio of ~5% resolves this issue and gives 100% NO$_2$ yield at 400ºC.
The sampler, measuring at 2.5 inch wide and ~10 inch tall, with the front cover removed. The lowest section (E) is positioned inside the GC oven to eliminate any cold spots in the sample transfer line. The functions of the marked sections are as follows. A: linear slide carrier to move the adsorption medium between the cold block during trapping and the hot block during the desorption stage. B: Union section made from PEEK (Polyether ether ketone) joining the glass sampler lining to the stainless steel Swagelok fittings. C: Cold block with internal channels for circulating coolant. D: Area to be heated by nichrome wire insulated by high temperature cement. E: Press joint for direct connection to the GC column.
Figure 5.4
Simplified schematic of the data acquisition module. The direction of the arrows indicate control relationships.
Figure 5.5
GC-TD-LIF chromatogram of a sample mixture of the 3 isoprene hydroxy nitrates as synthesized in Chapter 2. A: 3-methyl-2-nitroxybut-3-ene-1-ol; B: (Z)-2-methyl-4-nitroxybut-2-ene-1-ol; C: (E)-2-methyl-4-nitroxybut-2-ene-1-ol.
Figure 5.6
Pre-concentrator sampler efficiency tested on 672 ppb of 2-ethylhexyl nitrate sample in N\textsubscript{2} at 4 different total volumes collected in units of cm\textsuperscript{3} under standard condition (scc). The measured concentration is obtained by peak area integration of the resulting chromatogram expressed in ppb·scc. The slope is the inferred nitrate sample concentration.
Figure 5.7
Typical alkyl nitrate transmission efficiency calculated using the thermal dissociation parameters measured for n-propyl nitrate as a function of retention time under GC temperature program shown.
Chapter 6

Conclusion

6.1. Summary

Atmospheric oxidation is a complex process with contributions from both natural processes and human perturbations. For organic molecules their oxidation involves multiple pathways operating in parallel, leading ultimately to the common endpoint of CO$_2$. It is because of the variety of the intervening processes that the organic compounds in the atmosphere are manifold and contain a diverse array of functional groups as well as a diverse array of products deriving from the individual oxidative sequences of primary emissions. In principle, observations of this ensemble of organic molecules contain all the information about the emission and oxidative processes in the atmosphere. However, it is impossible to measure all the compounds, and simplifications are necessary to condense the complexity in order to understand the key processes. In this dissertation I demonstrate that it is possible to use a subset of molecular species, namely organics that contain nitrooxy groups, to gain insight into some of the dominant atmospheric processes, in particular those with close ties to the formation of O$_3$ and organic aerosol.

In Chapter 2, I investigated the daytime chemical fate of major isomers of isoprene-derived hydroxy nitrates by conducting an environmental chamber study under high NO$_x$ conditions to simulate forested regions influenced by anthropogenic emissions. The results indicate that these particular hydroxy nitrates are short-lived (2 to 3 hours), yet retain their nitrooxy moiety in the subsequent product molecules. The retention of the nitrooxy group lengthens the lifetime of the compound class of organic nitrates, making them more important as a reservoir of NO$_x$ and extending their influences over greater distances. The co-production of a di-nitrate compound was also observed and may play a role in aerosol formation in forested regions.

In Chapter 3, another pathway for atmospheric organic nitrate formation—specifically from heterogeneous oxidation on organic aerosol surfaces—was explored. In this study, I tracked the composition change of squalene aerosol exposed to NO$_3$ in a flow tube reactor. I demonstrated that, for highly oxidized aerosol, the organic matrix may become increasingly activated toward further heterogeneous oxidations, as manifested by the increase in the effective reactive uptake coefficient observed. This effect accelerates organic aerosol aging, and has implications for rates of radical reactions in the condensed phase for regions with high anthropogenic activities.

In Chapter 4, I studied the source of alkyl nitrates under the influence of oil and gas extraction operations in a field study in northeastern Utah in 2012. For this alkane-dominated environment due to hydraulic fracturing, in Part A, I presented direct field observations of the temperature dependence of the ensemble-averaged alkyl nitrate yield and its related effect on local O$_3$ production rates. Using two independent methods of analysis, I demonstrated that the observed enhancement in alkyl nitrate yield at low temperatures is large and can be predicted.
based on prior laboratory measurements on individual alkanes. The temperature sensitivity of the alkyl nitrate yield results in a much larger temperature dependence of the local \( \text{O}_3 \) production rate than would have been predicted by the temperature dependence of the OH reactivity of the VOCs alone. It also causes large changes in the \( \text{O}_3 \) production rate compared to standard models that neglect this temperature dependence. In Part B, the observation of particulate organic nitrate concentrations is described. The organic nitrates partitioned predominantly into the sub-0.5 µm size range, consistent with previous impactor observations. With constraints from gas phase organic nitrates and VOC measurements, I demonstrated that both gas phase condensation (secondary organic aerosol pathway) and heterogeneous oxidation by \( \text{NO}_3^- \) are important sources of the particulate organic nitrates observed.

In Chapter 5, I provided a detailed description of the GC-TD-LIF system used for quantification and identification of multi-functional organic nitrates. This system provides better sensitivity and is easier to operate than the previous iteration which used luminol solution for detection.

6.2. Outlook

6.2.1. Isoprene hydroxy nitrate chemistry

Explicit measurements of rate constants and product distributions of the 3 major hydroxy nitrate isomers from first generation isoprene oxidations are presented in this dissertation. However, uncertainties persist regarding the fate of the other 5 isomers for which the product distribution can only be inferred from the current dataset by arguments of similarity. To completely describe the chemistry of these molecules, the oxidation rates and product channels for at least 2 other hydroxy nitrates, namely the cis-δ-4,1 and β-1,2 hydroxy nitrates, should be measured. The β-1,2 hydroxy nitrate is more difficult to synthesize and purify than the δ-1,4 isomers but has the highest yield from isoprene OH oxidation under high \( \text{NO}_x \) conditions, making it especially important that its oxidation be measured directly. It will also be important to measure the product distribution of \( \text{NO}_3^- \)-initiated oxidation of isoprene hydroxy nitrates, as the isoprene nitrates can exist at nighttime either as residual compounds from daytime chemistry or direct products due to nighttime chemistry of \( \text{NO}_3^- \). Lastly, the aerosol forming properties of di-nitrates should be examined, with focus on accommodation coefficients. For example, preliminary results from total particulate organic nitrate measurements in a forested site (Southern Oxidant and Aerosol Study) suggest that a substantial portion of the organic nitrate compounds observed exist in the aerosol phase. To understand this result, it would be useful to examine the uptake of biogenically-derived multi-functional nitrates onto organic and aqueous aerosols. Hydrolysis of tertiary nitrates has been reported to be rapid\(^{18}\) and this chemistry is likely the cause for the irreversibility of the gas-particle partitioning. Nonetheless, direct confirmation of hydrolysis rates for the specific compounds that are produced most rapidly would be an important contribution.

6.2.2. Condensed phase radical chemistry
Condensed phase alkyl radical reactions were a dominant feature of the NO$_3$ + squalene aerosol experiment. It was suggested in Chapter 3 that the aerosol organic matrix remained a fluid and I estimated a lower limit to the liquid-phase diffusivity. However, an alternative explanation to overcome the diffusion limit for the oxidation is through radical propagation reactions. It would therefore be interesting to explore the possibility of radical propagation through hydrogen exchange or the opening of double bonds on neighboring molecules in the condensed matrix. If this radical propagation condition is satisfied, the condensed phase oxidation may be initiated at the particle surface but effectively oxidizes molecules buried internally, regardless of whether internal mixing can be achieved. Understanding this process will have implications for the aerosol aging mechanisms as it accelerates the aging process through secondary reactions and avoids the kinetic limitations imposed by aerosol surface freezing.

6.2.3. Constraining secondary organic aerosol (SOA) mass through organic nitrate measurements

Organic nitrate formation in urban areas occurs along the same pathway as atmospheric oxidation, suggesting that there may be a generic link between aerosol mass and organic nitrates in the atmosphere. For the simplest case, consider organics with moderate molecular weight, such as large alkanes observed in Utah. When oxidized once in the presence of NO, either an organic nitrate or an oxygenate is formed. The branching ratio between the two channels can be estimated using the alkyl nitrate yield from an appropriate RO$_2$ precursor. Assuming the oxygenate has the same structure as the organic nitrate except that an OH group is in place of the nitrooxy group, the relative degree of partitioning of the two molecules into the particulate phase is controlled by their respective vapor pressures. Interestingly, a group contribution method for vapor pressure estimation (SIMPOL.1$^{59}$) assigns very similar vapor pressure reduction factors to both nitrooxy and hydroxy groups at ambient temperatures. This suggests that, to first order, the relative contribution of the product organic nitrate and alcohol is set by the alkyl nitrate yield of the precursor. Given that the VOC composition at a particular location is measured, and the appropriate product distribution of the alkoxy radical is taken into account, such as isomerization reactions for long carbon chains, an ensemble-averaged ratio between particulate-phase organic nitrate and oxygenates could be obtained. This relationship could be tested under conditions where SOA mass is constrained independently by concurrent particulate organic nitrate measurements. Furthermore, with the calculated ratio, estimates of aerosol organic mass as a result of partitioning from gas phase oxidation products can be made using aerosol organic nitrate content, and from which a better understanding of the source of organic aerosols under various conditions can potentially be gained.

The above questions are outstanding issues that I believe to be important and follow directly on advances made in this dissertation. Answers to these questions should provide a better understanding of and predictions for tropospheric chemistry in a wide range of environments and
therefore lead to more accurate estimates of human exposure to toxics and the effects of atmospheric chemistry on climate.
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Appendix A (Chapter 2)

A1. NMR assignments

(E)-2-methyl-4-nitrooxybut-2-ene-1-ol (trans-6-1,4 hydroxy nitrate)

NMR spectrum of purified sample of trans-6-1,4 hydroxy nitrate was measured with a Bruker 400MHz instrument in CDCl₃ (Sigma Aldrich, 100% D). Hydrogen on C3 is shown as a triplet centering at 5.640 ppm with coupling constant of 7.2 Hz to the hydrogen on C4 at 4.985 ppm. Hydrogen on carbon 1 and the methyl group are observed as singlet, at 4.074 and 1.757 ppm, respectively. Other peaks upfield from 1.5 ppm are residual solvent peaks such as hexane and water.
(Z)-2-methyl-4-nitrooxybut-2-ene-1-ol (cis-δ-1,4 hydroxy nitrate)

Measured under the same condition as the trans-δ isomer. Similar peak assignment but slight difference in chemical shift of hydrogens on C3 and C4, due to relative position with respect to the methyl group.
3-methyl-2-nitrooxybut-3-ene-1-ol (β-4,3 hydroxy nitrate)

Purified β-4,3 sample after HPLC separation. The 2 singlets at 5.120 and 5.082 ppm locations are the 2 distinct hydrogens at the end of double bond. The triplet at 5.312 ppm couples to the doublet centered at 3.776 ppm with a coupling constant of 5.2 Hz, corresponding to the single hydrogen on the nitrooxy carbon and the 2 equivalent hydrogens on the hydroxy carbon. The methyl group hydrogen appears as a singlet at 1.794 ppm. The peak at 1.555 ppm is due to water. Hydrogen on the OH group is broad.
A2. Wiggle reduction for CIMS signal

It may be observed that the CIMS signal has certain fluctuation during the decay. Such fluctuation was thought to relate to temperature of the analog-to-digital conversion board currently being used. The temperature fluctuation on the ADC board affects the counting of the ions with a fixed pre-set discrimination threshold. Overall the temperature fluctuation gives a signal variation of approximately 6%, and may be corrected by observing that similar fluctuation is present for the total ion counts. A long running average (3600 sec) is applied to the total normalized CIMS ion signal to obtain the baseline of the correction. The correction factor is then calculated by dividing the 1 Hz CIMS total ion signal to the long-averaged value. The resulting correction factor is a time series that has the same fluctuation as the signal, but with a normalized value centering at unity. By applying the correction as a multiplicative factor, a smoother decay is obtained, as shown in figure below.
A3. Possible interferences and minor reactions

In determining rate constants using relative method, interferences arise when more than one oxidant contribute to the consumption of the intended reactant and reference compounds. Under our OH experimental conditions, other possible oxidants are O₃, HO₂, RO₂ and O³P. Ozone reaction with propene and hydroxyl nitrates are much slower than OH reaction, with a rate constant around $1 \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹. With the measured O₃ concentration, we estimate the contribution to be less than 4%, well under our uncertainty. For HO₂, due to the excess H₂O₂ and NO in our system, the ratio of HO₂ over OH is generally around 5. Since HO₂ reaction with alkene is more than 6 orders of magnitude slower¹⁶¹ than OH, the HO₂ direct contribution should be negligible. The rate constant of reaction between alkene and alkylperoxy radicals are expected to be slow¹⁶², likely less than $1 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ and should not be able to compete under 100 ppbv of NO. Lastly, O³P is formed under UV irradiation of accumulated NO₂ in our chamber, and has been shown to react with alkene by addition reaction to yield oxirane¹⁶³ or, through hydrogen shift, ketones. Direct observation of the corresponding mass at m/z = 248 has been observed, with a tentative yield of 1.3% assuming the same sensitivity as trans-δ-1,4-hydroxy nitrate. Note that both oxirane and the isomerized ketones have the same mass. Assuming O³P reaction with hydroxy nitrate yields near 100% m/z = 248, this corresponds to an additional loss to our reactant of 1.3%. Using box model simulation with measured UV spectrum from the light banks and absorption cross section data, we estimate the fraction of reactant reacted with O³P to be of 0.6% using a rate constant of $3.5 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (Paulson et al., 1995¹⁶⁴), both considered to be insignificant.

Potential mass interferences from oxidation products other than ones originating from hydroxy nitrate exists and can affect estimation for product yield. Hydroxy acetone, a direct product from δ hydroxy nitrates monitored at m/z = 159 can also be formed from a minor channel in OH oxidation of propene from the corresponding β-hydroxy alkoxy radical reaction with O₂. Under our experimental condition the yield is estimated to be 1.4%. For δ hydroxy nitrate experiments the amount of nitrate reacted is very similar to the amount propene reacted, hence the net contribution of m/z = 159 from propene is only around 3%. Photolysis of some of the carbonyl compounds formed has also been considered, given the availability of literature data and we have found that the loss is too slow to have significant modification to our observed products. Due to the limited photolysis data for functionalized organic nitrates, we use nitrooxy acetone¹⁶⁵ as a surrogate for ethanal nitrate (m/z = 190) and methyl vinyl ketone nitrate and methacrolein nitrate (m/z = 234) and obtained a photolysis lifetime of ~48 hours from our light bank emission spectra, much longer than our typical experiment running time of ~2 hours.
In order to achieve a reasonable representation of RO$_2$+RO$_2$ chemistry, 2 collective species are introduced, designated as (t)RO$_2$ and (p,s)RO$_2$ standing for the collective concentration of tertiary and non-tertiary peroxy radicals, respectively. The reason for such distinction is to account for the availability of $\alpha$-hydrogen when proceeding through the alcohol and carbonyl forming channel of RO$_2$+RO$_2$ reactions. In cases when both RO$_2$ radicals are tertiary, this channel will be prohibited and an enhancement in alkoxy radical forming channel is expected. Alternatively when a tertiary RO$_2$ reacts with a primary or secondary RO$_2$, the tertiary RO$_2$ can only transform into the associated alcohol while the non-tertiary counterpart forms a carbonyl. Considerations for this functional group dependence and channel suppression are incorporated in our parameterizations. The collective species are not “consumed” when propagating the master equation, as equations 7~10 are formulated in such a manner that the product stoichiometry corresponds to the consumption of one ISOPOO$_x$ molecule only (not one ISOPOO$_x$ and one (x)RO$_2$). The product from all other RO$_2$ partner are calculated when iterating through all the RO$_2$ species. Note that when calculating (t)RO$_2$ and (p,s)RO$_2$ from lumped RO$_2$ species an estimation of the tertiary fraction of the lumped species may be necessary. For example, under the criteria of mass balance, ISOPNOO$_\delta$ should be considered as consisting of 0.91 (t)RO$_2$ and 0.09 (s,p)RO$_2$, while ISOPNOO$_\beta$ contains 0.36 (t)RO$_2$ and 0.64 (s,p)RO$_2$. Values for (t)RO$_2$ and (s,p)RO$_2$ are refreshed in each simulation step to reflect the current RO$_2$ concentration.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>k (298K) cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ISOPNOO$_\delta$ + (t)RO$_2$ $\rightarrow$ 0.83 HO$_2$ + 0.05 ROOR + 0.06 R=O + 0.1 MVKN + 0.42 PROPNN + 0.3 ETHLN + 0.3 HACET + 0.42 GLYC + 0.1 HCHO</td>
</tr>
<tr>
<td>2</td>
<td>ISOPNOO$_\delta$ + (p,s)RO$_2$ $\rightarrow$ 0.47 HO$_2$ + 0.02 ROOR + 0.03 R=O + 0.65 DHDN + 0.13 PROPNN + 0.11 ETHLN + 0.11 HACET + 0.33 GLYC + 0.03 HCHO</td>
</tr>
<tr>
<td>3</td>
<td>ISOPNOO$_\beta$ + (t)RO$_2$ $\rightarrow$ 0.31 NO$_2$ + 0.19 HO$_2$ + 0.03 ROOR + 0.44 R=O + 0.13 MVKN + 0.06 MACRN + 0.31 HACET + 0.31 GLYC + 0.19 HCHO</td>
</tr>
<tr>
<td>4</td>
<td>ISOPNOO$_\beta$ + (p,s)RO$_2$ $\rightarrow$ 0.18 NO$_2$ + 0.1 HO$_2$ + 0.03 ROOR + 0.22 R=O + 0.46 DHDN + 0.04 MVKN + 0.06 MACRN + 0.18 HACET + 0.18 GLYC + 0.1 HCHO</td>
</tr>
</tbody>
</table>

$^{\dagger}$ Estimated using the rates from Jenkin and Hayman (1995)$^{168}$
ROOR = Organic peroxide
Appendix B (Chapter 3)

B1. Derivation of $\gamma$ from N$_2$O$_5$ loss

Consider an aerosol particle suspended in air with radial transport of reactive nitrogen onto the particle surface. In the far field where transport is governed by Fick’s diffusion, the total radial molecular flux ($F$, number of molecules per second) is proportional to the gradient of reactive nitrate concentration, as shown in equation b1 where $r^*$ represents the radius of inner boundary beyond which diffusion transport is assumed, $\rho(\infty)$ and $\rho(r^*)$ the concentration at infinity and at the boundary, respectively and $D_{N_2O_5}$ the diffusion constant. Within the boundary, typically within one mean free path above the particle surface, simple molecular collision is assumed for surface-bound transport, represented as a function of $\rho(r^*)$ in equation b2 where $f$ denotes the equilibrium ratio of [NO$_3$]/[N$_2$O$_5$], $A$ the surface area of the particle under consideration and $\langle v \rangle$ the average molecular speed of NO$_3$. It is noted here that the factor (1/4) comes from accounting for half of molecules having velocity component going toward the particle surface and steric angle considerations. By requiring $F_d = F_c$ under steady state condition, $\rho(r^*)$ may be solved and the flux presented as a function of $\rho(\infty)$. Assuming the concentration depletion region from each particle does not overlap, the N$_2$O$_5$ loss rate through NO$_3$ uptake is shown in equation b3 in which $n_p$ denotes the particle number concentration.

\begin{equation}
F_d = (\rho(\infty) - \rho(r^*)) r^* 4\pi D_{N_2O_5} \tag{b1}
\end{equation}

\begin{equation}
F_c = \rho(r^*) f A \frac{\langle v \rangle}{4} \tag{b2}
\end{equation}

\begin{equation}
- \frac{d[N_2O_5]}{dt} = n_p \frac{[N_2O_5]}{r^* 4\pi D_{N_2O_5} + \frac{4}{f\gamma A(v)}} \tag{b3}
\end{equation}

Derivation of equation b3 assumes diffusional transport of reactive nitrogen as N$_2$O$_5$, based on the fact that N$_2$O$_5$ has a much longer lifetime than NO$_3$. Also there is minimal NO$_2$ concentration enhancement near the particle surface from loss of NO$_3$ by N$_2$O$_5$ decomposition and $f$ is calculated from directly measured NO$_2$ concentration. Noting that diffusion resistance is only around $10^{-5}$ of the collisional resistance for the particle size range we used, dropping it in equation b3 gives the corresponding simplified formulation for second order $k$ (per area density per second) measurable in this experiment (equation 3.2).
B2. Brief description of box model

A box model with simplified aerosol evolution module has been developed to simulate surface uptake behavior of squalane. Gas phase and condensed phase components are represented in the same manner, while aerosol surface concentrations are allowed to evolve due to coagulation and wall loss. Condensed phase components are assumed to be homogeneous and not size dependent. For the aerosol module, measured particle distributions were re-binned with uniform bin width (log(2)/3) under log scale so that coagulation of 2 particles of the same size will fall to the next size bin. Only brownian and 2-body coagulations were accounted within each time step assuming unity coagulation efficiency for liquid particles.

Reactions incorporated in squalane simulations are listed below. All rate constants are calculated at 293 K and 1 atm. “Surface” denotes surface concentration from aerosol in unit of cm\(^2\)/cm\(^3\). C_NO represents the collective species from all chain-termination products in equation 3 in the aerosol phase. It is noted that the wall loss reactions (4 and 5) are set using blank runs with no particle added to the flow tube and are flow tube dependent. Measured particle size distributions, NO\(_2\) concentration and N\(_2\)O\(_5\) concentrations are used as starting parameters for each simulation run for various aerosol loading conditions.

<table>
<thead>
<tr>
<th>#</th>
<th>Rate expression</th>
<th>Rate constant 293K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO(_2) + NO(_3) → N(_2)O(_5)</td>
<td>1.25×10(^{-12}) cm(^3) s(^{-1})</td>
<td>ATK</td>
</tr>
<tr>
<td>2</td>
<td>N(_2)O(_5) → NO(_2) + NO(_3)</td>
<td>2.39×10(^{-2}) s(^{-1})</td>
<td>ATK</td>
</tr>
<tr>
<td>3</td>
<td>NO(_3) + NO(_3) → NO(_2) + NO(_2) + O(_2)</td>
<td>1.99×10(^{-16}) cm(^3) s(^{-1})</td>
<td>DEM</td>
</tr>
<tr>
<td>4</td>
<td>NO(_3) → wall loss</td>
<td>0.41 s(^{-1})</td>
<td>This study</td>
</tr>
<tr>
<td>5</td>
<td>NO(_3) → NO(_2) (wall conversion)</td>
<td>1.3 s(^{-1})</td>
<td>This study</td>
</tr>
<tr>
<td>6</td>
<td>NO(_3) + Surface → C_NO(_3)</td>
<td>13 cm s(^{-1})</td>
<td>This study</td>
</tr>
<tr>
<td>7</td>
<td>NO(_3) + Surface → NO(_2)</td>
<td>24 cm s(^{-1})</td>
<td>This study</td>
</tr>
<tr>
<td>8</td>
<td>N(_2)O(_5) + Surface → C_NO(_3) + NO(_2)</td>
<td>0.13 cm s(^{-1})</td>
<td>This study</td>
</tr>
<tr>
<td>9</td>
<td>N(_2)O(_5) + Surface → NO(_2) + NO(_2)</td>
<td>0.22 cm s(^{-1})</td>
<td>This study</td>
</tr>
</tbody>
</table>

ATK: Atkinson et al., 2004\(^{125}\); DEM: DeMore et al., 1997\(^{167}\)
B3. Calculation of oxidation ratio as a function of time

Consider a particle of certain diameter, the inbound flux of NO$_3$ molecule can be calculated using known value of the particle surface area ($A$), molecular collision rate ($Z_{NO_3}$) and reactive uptake coefficient ($\gamma$) for any given instant. The time integration of the NO$_3$ flux yields the total number of NO$_3$ molecules ($N_{NO_3}$) reacted in the condensed phase. Dividing $N_{NO_3}$ by the number of squalene molecules in the particle gives us the oxidation ratio ($x$), as shown in equation b4.

$$N_{NO_3} = \int_0^\tau Z_{NO_3} \cdot A \cdot \gamma(x) \, dt \quad ; \quad x = \frac{N_{NO_3}}{N}$$  \hspace{1cm} (b4)

Since reactive uptake coefficient is a function of oxidant ratio $x$ as shown in our experiment, we may rearrange and collect terms in equation S4. Integrating on both sides gives us equation b5.

$$\int_0^{x\tau} \frac{1}{\gamma(x)} \, dx = \int_0^\tau \frac{Z_{NO_3} \cdot A}{N} \, dt$$ \hspace{1cm} (b5)

Equation b5 relates oxidation ratio to the reaction time in an atmosphere specified by the NO$_3$ collision rate and aerosol surface area and may be integrated numerically to give $x$ at time $\tau$. It is implied that diffusion in the gas phase does not become limiting in supporting the inbound NO$_3$ flux, which is true in our experimental condition. For a typical nighttime condition of 5 ppb NO$_2$ and the NO$_3$ uptake coefficient of 1 with established equilibrium between NO$_3$ and N$_2$O$_5$, the N$_2$O$_5$ concentration near the surface of a 126 nm diameter particle is only attenuated by 5% comparing with concentration at theoretical infinite separation from particle hence we may ignore diffusion transport in this case.
Appendix C (Chapter 4)

C1. O₃ pyrolysis correction for ΣANs (380°C) channel

It was necessary to correct for apparent negative signals observed in the ΣANs signal (ΣANs channel showing less signal level than the ΣPNs channel). The cause of this interference was O₃ pyrolysis to yield O atom in the TD oven at elevated temperature. In the absence of organic molecules, the O atom can serve as a promoter for NO and NO₂ interconversion reaction, as illustrated in Equation c1.1 to c1.3.

\[
\begin{align*}
O_3 & \underset{M}{\longrightarrow} O_2 + O \quad \text{\quad (c1.1)} \\
O_2 + O & \underset{M}{\longrightarrow} O_3 \quad \text{\quad (\neg \text{c1.1})} \\
NO_2 + O & \longrightarrow NO + O_2 \quad \text{\quad (c1.2)} \\
NO + O & \underset{M}{\longrightarrow} NO_2 \quad \text{\quad (c1.3)}
\end{align*}
\]

NO and NO₂ are interconverted at a cost of one O atom whose steady state concentration is generally controlled by the forward and reverse reaction of c1.1. If sufficient time is given, NO and NO₂ will ultimately reach an equilibrium ratio which can be calculated from the reaction rate \( k_{1.2} \) and \( k_{1.3} \) with pressure dependence. From the O₃ pyrolysis rate and the gas residence time of 0.17 second in our TD oven region, only ΣANs channel at 380°C should generate sufficient O atom to significantly alter the NO₂ concentration. To confirm this effect, we performed a series of lab experiments under NO₃ and O₅ concentrations covering the range observed during the UBWOS campaign in the presence of ~2 ppb of 2-ethylhexyl nitrate, a simple alkyl nitrate standard available from Sigma Aldrich as a surrogate for the collection of ΣANs in Utah. The Figure below demonstrates the result from a temperature scan experiment when the inlet oven temperature of cell 1 was scanned upward from 180°C to 380°C, the operating temperature of ΣANs channel in the field. The red trace represents the NO₂ signal from cell 1, while the black trace is the NO₂ signal from cell 3 whose inlet was unheated. Since there was no peroxy nitrate in the system, at 180°C cell 3 only detect the same amount of NO₂ as the ambient temperature cell 1. However, starting from ~200°C alkyl nitrate started to thermal dissociate, giving extra NO₂ signal as the red trace increased relative to the black trace. At temperature beyond 280°C effects due to O₃ pyrolysis started to reduce the excess NO₂ signal, presumably by the interconversion reaction mentioned above and we see the red trace eventually dropped below the black trace at around 320°C. This interference thus generated substantial negative ΣANs signal when we subtract the 180°C channel from 380°C channel. Indeed, significant portions of uncorrected night time ΣANs signals throughout the campaign yielded negative values including negative spikes correlated with positive NO₂ spikes from nearby road traffic emissions. This effect was most prominent when high NO₂ concentration existed so that the excess ΣANs signal was relatively small on the 380°C channel. Considering that under the same O₃ concentration the fraction of NO₂ converted due to O atom chemistry was a constant, larger overall NO₂ concentration corresponded to a larger overall NO₂ reduction which could easily overwhelm the original ΣANs signal to introduce negative values when high temperature channel was subtracted.
from lower temperature ones. For example, we have performed high temperature box model simulations on O$_3$ pyrolysis reactions inside the TD oven with a residence time of 0.17 second. At an O$_3$ concentration of 30 ppb the amount of NO$_2$ loss through 380ºC was around 6%. This indicates that if the ΣANs fraction within a sample is less than 6% of the total concentration from NO$_2$, ΣPNs and ΣANs combined, a negative value will result. The O atom chemistry outlined in Equation c1 was further complicated by the presence of organics, especially when initial NO$_2$ concentration was small as signal loss in lab experiments was always more than can be explained in the absence of organics. Since we were uncertain of the effect of possible chain reactions involving organic radicals initiated by O atom, an empirical equation derived directly from in-lab observations under NO$_x$ and O$_3$ concentrations relevant to UBWOS condition was currently used for such correction. Equation c2 shows the relation of fractional signal lost ($r$) as a function of the observed total signal $S_{380}$ of the 380ºC channel (NO$_2$ + ΣPNs + ΣANs) and O$_3$ concentration with all parameters obtained through fitting of experimental data. The corrected signal ($S'_{380}$) was thus obtained with Equation c3.

$$r = (0.0694 \times ln(S_{380}) - 0.308) \times (0.0115 \times [O_3] + 0.557) \quad (c2)$$

$$S'_{380} = \frac{S_{380}}{1 + r} \quad (c3)$$
C2. VOC $\alpha$ calculation considering multiple generation RO$_2$ formation

$\alpha$ for ethane

\[
\begin{align*}
\text{H}_3\text{C} - \text{CH}_3 & \xrightarrow{\cdot \text{OH}} \text{H}_3\text{C} - \cdot \text{O} - \cdot \text{O} \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} \xrightarrow{(0.981)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \xrightarrow{(0.019)} \text{H}_3\text{C} - \cdot \text{O} + \text{HO}_2 \\
\text{H}_3\text{C} & \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} - \text{NO}_2
\end{align*}
\]

Estimating $\alpha$ for ethane is relatively straightforward. Daytime oxidation of ethane starts with an initial hydrogen extraction by OH radical followed by O$_2$ addition to the alkyl radical formed. Only a single isomer of alkyl peroxy radical is involved and no significant decomposition channel exists for the ethyl alkoxy radical formed from NO reaction that does not yield organic nitrate, as shown in Figure above. We simply state here and will demonstrate in later section that the dominant fate of RO$_2$ radicals in the basin were reaction with NO because RO$_2$ + RO$_2$ and RO$_2$ + HO$_2$ reactions are minor during the day. The number in bracket is specific branching ratio of the processes represented. Branching ratios yielding organic nitrates are colored in blue. The overall nitrate branching ratio in this simple case is the same as the specific branching ratio of the ethylperoxy radical at 0.019.

$\alpha$ for propane

\[
\begin{align*}
\text{H}_3\text{C} - \text{CH}_3 & \xrightarrow{\cdot \text{OH}} \text{H}_3\text{C} - \cdot \text{O} - \cdot \text{O} \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} \xrightarrow{(0.979)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \xrightarrow{(0.021)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \\
\text{H}_3\text{C} & \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} - \text{NO}_2 \\
\text{H}_3\text{C} - \text{CH}_3 & \xrightarrow{\cdot \text{OH}} \text{H}_3\text{C} - \cdot \text{O} - \cdot \text{O} \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} \xrightarrow{(0.948)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \xrightarrow{(0.948)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \\
\text{H}_3\text{C} & \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} - \text{NO}_2 \\
\text{H}_3\text{C} - \text{CH}_3 & \xrightarrow{\cdot \text{OH}} \text{H}_3\text{C} - \cdot \text{O} - \cdot \text{O} \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} \xrightarrow{(0.979)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \xrightarrow{(0.979)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \\
\text{H}_3\text{C} & \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} - \text{NO}_2 \\
\text{H}_3\text{C} - \text{CH}_3 & \xrightarrow{\cdot \text{OH}} \text{H}_3\text{C} - \cdot \text{O} - \cdot \text{O} \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} \xrightarrow{(0.948)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \xrightarrow{(0.948)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \\
\text{H}_3\text{C} & \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} - \text{NO}_2 \\
\text{H}_3\text{C} - \text{CH}_3 & \xrightarrow{\cdot \text{OH}} \text{H}_3\text{C} - \cdot \text{O} - \cdot \text{O} \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} \xrightarrow{(0.979)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \xrightarrow{(0.979)} \text{H}_3\text{C} - \cdot \text{O} + \text{NO}_2 \\
\text{H}_3\text{C} & \xrightarrow{\text{NO}} \text{H}_3\text{C} - \cdot \text{O} - \text{NO}_2
\end{align*}
\]
To calculate the overall nitrate yield for propane, the dominant product channels should be traced, as illustrated in Figure above. 2 isomers are formed through hydrogen extractions from either the primary or secondary carbon, giving n-propylperoxy and iso-propylperoxy radical in a relative yield of 24% and 76%, respectively. The overall nitrate branching ratio can then be calculated if the specific $\alpha$ for each peroxy isomer is known. Starting from n-propylperoxy radical, the direct reaction with NO gives n-propyl nitrate with a relative yield of 2.1% calculated according to the Carter and Atkinson’s method at 273K and 842 mBar, representative of campaign condition. The remaining portion of the channel proceeding through alkoxy radical reactions has a further branching of decomposition reaction (rather than reacting with O$_2$) to form a formaldehyde and an ethyl radical which promptly reacts with O$_2$ to give ethylperoxy radical. The relative yield of decomposition versus O$_2$ reaction can be calculated from the respective reaction rates reported in the literature. We used a decomposition rate of 846 1/s$^{166}$ and the product of O$_2$ reaction rate with O$_2$ concentration giving a first-order rate constant of $4 \times 10^4$ s$^{-1}$ for the O$_2$ channel. Branching ratios are hence 2% and 98% for decomposition and O$_2$ reaction. The ethylperoxy radical from the decomposition channel can then react further with NO to give organic nitrates with a yield of 0.019, calculated in the previous section. Summing up both yields scaled by the individual channel strength, we have the specific nitrate yield of n-propylperoxy radical as: $(0.019 \times 0.02 \times 0.979 + 0.021) = 0.0214$. Note the correction from the additional ethylperoxy radical nitrate yield is almost negligible, due to the decomposition channel strength of only 2%. However, For larger molecules, typically starting from n-butane, isomerization reactions can contribute substantially and higher-generation nitrate yield corrections is generally non-negligible. For iso-propylperoxy radical the specific nitrate yield was calculated using the same principle, only that after decomposition reaction a methylperoxy radical is formed. Since methylperoxy radical has little yield for methylnitrate formation, the total specific nitrate yield for iso-propylperoxy radical is just the direct yield of 5.2%. The overall $\alpha$ for propane-OH reaction is hence the ensemble average of the specific nitrate yield of all peroxy isomers, namely: $(0.24 \times 0.021 + 0.76 \times 0.052) = 0.045$.

$\alpha$ for higher alkanes and other organics

Using the method detailed above for propane, we carried out an extended estimation for alkanes up to undecane which is the largest alkane reported from GC-MS data. The results are summarized in Table 2. It is noted here that certain simplifications were necessary for this calculation. For example, in estimating $\alpha$ for more complex RO$_2$ radicals from higher-generation oxidation products we ignored the possible contribution of other oxygen-containing functional groups toward the estimated yield given by the Carter and Atkinson parameterization so that only carbon number was considered. Further, rate constants used to estimate the relative branching ratios of alkoxy radical reactions were limited to available literature values, generally around 298K. As carbon chain length becomes longer, experimental data regarding O$_2$ reaction, isomerization and decomposition rates become scarce and the data available for the most similar structure are used.
C3. Differences in definition of $\gamma$ used in this work

The $\gamma$ value, used to denote the amount of O$_3$ molecule generated from OH-initiated oxidation of an organic molecule in this work, is different from the definition of previous works that focus on only single generation RO$_2$ chemistry in 2 respects, described as following. First, $\gamma$ has commonly been given a value of 2 for 2O$_3$ molecules being generated per OH-initiated oxidation of VOCs, from the formation of HO$_2$ and NO$_2$ each. This is a good approximation for small alkanes of which isomerization is not important, but can be erroneous otherwise. For example, in the absence of organic nitrate formation channel, we estimate $\gamma$ for n-hexane to be 3.2 due to the efficient isomerization reaction of hydrogen abstraction by the 2-alkoxy or 3-alkoxy radical produced, generating a new alkyl radical and an alcohol group. The presence of large alkanes, up to undecane, necessitate a more careful treatment. Second, $\gamma$ has been used to calculate the ratio of O$_3$ production rate over $\Sigma$ANs production rate, formulated as $\gamma(1-\alpha)/\alpha$. The factor $(1-\alpha)$ in the numerator implies that $\gamma$ was estimated under the assumption of zero nitrate formation. $(1-\alpha)$ therefore accounted for the fraction of reaction that actually proceeded to form O$_3$. This is only exact if VOC + OH reaction only forms a single generation of RO$_2$ molecule, once again a valid assumption for small VOC only. For larger alkanes there is a non-negligible fraction of higher generation RO$_2$ reactions from isomerization reactions and we must account for the effective number of NO$_2$ and HO$_2$ formed in a cumulative manner over extended generations. This means $\gamma$ and $\alpha$ are related by the structure of the molecule under consideration. Our listed $\gamma$ values in table 2 is then the better average number of O$_3$ generated per OH-initiated oxidation with alkyl nitrate formation considered, or in the same spirit, the “$\gamma(1-\alpha)$” value considered over multi-generation reactions. In Table 2, we observe an increasing trend of $\gamma$ going from methane to around hexane as larger alkanes are more susceptible to isomerization and further radical reactions, converting more NO to NO$_2$. This trend does not continue, however, with further increase of alkane size because of the competing effect of increasing organic nitrate yield which reduces the the amount of alkoxy radical formed.
C4. Derivation for aerosol specific volume–nitrate concentration relationship

The third panel in Figure 4b.1 shows the relative importance of total aerosol volume contributions from particles above or under 500 nm size. While we have demonstrated the relative domination of organic/inorganic component has a rough boundary at 500 nm, simply treating this as a cut-off point will likely lead to non-negligible underestimation of organic component that exists in the over 500 nm size range which contained about half of total PM2.5 aerosol volume. We therefore propose a method that utilizes our PM2.5 pΣAN data as tracers and does not require assumptions made on the organic content of the various aerosol size ranges. This method is based on the observation that mineral dust or inorganic salts generally have higher density than organic molecules. But instead of focusing on density which is not an additive parameter, specific volume (cm$^3$/g) is used to factor out the inorganic component by linear combination. Under the particular environment of winter time Utah, we assume no significant aqueous phase present. As mineral dust and salt are not typically soluble in organic phase, the total volume of the aerosol can be treated as a linear combination of volumes from individual immiscible components, such as the equation presented below:

$$\tilde{\nu} = \sum_i \tilde{v}_i \cdot f_i \quad (c4)$$

$$\sum_i f_i = 1 \quad (c5)$$

In Equation c4, $\tilde{\nu}$ is the overall specific volume of the PM2.5 aerosol phase, while $\tilde{v}_i$ and $f_i$ are specific volume and mass fraction of component $i$ in the aerosol phase, respectively. Mass fractions from all aerosol components should add up to 1 (Equation c5). We now name 3 components in the aerosol phase to be considered explicitly. First component $f_{dust}$ represent collectively the inorganic component, including mineral dust and salt. The second and third component both represent the organic phase, but was broken in terms of functionality. We represent the organic nitrate functionality as $f_{HNO3}$ and the rest of the organic group as $f_{CH2}$. The presence of oxygenated groups are treated later in the main text by further breaking down the $f_{CH2}$ component. For the time being, this effectively represent the organic molecules as a nominal equation of $(CH_2)_n(HNO_3)_m$. The inclusion of an extra hydrogen to the -ONO$_2$ group is for valence balance of a fully saturated molecule. The resulting representation for $\tilde{\nu}$ is therefore:

$$\tilde{\nu} = \tilde{\nu}_{dust} \cdot f_{dust} + \tilde{\nu}_{HNO3} \cdot f_{HNO3} + \tilde{\nu}_{CH2} \cdot f_{CH2} \quad (c6)$$

Since it was observed that the nitrate group is a rather consistent component of the organic aerosols (Figure 4b.3), we expect $f_{CH2}$ to vary with $f_{HNO3}$ by a constant coefficient $\gamma$. By further assuming that the specific volume of the nitrate group is the same as the CH$_2$ fragment in a large organic molecule (subsequently called $\tilde{\nu}_{org}$) and using the constraint from Equation c5, we can simplify Equation c6 into Equation 1 in Chapter 4b.
\[ \tilde{v} = \tilde{v}_{dust} + (\tilde{v}_{org} - \tilde{v}_{dust}) \cdot (1 + \gamma) \tilde{f}_{NO3} \]  

We see that this equation predicts a linear relationship between PM2.5 specific volume and mass fraction of the nitrooxy group in the aerosol phase, under conditions where the inorganic and organic components have relatively constant specific mass. We demonstrate that this relation is indeed observed during UBWOS 2012 in Figure 4b.4.
C5. Estimation of ΣAN contribution using extrapolated VOC reactivity.

\[ \begin{align*}
R + OH & \xrightarrow{NO,O_2} R(ONO_2) \quad (\text{Reaction } c1) \\
\xrightarrow{NO,O_2} (1 - \alpha) \cdot \alpha & \rightarrow R(OH)(ONO_2) \quad (\text{Reaction } c2) \\
\xrightarrow{NO,O_2} (1 - \alpha)^2 & \rightarrow R(=O)(OH) \quad (\text{Reaction } c3)
\end{align*} \]

To estimate specific contributions of organic nitrates to the aerosol formation, we traced oxidation of long-chain alkanes up to the second generation RO2 products. Consider a simple alkane R, the dominant OH reaction is abstraction of hydrogen to give the first generation RO2 radical which upon reaction with abundant NO during UBWOS condition leads to alkyl nitrate compound R(ONO2) and alkoxy radical RO of relative yield \( \alpha \) and \((1-\alpha)\). For R with carbon chain length over 6, the isomerization dominates the fate of RO by hydrogen abstraction within the same molecule through a 6-membered ring transition state (rate constant typically \( >10^4 \text{ s}^{-1} \)). The result is a hydroxy peroxy radical upon reaction with O2 (second generation RO2). The same NO reaction proceeds to give a second generation hydroxy nitrate R(OH)(ONO2) and a hydroxy alkoxy radical, which may promptly react \( (>10^5 \text{ s}^{-1}) \) with the hydrogen on the hydroxy group carbon to give a hydroxy carbonyl R(=O)(OH) which is assumed to represent the rest of the non-nitrate functionality under our simplification. It is also assumed that the organic nitrate yield are not affected by the presence of non-neighboring OH group to give the simplified branching ratios shown in Reactions c1 to c3. We then calculate the vapor pressure of each molecule surrogate using group contribution method SOMPOL.1, of a given carbon chain length in the R group at 273K.

In order to obtain a converging estimation with respect to the long-carbon chain end of the VOC spectrum, it is necessary to extrapolate the contribution of heavy VOCs beyond the measurement which terminates at undecane. Using a linear fit in the log space of the grouped VOC reactivity with specific carbon number, we obtained a estimation shown in Equation c7 for the 1/29 accumulation period where \( kx \) is the total reactivity in s\(^{-1} \) of alkanes with carbon number \( n \).

\[
\ln(kx) = -0.5893 \cdot n + 3.9223 \quad (c7)
\]

\[
S_n\{R(OH)(ONO_2)\} = kx \cdot [OH] \cdot (1 - \alpha) \alpha \cdot K_p \quad (c8)
\]

The total aerosol source of each of the 3 type of molecules in each carbon number class is then calculated in the same way shown for the hydroxy nitrates of size n (Equation c8). Note \( K_p \) is the fraction of the species in the aerosol phase, calculated using Equation 6 in Chapter 4b. The total nitrate groups incorporated into the aerosol phase is the calculated by summing over all carbon groups of alkyl nitrates and hydroxy nitrates. Other functional groups is calculated similarity with application of appropriate weightings. For example, the total CH2 group contribution is calculated according to Equation c9.
\[
\sum_{n} n \cdot (S_n\{R(ONO_2)\} + S_n\{R(OH)(ONO_2)\} + S_n\{R(=O)(OH)\}) = c_9
\]

(c9)
Appendix D (Chapter 5)

D1. Assembly program for ADC control chip AT89S51

Use C51 (8051) assembler. Check sum for intell Hex: 0F79E8

ORG 0000H
CLR RS1
CLR RS0 ; REGISTER BANK=0
SETB IT0
SETB IT1
CLR IE0 ; CAL FLAG
CLR IE1 ; READ FLAG
MOV SCON, #00010001B
MOV IE, #00000000B
MOV R0, #30H
MOV R7, #00000111B
MOV R4, #00000100B
MOV R5, #00001001B
MOV R6, #01010111B
MOV R3, #03H
MOV R2, #00H
MOV R1, #04H
MOV P1, #11111111B
MOV P2, #11111111B
MOV P0, #11111111B

JB P1.0,CONTROLREAD ; DUMP PREVIOUS DATA
CLR P1.1
CLR RI
DUMP:
JB P1.0,CONTROLREAD
JNB RI,DUMP
CLR RI
SJMP DUMP

CONTROLREAD:
CLR P1.4
SETB P1.1
NOP
NOP
NOP
NOP
NOP
NOP ; INITIAL WAIT
CLR P1.3 ; A0 LOW
CLR P1.1
CLR RI

CONTROLLOOP: ;READ IN BYTES
JNB RI,CONTROLLOOP
MOV @R0,SBUF
INC R0
DEC R3
MOV A,R3
JZ CHECK
CLR RI
SJMP CONTROLLOOP

CHECK: ;CHECK OPERATION MODE
SETB P1.1
MOV R3,#03H
MOV R0,#30H
MOV A,@R0
ANL A,R7
JZ CALIBRATE
LJMP CONTROLREAD

CALIBRATE:
CLR REN
CLR TI
CLR P1.2
MOV SBUF,@R1

WRITEWAIT:
JNB TI,WRITEWAIT
CLR TI
INC R1
DEC R3
MOV A,R3
JZ CALIBRATIONWAIT
MOV SBUF,@R1
SJMP WRITEWAIT

CALIBRATIONWAIT:
SETB P1.2
SETB P1.3
SETB P1.1 ;REDUNDANT
MOV R3,#03H
MOV R1,#04H
CALOOP:
JB P1.0,CALOOP
SETB P1.4
SETB REN ;RECEIVE ENABLE
SETB P1.5 ;INDICATOR LIGHT
CLR IE0
CLR IE1
LOOP:
JB IE1,OUTPUT
JB IE0,RECAL
JB P1.0,LOOP
MOV P0,#11111111B ;CLEAR BUS
CLR P1.1
CLR RI

WAIT: ;READ from ADC
JB P1.0,DONE
JNB RI,WAIT
WRITE:
MOV @R0,SBUF
INC R0
CLR RI
SJMP WAIT

DONE:
SETB P1.1
MOV @R0,SBUF
MOV R0, #30H
CPL P1.5 ;INDICATOR LIGHT
LJMP LOOP

RECAL:
CLR IE0
LJMP CONTROLREAD

OUTPUT:
CLR IE1
OUTLOOP:
JNB P1.6,LOOP ;CHECK CLEAR SIGNAL
MOV A,P2 ;OUTPUT TO USB BOX
CPL A
JZ OUTLOOP
CJNE A,#01H,NEXT2
MOV P0, @R0
LJMP OUTLOOP

NEXT2:
RR A
CJNE A,#01H,NEXT3
MOV P0,31H
LJMP OUTLOOP

NEXT3:
RR A
CJNE A,#01H,OUTLOOP
MOV P0,32H
LJMP OUTLOOP

END
D2. Assembly program for FIFO buffer and interface chip AT89S51

Use C51 (8051) assembler. Check sum for intel Hex: 1F6905

ORG 0000H  
LJMP MAIN  

ORG 0003H  ;EXTERNAL INTERRUPT  
SETB TR0  
RETI  

ORG 000BH  
CLR TR0  
SJMP READ  

READ:  
CLR EA  
SETB P3.4  
MOV A,R1  
CJNE A,00H,SKIP  
CLR P3.4  
SKIP:  
MOV @R0,P1  ;byte 0  
SETB P3.5  
INC R0  
MOV @R0,P1  ;byte 1  
SETB P3.6  
INC R0  
MOV @R0,P1  ;byte 2  
CLR P3.5  
INC R0  
WAIT1:  
INC R2  
CJNE R2,#08H,WAIT1  
MOV R2,#00H  
MOV @R0,P1  ;byte 3  
CLR P3.7  
INC R0  
WAIT2:  
INC R2  
CJNE R2,#08H,WAIT2  
MOV R2,#00H  
MOV @R0,P1  ;byte 4
CLR P3.6
INC R0
WAIT3:
INC R2
CJNE R2,#08H,WAIT3
MOV R2,#00H

MOV @R0,P1 ;byte 5
INC R0

SETB P3.5
WAIT4:
INC R2
CJNE R2,#05H,WAIT4
MOV R2,#00H

SETB P3.7
CLR P3.5
CJNE R0,#0FCH,DONE ;TOP OF BUFFER
MOV R0,#30H
DONE:
CLR IE0
SETB EA
MOV A,R4
RETI

MAIN:
CLR RS1
CLR RS0
SETB IT0
SETB IT1
CLR IE0
CLR IE1
MOV IE,#00000011B
MOV TMOD,#00000010B ;TIMER0 AUTORELOAD
CLR TF0
CLR TR0
MOV TH0,#10011100B ;RELOAD VALUE
MOV TL0,#00000000B
MOV R0,#30H
MOV R1,#30H
MOV P1,#11111111B
MOV P2,#11111111B
MOV P3,#10011111B
MOV P0,#11111111B
MOV R2,#00H
MOV R3,#00H

INITIALWAIT:
INC R2
CJNE R2,#0FFH,INITIALWAIT
MOV R2,#00H

CLR IE0
JB P3.2,BACK
SETB IE0

BACK:
SETB EA
LOOP:

JB P3.1,STANDBY ;CHECK STANDBY

MOV A,R1
CJNE A,00H,SEND
SJMP LOOP

STANDBY:
CLR EA
CLR TR0
CLR TF0
MOV TL0,#00H
MOV P3,#00111111B
MOV R1,00H

STDWAIT:                ;WAIT FOR P3.1 LOW
JB P3.1,STDWAIT
MOV P3,#10011111B
CLR IE0
SETB EA
SJMP LOOP

SEND:                  ;SEND DATA TO USB
JNB P3.0,SEND
CLR EA
SENDWAIT:              
INC R2
CJNE R2,#03H,SENDWAIT
MOV R2,#00H

RESUME:
SETB P3.0
CLR EA
MOV P0, @R1
SAMPLE: ;CHECK
MOV A, P2
NOP
NOP
CJNE A, P2, SAMPLE
MOV R4, A
CLR P3.0
INC R1
INC R3
CJNE R3, #06H, WAITLOOP
SETB P3.0 ;HIGH Z
SJMP WRAPUP
WAITLOOP:
SETB EA
WAITHERE:
CJNE A, P2, RESUME
SJMP WAITHERE

WRAPUP:
SETB EA
HERE: ;LAST CHANGE
CJNE A, P2, COMPLETE
JB P3.0, COMPLETE
SJMP HERE
COMPLETE:
CLR EA
MOV R3, #00H
CJNE R1, #0FCH, BACK
MOV R1, #30H
LJMP BACK

END
D3. Wiring schematics for data module

Time base and 24 bit counter board
ADC control board