Atmos. Chem. Phys. Discuss., 14, 6721–6757, 2014
www.atmos-chem-phys-discuss.net/14/6721/2014/
doi:10.5194/acpd-14-6721-2014

Atmospheric Chemistry and Physics
Discussions
Open Access

Hydroxy nitrate production in the OH-initiated oxidation of alkenes

A. P. Teng[1], J. D. Crounse[1], L. Lee[2], J. M. St. Clair[1], R. C. Cohen[2,3], and P. O. Wennberg[1,4]

[1]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA
[2]Department of Chemistry, University of California Berkeley, Berkeley, CA, USA
[3]Department of Earth and Planetary Sciences, University of California Berkeley, Berkeley, CA, USA
[4]Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA, USA

Received: 10 February 2014 – Accepted: 14 February 2014 – Published: 13 March 2014

Correspondence to: A. P. Teng (ateng@caltech.edu)

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

Abstract

Alkenes generally react rapidly by addition of OH and subsequently O_2 to form beta hydroxy peroxy radicals. These peroxy radicals react with NO to form beta hydroxy nitrates with a branching ratio α. We quantify α for C_2–C_8 alkenes at 296 K ±3 and 993 hPa. The branching ratio can be expressed as $\alpha = (0.042 \pm 0.008) \times N - (0.11 \pm 0.04)$ where N is the number of heavy atoms (excluding the peroxy moiety), and listed errors are 2σ. These branching ratios are larger than previously reported and are similar to those for peroxy radicals formed from H abstraction from alkanes. We find the isomer distributions of beta hydroxy nitrates formed under NO-dominated peroxy radical chemistry to be similar to the isomer distribution of hydroxy hydroperoxides produced under HO_2-dominated peroxy radical chemistry. With the assumption of unity yield for the hydroperoxides, this implies that the branching ratio to form beta hydroxy nitrates from primary, secondary, and tertiary RO_2 are similar.

Deuterium substitution enhances the branching ratio to form hydroxy nitrates in both propene and isoprene by a factor of ~ 1.5. These observations provide further evidence for importance of the ROONO lifetime in determining the branching ratio to form alkyl nitrates.

We use these measurements to re-evaluate the role of alkene chemistry in the Houston region. We find that small alkenes play a larger role in oxidant formation than previously recognized.

1 Introduction

The formation of alkyl nitrates is an important process controlling tropospheric oxidants and the lifetime of NO_x. During day time, alkyl nitrates form via a minor chain terminating branch in the reaction of peroxy radicals with NO. The major branch in this chemistry recycles HO_x and produces ozone. The fate of alkyl nitrates is thought to be determined by either: (1) deposition leading to loss of atmospheric NO_x or (2) further reactions that lead to recycling of NO_x or conversion of the organic nitrates to HNO_3. Thus, $RONO_2$ can serve as both a permanent sink, and as a transport mechanism for NO_x.

Alkyl nitrates also play an important role in organic aerosol formation (Rollins et al., 2012; Brown et al., 2009). Aerosol nitrates have been observed to form as a result of NO_3 chemistry, though our understanding of the gas phase mechanisms leading to aerosol nitrate remains incomplete.

Knowledge of the branching ratio to form alkyl nitrates from specific VOC is important for diagnosing the role of individual VOC in ozone and aerosol formation. This knowledge can then guide specific control strategies to mitigate pollution (Ryerson et al., 2003; Rosen et al., 2004; Farmer et al., 2011).

Many previous studies have been conducted to determine the branching ratio to form alkyl nitrates from specific VOCs. These studies suggest that the branching ratios increase with increasing carbon number, increasing pressure, and decreasing temperature (Orlando and Tyndall, 2012 and references therein). This behavior has been interpreted as evidence that the lifetime of the O-ONO intermediate controls the fraction of the nascent complex that follow the curve crossing to the $-ONO_2$ surface. This crossing from the peroxynitrite (ROONO) to the nitrate ($RONO_2$) is, however, not well understood (Lohr et al., 2003; Barker et al., 2003; Zhang et al., 2002).

Alkenes react rapidly by addition of OH and subsequently O_2 to form beta hydroxy peroxy radicals. These peroxy radicals react with NO to form beta hydroxy nitrates. We define the fraction of OH that adds to carbon n as f_{an} out of the total OH + alkene reaction. The total fraction of OH + alkene that proceeds via addition is given as $f_a = f_{a1} + f_{a2} + \ldots + f_{an}$. The total fraction of OH + alkene that proceeds via H-abstraction is given as $f_b = f_{b1} + f_{b2} + \ldots + f_{bn}$, where the subscript indicates the carbon at which H-abstraction takes place. Therefore $f_a + f_b = 1$. We define the branching ratio (α_n) to represent the fraction of RO_2 + NO reaction that produces $RONO_2$, where the subscript n denotes the carbon alpha to the peroxy radical (Fig. 1). The isomer averaged branching ratio (α no subscript) to form beta hydroxy nitrates from OH addition to a mono-alkene is then defined in this paper as: $\alpha = f_{an} \times \alpha_{n+1} + f_{an+1} \times \alpha_n$.

Yields of hydroxy nitrates (Y_{HN}) are defined as the change in hydroxy nitrate concentration over the change in hydrocarbon (HC): $Y_{HN} = -d[HN]/d[HC]$. Isomer averaged branching ratios (α) to form hydroxy nitrates from hydroxy peroxy radicals can be calculated from beta hydroxy nitrate yields by normalizing for the fraction of the alkene reactions with OH that proceed via OH addition: $\alpha = Y_{HN}/(f_a/(f_a + f_b)) = Y_{HN}/f_a$. For alkenes studied here, f_a is greater than 0.75.

Previous studies have suggested that the branching ratio to form beta hydroxy nitrates from reaction of beta hydroxy peroxy radicals with NO is lower than that for peroxy radicals produced from reactions of alkanes of the same carbon number with OH (O'Brien et al., 1998). The lower nitrate branching ratios for beta hydroxy peroxy radicals have been attributed to the beta hydroxy group weakening the O-ONO bond, shortening the lifetime of the OONO complex toward decomposition to NO_2, and thereby reducing the time available to sample the curve crossing to the nitrates ($RONO_2$) (Muthmuruthma et al., 1993; O'Brien et al., 1998; Matsunga and Ziemann, 2009, 2010). This interpretation is clouded, however, by the large scatter in the measured yields of alkyl nitrates from alkenes. Several studies report total alkyl nitrate yields similar to those of the equivalent size alkane (Atkinson et al., 1985; Tuazon et al., 1998; Patchen et al., 2007; Aschmann et al., 2010) while others generally report yields ~ 1/2 as large (e.g. O'Brien et al., 1998). The wide distribution of measured nitrate yields may reflect the challenges in quantifying hydroxy nitrates. Consistent with this interpretation, lower nitrate yields were obtained using HPLC or GC methods while higher yields were found in experiments that used remote sensing (e.g. long-pass FTIR) or direct sampling techniques.

In this study, we use CF_3O^- CIMS to quantify the hydroxy nitrates formed during the OH oxidation of alkenes in the presence of O_2 and NO. In addition, we utilize gas chromatography with both CF_3O^- CIMS and thermal dissociation NO_2 laser-induced fluorescence (TD-LIF) to resolve and quantify isomeric distributions of these hydroxy nitrates. The TD-LIF instrument provides independent confirmation that the observed signals are alkyl nitrates and enables determination of the sensitivity of the CIMS instrument for the nitrates for which standards are not available. The combination of direct sampling and chromatographic separation demonstrates that losses of the hydroxy nitrates in our GC analysis are minimal, and provides confidence in the apportionment of isomer yields of the hydroxy nitrates.

Here we describe the measurements of beta hydroxy nitrates from OH oxidation of alkenes, their branching ratios to formation, and their isomer distributions.

2 Materials and methods

1-propene [propene] (>99 %), d_6-propene (> 99 %), 1-butene [but-1-ene] (> 99 %), cis-2-butene [*cis*-but-2-ene] (> 99 %), methylpropene [2-methylpropene, isobutylene, isobutene] (> 99 %), 2-methyl 2-butene [2-methyl but-2-ene] (> 99 %), isopropyl nitrate [nitric acid, 1-methylethyl ester] (> 99 %), 1-hexene [hex-1-ene] (> 99 %), 1-octene [oct-1-ene] (> 98 %) purity were purchased from Sigma Aldrich and used without further purification. Hydrogen peroxide (30 % by weight in water) was purchased from Sigma Aldrich. Ethene [ethylene] (> 99 %) was purchased from Scotty Specialty Gases. A nitric oxide [NO] (1994 ± 20 ppmv in ultra high purity N_2) gas tank for chamber experiments was prepared by Matheson. A second nitric oxide [NO] (5 ppmv in ultra high purity N_2) gas tank for TD-LIF calibration was prepared by Matheson.

2.1 Environmental chamber experiments

The CIMS and thermal dissociation laser-induced fluorescence instrument (TD-LIF) instruments and the teflon reaction chamber have been described previously (Crounse et al., 2013; Lee et al., 2014). Briefly, photochemical experiments were conducted in a 1 m^3 enclosure composed of fluorinated ethylene propylene copolymer (Teflon-FEP, Dupont). UV photolysis of hydrogen peroxide provided the primary HO_x source. Experiments to determine the hydroxy nitrate yields were typically conducted with initial mixing ratios of 0.08–2 ppmv of alkene, 0.2–2 ppmv (±10 %) of hydrogen peroxide and 0.5–4 ppmv (±5 %) of NO. Experiments to determine hydroxy hydroperoxide isomeric distributions were conducted with initial mixing ratios of 15–30 ppbv alkene and 2 ppmv of hydrogen peroxide. All experiments were performed at ambient pressure, approximately 993 hPa. Table 1 provides a complete list of experiments.

Alkene addition to the environmental chamber was accomplished by first flushing a 500 cm^3 glass bulb with the alkene and then filling it to the desired pressure (5–20 hPa). The bulb was then filled with N_2 gas to 993 hPa. If required, the alkene was serially diluted by pumping the bulb down to the desired pressure (5–400 hPa) and backfilling again with N_2 to atmospheric pressure. The concentrations of ethene, propene, 1-butene, cis-2-butene, 2-methyl propene, 2-methyl butene, and 1-hexene determined by pressure methods were verified by FT-IR spectroscopy. FT-IR cross sections were obtained from the PNNL database (Johnson et al., 2002; Sharpe et al., 2004) for all compounds except cis-2-butene and d_6-propene. Determinations of the concentrations of d_6-propene and cis-2-butene were based on manometry, and checked against GC-FID measurements relative to the other gases added in the same experiment assuming equivalent FID signal per carbon atom. These independent methods agreed to within 3 %. Experimental conditions are listed in Table 3. NO addition was accomplished by evacuating a 500 cm^3 glass bulb, and filling from the standard tank to the desired pressure. NO was added to the enclosure only after at least 0.25 m^3 of air was added to avoid conversion of NO to NO_2. All pressure measurements were obtained using 13.3 hPa or 1333.3 hPa full scale absolute pressure gauges (MKS Baratron™).

The composition of the chamber was monitored by sampling from the enclosure at ~ 2000 sccm through a single 4 mm ID perfluoroalkoxy line with instruments sampling in series: (1) ToF-CIMS (Tofwerk, Caltech), (2) Triple Quadripole MS-MS CIMS (Varian, Caltech), (3) GC-FID (HP 5890 II), (4) NO_x Monitor (Teledyne 200EU), (5) O_3 Monitor (Teledyne 400E). The specifics of the ToF-CIMS and MS-MS CIMS have been described elsewhere (Crounse et al., 2006, 2011, 2012, 2013; Paulot et al., 2009; St.

Clair et al., 2010). The TD-LIF quantitatively converts alkyl nitrates to NO_2 by thermal dissociation in a 400 °C oven. NO_2 is then measured by laser-induced fluorescence (Lee et al., 2014). Reaction products were monitored using CF_3O^- chemical ionization mass spectrometry (CIMS) methods. Using CF_3O^- cluster ion signals of $(M+85)$ m/z, where M is the molecular weight of the neutral species, products from alkene oxidation were detected. The following m/z were used for hydroxy nitrate determination: ethene, 192; propene, 206; d_6-propene, 212; 1-butene/cis-2-butene/methylpropene, 220; 2-methyl,2-butene, 234; 1-hexene 248; 1-octene, 276. For hydroxy hydroperoxides, the following m/z were used for quantification: propene, 177; 1-butene/methylpropene, 191; 2-methyl 2-butene, 205; 1-hexene, 219.

The alkene concentrations were monitored by GC-FID. Chamber air was sampled into a 10 cm^3 stainless steel sample loop using a six-port valve. The sample was transferred to the head of the column in the oven at temperatures between 308–373 K, depending on the hydrocarbon. In the case of ethene, samples were cryotrapped with liquid nitrogen on the head of the column. A megabore (0.53 mm) 30 m Plot-Q column (JW Chemicals) was used to separate compounds using 7–9 $stdcm^3\,min^{-1}$ N_2 carrier gas. A suitable temperature ramp was selected for each compound.

2.2 Photooxidation

After addition of the reagents, the chamber air was monitored for at least 20 min to assure a well-mixed reactor. UV lights were then turned on, initiating photooxidation of hydrocarbon. The CF_3O^- CIMS and GC-FID were used to monitor the reaction progress. For relative nitrate branching ratio experiments, we minimized the fraction of the hydrocarbon oxidized ($< 10\,\%$) to ensure that little of the nitrates are photochemically removed. Experiments were initiated at 293 K, and the temperature increased slowly 2–4 K after the lights were turned on. After an appropriate oxidation period, lights were turned off, and the contents of the bag were monitored for at least ten minutes to precisely determine the concentrations of the gas-phase products.

2.3 Post-experiment GC-CIMS/LIF monitoring

Following each experiment, products were analyzed using gas chromatography. For each GC run, a controlled mass of air ranging from 200–2500 std cm^3 was cryofocused at 240–280 K on the head of a 4 m HP 612, 4 m RTX-1701, or 1 m RTX-1701 megabore column. Temperature ramping for every compound was: 30 °C, hold 0.1 min, 3 °C min^{-1} from 30–60 °C, 10 °C min^{-1} to 130 °C, hold 3 min. Carrier gas flow was constant and set by a mass flow controller (MKS) to be 8.7 std cm^3 min^{-1} N_2.

Following the GC, the column effluent was split and directed to both the ToF-CIMS instrument and to the TD-LIF system. The ToF-CIMS instrument was operated in the same manner as during the photochemistry with diluted column effluent substituting for the ambient flow. With this split flow configuration, the concurrent elution of alkyl nitrates was monitored by both the ToF-CIMS and TD-LIF instruments, enabling absolute calibration of the CIMS sensitivity to the individual alkyl nitrates. Following each photochemistry experiment, at least three replicate GC runs were conducted. To determine transmission through the GC, the integrated CIMS signal at the appropriate m/z from the GC effluent was compared to direct sampling measurement of the same m/z. For hydroxy hydroperoxide experiments and relative nitrate yield experiments, no TD-LIF measurement was used.

The determination of the split ratio (approximately 10 : 1) between the CIMS and TD-LIF NO_2 instrument was performed using an isopropyl nitrate standard (80 ppbv in air) prepared in the same fashion as the alkenes above. The gas standard was both directly sampled from the chamber and following cryo-collecting ~ 200 cm^3 on an HP 612 column and eluting the peak in the usual GC configuration. The signal level in the TD-LIF instrument was recorded as the GC ramped through its usual temperature program. Signal levels were also compared between direct measurement of ~ 80 ppbv isopropyl nitrate within a Teflon bag into the TD-LIF system and collecting for four minutes on a cooled sample loop. A separate check was also conducted with prepared standards of isoprene hydroxy nitrates in which the standard was directly sampled from the chamber and through the GC system. The TD-LIF was also calibrated at the end of each photochemistry experiment with gas standard of 5 ppmv NO_2 in N_2 (Matheson) under matching pressure conditions.

3 Results and discussion

In this section, we proceed through the following analysis:

1. We estimate the fraction of the reaction of OH that proceeds via addition, f_a. This allows us to normalize subsequent measurements of Y_{HN} to produce branching ratios, α.

2. We determine branching ratios to form hydroxy nitrates, α, from alkenes relative to $\alpha_{HN\_propene}$. This method allows us to determine the most internally precise α while oxidizing only a small fraction of the alkene, thereby avoiding the complication of secondary chemistry.

3. We measure the absolute branching ratios, α, of a subset of compounds. We find that the branching ratios are well described by a linear relationship: $\alpha = m \times N + b$, where α is isomer-averaged branching ratio, and N is the number of heavy atoms in the peroxy radical (not counting the peroxy radical oxygens).

4. We place all relative nitrate branching ratios on an absolute basis using the relationship derived in (3).

5. We determine specific isomer distributions for alkenes using the GC chromatograms of hydroxy nitrate isomers.

6. We infer OH addition branching ratios by analyzing GC chromatograms of hydroxy hydroperoxides from alkenes.

7. We determine the dependence of the alkyl nitrate branching ratios on the type (i.e., primary, secondary or tertiary) of beta hydroxy RO_2 radicals by comparing (5) and (6).

3.1 Normalizing nitrate yields for H-abstraction

To calculate the branching ratio for reaction of RO_2 with NO to form of beta hydroxy nitrates following addition of OH and O_2 to alkenes, it is necessary to estimate the fraction of the chemistry that proceeds via OH addition ($f_a/(f_a + f_b)) = f_a$. A quantitative determination of f_b from our experimental data is not possible because CF_3O^- CIMS is insensitive to simple carbonyl or nitrate compounds. There have been few studies of H-abstraction from alkenes by OH at ambient temperatures. The H-abstraction channel by OH has been measured for propene and cis-2-butene to be less than 3 %, and for 1-butene to be 8 ± 3 % (Krasnoperov et al., 2011; Loison et al., 2010 and references therein). Aschmann and Atkinson (2008) measured OH rate constants for a series of 1-alkenes and found that the OH rate constant increases per additional CH_2 group was 2×10^{-12} cm^3 molec^{-1} s^{-1}, roughly 25 % higher than the empirically derived increase in OH rate constant per additional CH_2 group for *n*-alkanes (1.4×10^{-12} cm^3 molec^{-1} s^{-1}, Kwok and Atkinson, 1995). Theoretical work by Pfrang et al. (2006a, b) has predicted that the chain length should not affect the rate of OH addition to 1-alkenes, which implies the increase in rate constant from 1-butene to 1-octene is attributable to the H-abstraction channels. Using this additivity relationship, the abstraction fraction (f_b) for 1-octene is calculated to be 28 %. For this analysis, we assume that f_b is 8 % for 1-butene and that the abstraction rate increases 1.4×10^{-12}cm^3 molec^{-1} s^{-1} per additional CH_2 group as suggested by Kwok and Atkinson (1995), as non-allylic CH_2 groups are expected to be similar to CH_2 groups in alkanes. This calculation suggests 15 % H-abstraction for 1-hexene, and 22 % for 1-octene.

To estimate abstraction rates for methyl-substituted alkenes, we use an overall k_{OH} of 1.4×10^{-12} cm^3 molec^{-1} s^{-1} for 1-butene (Atkinson and Arey, 2003), Kwok and Atkinson's (1995) suggested k_{OH} for a CH_3 group of $0.14 \times 10^{-12}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$, and an 8 % H-abstraction (f_b). We estimate an $k_{OH,abstraction}$ rate constant for a secondary allylic hydrogen of 2.4×10^{-12}. Using an overall k_{OH} of $26.3 \times 10^{-12}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$ for propene (Atkinson and Arey, 2003) and an upper limit of 3 % abstraction, we derive an upper limit $k_{OH,abstraction}$ rate constant of primary allylic hydrogen of $0.8 \times 10^{-12}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$. Assuming vinylic hydrogen abstraction rates are negligible, we estimate f_b for cis-2-butene, methylpropene, and 2-methyl 2-butene to all be < 3 %.

3.2 The relative yields of hydroxy nitrates from alkene oxidation

All hydroxy nitrate branching ratios were measured relative to $\alpha_{HN\_propene}$. With minimal oxidation of total hydrocarbon (< 10 %), the measured CIMS signal of each compound can be used to determine the ratio of the yield of hydroxy nitrates ($Y = f_{a1} \times \alpha_2 + f_{a2} \times \alpha_1$):

$$\frac{Y_{HN\_alkene}}{Y_{HN\_propene}} = \frac{\text{CIMS\_signal}_{HN\_alkene}}{\text{CIMS\_signal}_{HN\_propene}} \times \frac{\text{sensitivity}_{HN\_propene}}{\text{sensitivity}_{HN\_alkene}} \times \frac{k_{OH,propene}}{k_{OH,alkene}} \times \frac{[\text{propene}]_{average}}{[\text{alkene}]_{average}} \quad (1)$$

To determine the ratio of the branching ratios, we multiply the ratio of the yields by the ratio of the fraction of OH addition (f_a):

$$\frac{\alpha_{HN\_alkene}}{\alpha_{HN\_propene}} = \frac{Y_{HN\_alkene}}{Y_{HN\_propene}} \times \frac{f_{a\_propene}}{f_{a\_alkene}} \quad (2)$$

Average concentrations throughout the experiment were calculated by averaging the initial and final alkene concentrations. The amount of alkene oxidized could not be accurately determined by GC-FID due to the small fractional change. Therefore the loss was estimated by using the calculated branching ratio for the hydroxy nitrates (see Sect. 3.2 for derivation of absolute branching ratios used in this calculation). The difference in the determination of Y_{HN} between using average vs. the initial alkene concentrations was less than 5 % in all cases. CIMS signal measurements can be seen in Fig. 2.

Error in the estimate of the hydroxy nitrate branching ratios relative to $\alpha_{HN\_propene}$ from Eq. (2) are therefore determined solely by the relative errors associated with the direct sampling CIMS measurement, the ratio of the estimated OH reaction rates, errors associated with determining the relative initial concentrations, and, in the case of secondary loss, the relative ratio of the loss rates. Relative errors in the k_{OH} rate constants were taken from Atkinson et al. (1983, 1986), and Aschmann and Atkinson (2008), and are reported to be < 5 %. The k_{OH} rate for d_6-propene was assumed to be same as $k_{OH}$for propene (Stuhl et al., 1998). PNNL spectral database IR cross sections were used to determine alkene gas concentrations, with an associated error of 2 %. For compounds with no published IR cross sections, the GC-FID signal was used to corroborate the pressure measurement. This contributes an additional 3 % error. Errors in the CIMS quantification of hydroxy nitrates include background signal subtraction, signal to noise level, and time lag associated with lower volatility compounds. The combination of these errors are estimated to be lower than 10 % for all compounds. Additional uncertainty in sensitivity for d_6-propene 1-octene hydroxy nitrates, compounds which were not calibrated by using TD-LIF, was assumed to be 3 %. Estimates for secondary loss of hydroxy nitrates by reactions with OH for the relative yield experiments (k_{OH} estimates primarily from Treves and Ruddich, 2003 and scaled by Kwok and Atkinson, 1995) using the method by Atkinson et al. (1982) result in corrections of < 3 % and are neglected in this subset of experiments. For absolute yield determinations, the applied corrections are listed in Table 3.

To determine the relative nitrate yield, absolute sensitivities were derived from cryofocused gas chromatography and simultaneous measurement of hydroxy nitrate compounds by CF_3O^- CIMS and TD-LIF. The errors associated with this determination include: the split ratio of eluent flow between the CF_3O^- CIMS and TD-LIF, absolute sensitivity to NO_2 in the TD-LIF, and integration errors associated with determining a baseline for trailing peaks in both the CF_3O^- CIMS and the TD-LIF chromatograms. Combined errors for the split flow ratio and absolute NO_2 determination are 10 %. Reproducibility of sensitivity from repeat chromatograms had errors than < 5 %, except for propene (< 15 %), which was signal-to-noise limited. It is possible that co-eluting compounds detectable in the TD-LIF but not the CF_3O^- CIMS would bias the CIMS sensitivity low. For hydroxy nitrates from d_6-propene and 1-octene, the CIMS measurement was assumed to have the same absolute sensitivity as hydroxy nitrates from propene and 1-hexene respectively. These were estimated to have an additional uncertainty of 3 %. Sensitivities are listed in Table 2. An example chromatogram of GC-CIMS/TD-LIF from which sensitivities are derived is shown in Fig. 3.

3.3 Absolute beta hydroxy nitrate yields and branching ratios

An absolute yield of hydroxy nitrates for several of the alkenes was determined in experiments that proceeded beyond 10 % alkene loss. The longer reaction time was necessary in order to quantify with sufficient precision the amount of alkene oxidized. The concentration of hydroxy nitrates at the end of the experiment was determined by measuring the total TD-LIF peak signal which corresponded to a CIMS hydroxy nitrate signal. The initial concentration of alkene was determined by FT-IR and GC-FID, and total loss was determined by the fractional decay in peak area by the GC-FID. The yield was then calculated by dividing the concentration of hydroxy nitrates formed by the loss of alkenes. For each reaction, a correction factor, F, was applied to account for losses of hydroxy nitrates by OH (Atkinson et al., 1982) using rate coefficients estimated based on Treves and Ruddich (2003). Errors include those associated with determining initial alkene concentration, determining final alkene concentration, determining the split ratio between the CIMS and TD-LIF, and the absolute calibration of the TD-LIF. Branching ratios to form beta hydroxy nitrates were then derived from beta hydroxy nitrate yields by normalizing by the fraction of OH + alkene reactions that proceeds via OH addition. See Sect. 3.4 for more details. Tabulated values are listed in Table 3. In Fig. 4, we show the dependence of the branching ratio on the number of heavy atoms in the peroxy radical.

3.4 Absolute hydroxy nitrate branching ratios from relative measurements

To place the relative nitrate yields of the alkenes (3.2) on an absolute basis, we scale the relative branching ratios by the observed dependence of the absolute branching ratios on *N* derived in Sect. 3.3. Branching ratios to form beta hydroxy nitrates calculated using this method are listed in Table 4 and shown in Fig. 5.

Our method of placing the relative branching ratios on an absolute basis are prone to correlated errors if the two data sets are not independent of each other. We believe the data sets are sufficiently independent for the following reasons: (1) the absolute nitrate yields require a secondary loss by OH correction whereas the second set does not, (2) the determination of Δalkene relies on GC-FID for one set and initial reactant concentration and literature k_{OH} rate constants for the other set, (3) the yield of beta hydroxy nitrates are determined by GC-TD-LIF in the absolute yield experiments, and are determined by direct sampling ToF-CIMS measurements and GC-CIMS, (4) most of the deviations from the fits (Figs. 4 and 5) are not correlated (i.e. only 2-methyl 2-butene is consistently lower than the linear fit). The two data sets, however, are prone to similar biases in the following ways: (1) initial alkene concentrations were measured by FT-IR and with the same reference spectra in both sets of experiments, (2) sensitivities for beta hydroxy nitrate and absolute beta hydroxy nitrates yields both rely upon GC-TD-LIF data.

The measured branching ratios to form beta hydroxy nitrates (Table 4) are consistent with Tuazon et al. (1998) FT-IR determination for the formation of total alkyl nitrates for methylpropene, cis-2-butene, and 2-methyl,2-butene. They are also consistent with Patchen et al. (2007) measured yields for 1-butene and 2-butene determined by CIMS using synthesized standards. Our branching ratios are, however, significantly higher than those determined by O'Brien et al. (1998) using gas chromatography. While the FT-IR determines the sum of all nitrate-containing compounds and the measurements presented here and by O'Brien et al. (1998) comprise only hydroxy nitrate isomers, the difference between the two quantities is expected to be quite small for the studied alkenes. Reasons for these discrepancies are not clear but may reflect losses in the chromatographic analyses.

As shown in Fig. 5, the hydroxy nitrate branching ratios from beta hydroxy peroxy radicals on a per heavy atom basis are similar to those observed for peroxy radicals derived from *n*-alkanes as measured by Arey et al. (2001). This suggests that destabilization of the O-ONO bond due to the presence of the beta hydroxy group is likely small. Deuteration also leads to an increased branching ratio to form nitrates, possibly due to increased O-ONO lifetime resulting from the lower frequency vibrational and rotational modes. The nitrate branching ratio of d_6-propene is 50 % higher than h_6-propene. A similar increase in nitrate branching ratio has been observed for deuterated isoprene (Crounse et al., 2011).

3.5 Nitrate yields from alkoxy isomerization

In addition to the beta hydroxy nitrates, dihydroxy nitrates form from those alkenes that are able to undergo 1,5 H-shift chemistry from the alkoxy radical (Fig. 6). The CIMS sensitivities for these nitrates could not be obtained because they had low transmission through the gas chromatograph. From ambient sampling, the CIMS signal for the dihydroxy nitrates, relative to the beta hydroxy nitrates, are: 1-butene, < 2 %, 1-hexene, > 10 %, 1-octene, > 5 %. For 1-butene, an upper limit is provided due to the small amount formed. For the dihydroxy nitrates from 1-hexene and 1-octene, significant uptake to the walls of the chamber was observed.

3.6 Hydroxy nitrate isomer attribution

An example GC chromatogram is shown in Fig. 7. Peaks were assigned from the GC chromatogram for 1-alkenes assuming the 1-OH addition product is the major isomer due to alkyl radical stabilization (i.e. $f_{a1} > f_{a2}$). For 2-methyl,2-butene, we assume 3-

OH addition is formed in higher abundance than 2-OH addition for similar reasons (i.e. $f_{a3} > f_{a2}$).

The individual isomeric distributions derived from gas chromatography are listed in Table 5. The transmission for all hydroxy nitrate isomers through the GC-CIMS/TD-LIF was measured to be 100 % ± 5 % except for 1-octene hydroxy nitrates (transmission = 92 %).

3.7 Branching ratios to form hydroxy nitrates is independent of alkyl substituents of RO_2

There has been significant controversy about whether the yield of nitrates from $RO_2 + NO$ is sensitive to the nature of R. A central question in this debate is whether the yields of nitrates from primary, secondary, and tertiary peroxy radicals are different (Orlando and Tyndall, 2012).

To determine the branching ratios of beta hydroxy alkyl nitrates from specific beta hydroxy peroxy radicals (α_1 and α_2), it is necessary to normalize by the fraction of OH adding to each carbon (f_{a1} and f_{a2}). To estimate these fractions, we measured the isomer distribution of beta hydroxy hydroperoxides formed from the reaction of RO_2 with HO_2. For these peroxy radicals, we assume that the yield of hydroperoxides from $RO_2 + HO_2$ reaction is unity (Raventos-Duran et al., 2007; Hasson et al., 2004; Spittler et al., 2000; Wallington and Japar, 1990a, b). Thus, the ratio of the hydroxy hydroperoxides to hydroxy nitrate isomers provides an estimate of the difference in nitrate branching ratio for the individual RO_2 isomers.

For propene, Cvetanovic (1976) (unpublished, as reported by Peeters et al., 2007) measured the hydroxy hydroperoxide distribution, finding a 65/35 split between OH at C_1 vs. OH at C_2. Peeters et al. (2007) presented a structure-activity relationship (SAR) for OH addition kinetics which predicts an 87/13 OH addition at C_1 vs. C_2 for 1-alkenes. For 1-butene, Peeters et al. (2007) determined a ratio of 85 : 15 using a mass spectrometer technique. Loison et al. (2010) used a similar technique, measuring the fraction of OH addition to each carbon using fragmentation patterns for the alkyl radical products. They measured a somewhat different ratio than the Peeters study: 70/30 split for OH addition at C_1 vs. C_2 for propene and 1-butene. Both studies were conducted in a flowtube at reduced pressure (2–5 Torr, Peeters et al., 2007; 0.8–3 Torr, Loison et al., 2010). Krasnoperov et al. (2011) measured branching ratios for OH + propene using O^{18} labeled reactants to determine product distributions at 60–400 torr. They derived a ratio at odds with all previous findings, showing even distribution between products from OH addition at C_1 and C_2. Feltham et al. (2000) also measured site specific OH addition sites in sub-100 K temperatures in an argon matrix for a series of alkenes and included for completeness in Table 5.

We undertook a series of experiments to measure the hydroxy hydroperoxide isomer distribution using the same approach as described above for the hydroxy nitrates. We assume the same sensitivity for the two isomers in each system. Isomer distribution data is listed in Table 5. We derive a ratio between f_{a1} and f_{a2} that agrees well with the findings of Loison et al. (2010). We also find that the hydroxy hydroperoxide isomer distribution are identical (within error) to the hydroxy nitrate isomer distribution. This suggests that the specific nitrate branching ratio (α_1 or α_2) is determined primarily by the size of the RO_2 radical and is independent of whether the RO_2 is primary, secondary, and tertiary. Additionally, the presence of the beta hydroxy group in relation to the peroxy radical does not appear to substantially alter the branching ratio toward formation of beta hydroxy nitrates as compared to those of *n*-alkanes of similar size.

4 Atmospheric chemistry implications

In this study, we determined the hydroxy nitrate branching ratios, α, for a wide suite of alkenes. We recommend a revised parameterization for α based on the size of RO_2 for conditions of 298 K and 1 atm: $\alpha = (0.042 \pm 0.008) \times N + (-0.11 \pm 0.04)$, where N = number of heavy atoms in the peroxy radical (excluding the peroxy radical moiety's two oxygen atoms), and listed errors are 2σ.

The revision of branching ratios has a substantial impact on the predicted role of alkenes in the chemistry of ozone and aerosol. For ozone production, the role of nitrate formation as a chain termination reaction can be estimated, assuming that the initial branching for the peroxy radical chemistry results in either formation of ozone or of organic nitrate. Typically, 2 ozone molecules are formed per peroxy radical reacting with NO to form NO_2. Neglecting entrainment or deposition and assuming an average alkyl nitrate branching ratio for the VOC mixture $\ll 1$, one finds (Rosen et al., 2004; Farmer et al., 2011; Perring et al., 2013):

$$\frac{\Delta O_3}{\Delta ANs} \approx \frac{P_{O_3}}{P_{ANs}} \approx \frac{2(1-\alpha)}{\alpha} \approx \frac{2}{\alpha} \tag{3}$$

Examination of Eq. (3) suggests that increasing the nitrate branching ratios decreases the projected ozone production per VOC reacted. In Houston, where alkene oxidation is thought to significantly contribute to ozone formation, Rosen et al. (2004) used this relationship to estimate the overall nitrate branching ratio (α). Using published branching ratios for alkenes (mostly O'Brien et al., 1998), Rosen et al. (2004) could not reconcile the observed ozone, alkyl nitrates and alkene precursors. Using our experimentally derived hydroxy nitrate branching ratios for alkenes, we find a substantial increase in predicted alkyl nitrate production of 0.1969 ppbv h^{-1}, compared to Rosen's estimate of 0.1516 ppbv h^{-1}. The revised yields close approximately half the gap in observed vs. predicted nitrates. Tabulated data is shown in Table 6.

5 Conclusion

We measured hydroxy nitrate branching ratios for reactions of NO with RO_2 derived from the OH addition to linear and methyl-substituted alkenes. We find these branching ratios to be similar to those found previously for RO_2 derived from the OH oxidation of *n*-alkanes on a per-heavy-atom basis. Measurements of the hydroxy hydroperoxide isomer distributions from HO_2-dominated oxidation of propene, 1-butene, 2-methyl 2-butene, methylpropene, and 1-hexene suggest that there is not a significant difference in nitrate branching ratio between primary, secondary and tertiary RO_2 radicals reacting with NO. We recommend the overall beta hydroxy nitrate branching ratio from beta hydroxy peroxy radicals reacting with NO to be: $\alpha = (0.042 \pm 0.008) \times N - (0.11 \pm 0.04)$, where N is the total number of heavy atoms (for alkenes, N is the total number of carbons plus 1 for the OH that adds), and listed errors are 2σ. The branching ratio dependence on the number of heavy atoms is found to be the same (within error) to that derived for *n*-alkanes (Arey et al., 2001).

The atmospheric implications of our findings have a direct impact on our understanding of the the globally important formation of alkyl nitrates. Overall, projected NO_x and ozone concentrations will be lower where alkenes play an important role in the VOC budget.

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Table 1. Experiment list.

#	H_2O_2, ppmv	NO, ppbv	VOC1, ppbv	VOC2, ppbv	VOC3, ppbv
1	2	500	propene, 96	ISOPN, 50	
2	2	500	propene, 93	ISOPN, 38	
3	2	500	propene, 110	ISOPN, 7.9	
4	2	500	propene, 114	ISOPN, 47	
5	2	500	propene, 108	ISOPN, 28	
6	2	500	propene, 112	ISOPN, 54	
7	2	500	propene, 194	ISOPN, 17	
8	2	500	1-butene, 131	1-Hexene, 105	
9	2	500	1-butene, 15	cis-2-butene, 120	
10	2	500	ethene, 1096	cis-2-butene, 115	
11	2	500	2-methyl 2-butene, 107		
12	2	500	methylpropene, 342		
13			methylpropene, 4200	ISOPN, 20	
14	2		propene,, 36	1-butene, 17	1-hexene, 33
15	2		propene, 30	butadiene, 14	2-methyl 2-butene, 20
16	2	1000	d_6-propene, 324	1-butene, 256	
17	2	1000	d_6-propene, 280	propene, 334.5	1-butene, 102
18	2	1140	ethene, 963	propene, 426	methylpropene, 261
			2-methyl 2-butene, 242	1-hexene, 254	1-octene, 326
19	0.2	1930	ethene, 2983	propene, 608	methylpropene, 309
			2-methyl 2-butene, 339	1-hexene, 263	1-octene, 314
20	0.2	950	propene, 1418	1-butene, 85	methacrolein, 902
			2,3 dimethyl,2-butene, 1096		
21	0.2	950	propene, 1380	methyl vinyl ketone, 1258	cis-2-butene, 674
			2,3-dimethyl 2-butene, 732		

Table 2. Sensitivities for hydroxy nitrates in CF_3O^- CIMS derived from GC-CIMS/TD-LIF technique.

Hydroxy Nitrates Derived From:	Measured CIMS CF_3O^- Sensitivity (normcts pptv^{-1}), 10^4
Ethene, 1-OH, 2-ONO_2	**3.3 ± 0.4**
Propene 1-OH, 2-ONO_2	5.0 ± 1.2
Propene 2-OH, 1-ONO_2	5.0 ± 1.4
Propene, both	**5.0 ± 1.0**
1-Butene 1-OH, 2-ONO_2	3.2 ± 0.4
1-Butene 2-OH, 1-ONO_2	2.8 ± 0.4
1-Butene, both	**2.9 ± 0.4**
cis-2-Butene, first diastereomer	2.8 ± 0.4
cis-2-Butene, second diastereomer	2.8 ± 0.4
cis-2-Butene, both	**2.8 ± 0.4**
Methylpropene 1-OH, 2-ONO_2	3.8 ± 0.4
Methylpropene 2-OH, 1-ONO_2	3.5 ± 0.7
Methylpropene, both	**3.7 ± 0.5**
2-Methyl,2-Butene 2-OH, 3-ONO_2	3.8 ± 0.4
2-Methyl,2-Butene 3-OH, 2-ONO_2	3.9 ± 0.5
2-Methyl,2-Butene, both	**3.9 ± 0.4**
1-Hexene, 1-OH, 2-ONO_2	2.6 ± 0.4
1-Hexene, 2-OH, 1-ONO_2	1.9 ± 0.4
1-Hexene, both	**2.4 ± 0.3**

Absolute sensitivities for all isomers were found by summing all peaks in both the CIMS and TD-LIF, and deriving a sensitivity from the total. Errors include the 10 % error from the split ratio and absolute NO_2 determination by the TD-LIF. Listed errors are 1σ. We note that the measured 1-hexene HN sensitivities are lower than other HNs measured in this study. This may reflect precision errors for this one compound, and thus biases the HN branching ratio for 1-hexene and 1-octene to be higher.

Table 3. Absolute Hydroxy Nitrate (HN) Yields from Alkenes.

Alkene	Δ Alkene ppbv/%	HN, ppbv	$k^{1}_{\mathrm{OH,HN}}$ ($\times 10^{-11}$) ($\mathrm{cm^3\,molec^{-1}\,s^{-1}}$)	F^2	Y_{HN} (%)	f_{a}	α
ethene	221/21 (±1)	2.6 ± 0.1	0.3	1.04	1.2 ± 0.2	1	1.2 ± 0.2
propene	37/40 (±2)	2.1 ± 0.3	0.6	1.06	5.9 ± 1.1	0.97	6.1 ± 1.1
propene	70/64 (±6)	3.1 ± 0.6	0.6	1.14	5.0 ± 1.1	0.97	5.2 ± 1.1
1-butene	71/55 (±2)	6.8 ± 0.5	0.7	1.10	10 ± 2	0.92	11 ± 2
cis-2-butene	85/74 (±3)	9 ± 1	0.6	1.09	12 ± 2	0.97	12 ± 2
methyl propene	166/49 (±2)	17 ± 1	0.5	1.04	11 ± 1	0.97	11 ± 1
2-methyl 2-butene	61/64 (±3)	6.2 ± 0.3	0.8	1.06	11 ± 1	0.97	11 ± 1
1-hexene	63/60 (±4)	9 ± 1	1.0	1.15	17 ± 2	0.85	20 ± 2

[1] Rate constants are from Treves and Ruddich, 2003 or estimated based on Treves and Ruddich, 2003.

[2] Correction factor F accounts for loss of hydroxy nitrates due to reaction with OH and was calculated according to Atkinson et al., 1982 using the estimated values for k_{OH}.

See text for more details on estimates for normalization for the fraction of OH + alkene that proceeds via OH addition, f_{a}.

Table 4. Branching Ratios to Form Hydroxy Nitrates (HN).

alkene	Relative CIMS sensitivity	Relative Y_{HN}	Y_{HN} (%)	f_{a}	α	previously reported $Y_{\mathrm{total}\ N}$ ($^{\mathrm{a}}$ = only Y_{HN})
ethene	0.65 ± 0.08	0.44 ± 0.09	2.3 ± 0.5	1	2.3 ± 0.5	0.86 ± 0.03[a]
propene	1.00	1.00	5.1 ± 1.9	0.97	5.3 ± 2.0	1.5 ± 0.1[a]
d_6-propene	1.00[c]	1.5 ± 0.1	7.7 ± 1.0	1	7.7 ± 1.0	
1-butene	0.59 ± 0.08	2.1 ± 0.3	10.5 ± 1.9	0.92	11.7 ± 2.1	2.5 ± 0.2[a]
cis-2-butene	0.55 ± 0.08	2.0 ± 0.3	10.2 ± 1.9	0.97	10.4 ± 1.9	3.4 ± 0.5[a], 6 ± 2.1[b]
methyl propene	0.74 ± 0.10	2.0 ± 0.3	10.4 ± 2.0	0.97	10.6 ± 2.0	9 ± 3.1[b]
2-methyl 2-butene	0.78 ± 0.11	2.3 ± 0.4	11.8 ± 2.3	0.97	12.2 ± 2.3	13 ± 4.5[b]
1-hexene	0.47 ± 0.07	3.6 ± 0.6	18.4 ± 3.6	0.85	21.6 ± 4.2	5.5 ± 1.0[a]
1-octene	0.47[c] ±0.07	4.1 ± 0.8	21.2 ± 4.1	0.78	27.1 ± 5.2	

[a] O'Brien et al.,1998, only hydroxy nitrate yield

[b] Tuazon et al. (1998)

[c] Estimated values. For d_6-propene hydroxy nitrates, the sensitivity is assumed to be the same as propene hydroxy nitrates. For 1-octene hydroxy nitrates, the sensitivity was assumed to be the same as 1-hexene hydroxy nitrates.

See the text for how the fraction of reactivity with OH occuring by addition (f_{a}) is estimated. Listed errors are 1σ.

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Table 5. Isomer distribution for hydroxy nitrates and hydroxy hydroperoxides formed from OH addition to alkenes.

alkene	product	$-ONO_2$ % isomer distribution	–OOH % isomer distribution	previously reported % distribution[b]
propene	1-ONO_2/OOH,2-OH	31 ± 7	32	$40^b/28^c/35^d/50^f/50^g$
	2-ONO_2/OOH,1-OH	69 ± 7	68	$60^b/72^c/65^d/50^f/50^g$
1-butene	1-ONO_2/OOH,2-OH	27 ± 7	27	$44^b/29^c/15^e/30^f$
	2-ONO_2/OOH,1-OH	73 ± 7	73	$56^b/71^c/85^e/70^f$
2-butene	2-ONO_2, 3-OH [(R,S) and (S,R)]	50 ± 7		
	2-ONO_2, 3-OH [(S,S) and (R,R)]	50 ± 7		
2-methylpropene	1-ONO_2/OOH,2-OH	11 ± 3	10^a	15^e
	2-ONO_2/OOH,1-OH	89 ± 3	90^a	85^e
2-methyl 2-butene	2-ONO_2/OOH,3-OH,3-methyl	18 ± 10	25	44^e
	3-ONO_2/OOH,2-OH,3-methyl	82 ± 10	75	66^e
1-hexene	1-ONO_2/OOH,2-OH	28 ± 7	23	42^b
	2-ONO_2/OOH,1-OH	72 ± 7	77	58^b
1-octene	2-ONO_2, 1-OH	14 ± 10		
	1-ONO_2, 2-OH	86 ± 10		

Transmission of all compounds shown is 100 % ± 5 % except for 1-hexene hydroxy hydroperoxides (transmission = 50 %) and 1-octene hydroxy nitrates (transmission = 92 %). We assume that the sensitivity of the CIMS is independent of isomer for the hydroxy hydroperoxides. The ratios derived from repeat chromatograms ($n > 6$) were reproducible to ±2 % for all compounds, except 2-methyl,2-butene which was equally reproducible, but was assigned ±7 % additional error due to the required deconvolution of the two overlapping peaks.

[a] Ratio is from a measurement of hydroxy hydroperoxide products formed during a photolysis experiment with isoprene hydroxy nitrates and methyl propene.

[b] O'Brien et al. (1998); [c] Loison et al. (2010); [d] Cvetanovic (1976); [e] Peeters et al. (2007); [f] Feltham et al., (2000); [g] Krasnoperov et al. (2011).

Table 6. Using revised alkyl nitrate yields to interpret 2000 TexAQ data.

Compound	ppbv	P_{O_3}, ppbv h^{-1}	% P_{O_3}	Yield	$P_{\text{sum(ANs)}}$, ppbv h^{-1}	% $P_{\text{sum(ANs)}}$
butanes	6.7	0.31	4.9	0.079	0.0092	4.69
pentanes	3.6	0.26	4.2	0.101	0.0103	5.27
ethene	4.8	0.58	9.2	0.024	0.0068	3.46
propene	1.3	0.46	7.3	0.052	0.0123	6.27
isoprene	0.2	0.25	4.0	0.14	0.0196	10.03
other alkanes	22.6	0.51	8.2	0.044	0.0270	13.67
Other C_4-C_{10} alkenes	1.7	1.22	19.5	0.1082	0.0754	38.52
aromatics	2.7	0.55	8.7	0.10	0.0303	15.50
aldehydes	7.4	1.42	22.7	0	0	0
CO, CH_4	2000	0.54	8.56	0	0	0
other	6.2	0.17	2.67	0.026	0.0051	2.59
Total		6.25	100	0.04	0.1916	100

Yield numbers have been updated using values from this study. Ethene, propene, 1-butene, cis-2-butene, methylpropene, 1-hexene, 2-methyl 2-butene use the yields determined here. The following values have been changed to reflect the estimated value based on this work: 1,3-butadiene: 0.10, trans-2-butene, 0.10; 2-methyl 1-butene, 0.13; 3-methyl 1-butene, 0.13; 1-pentene, 0.13; cis-2-pentene, 0.13, isoprene: 0.135, methacrolein: 0.033, methyl vinyl ketone: 0.040. Alkane values have been re-adjusted to better reflect the parameterization in Arey et al., 2001: i-butane from 0.255 to 0.077; i-pentane from 0.35 to 0.10; nonane from 0.05 to 0.17.

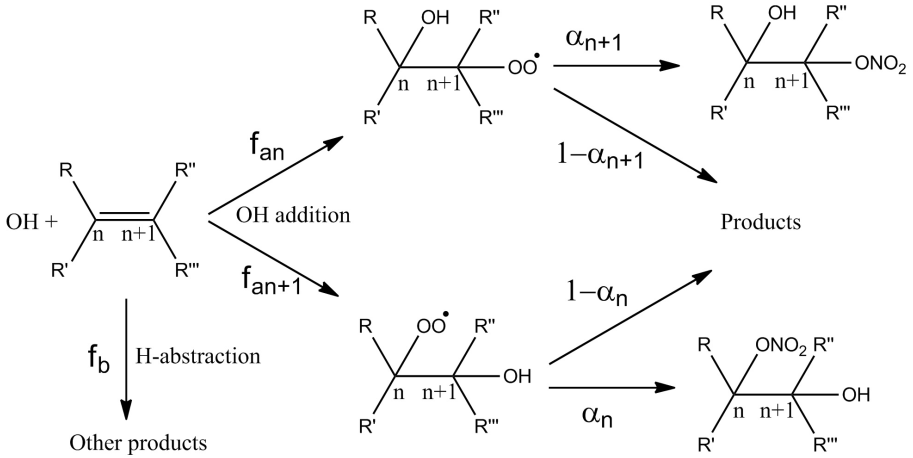

Fig. 1. Reaction Pathways of Alkenes with OH: OH oxidation with alkenes follows two pathways: OH addition (f_n and f_{n+1}) and H-abstraction (f_b, where $f_b = \Sigma(f_{b1} \ldots f_{bn})$). The sum of ($f_a + f_b$) equals 1. Subscripts indicate the carbon number at which either OH addition or abstraction occurs. For alkenes studied in this work at room temperature, the sum of f_{an} and f_{an+1} is much greater than f_b. See text for further discussion of estimations for f_b.

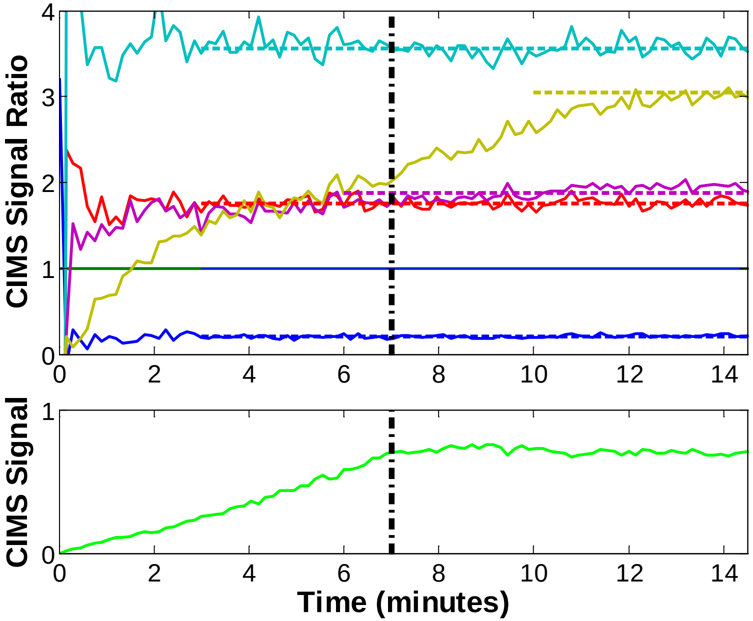

Fig. 2. Shown is an example oxidation experiment in which 6 alkenes are added to the chamber, and their hydroxy nitrate products are monitored simultaneously. The top panel shows CIMS hydroxy nitrate (HN) signals ratioed to propene HN (206 m/z) for: ethene HN (192 m/z, blue), methylpropene HN (220 m/z, red), 2-methyl,2-butene HN (234 m/z, teal), 1-hexene HN (248 m/z, purple), and 1-octene HN (276 m/z, gold). The bottom panel shows the absolute signal for propene HN (206 m/z). The lights were turned on at time = 0, and turned off at 7 min (vertical dashed line), at which point the oxidation stopped. For all compounds other than hydroxy nitrates from 1-octene, a ratio is plotted as a dashed line using averaged data from three minutes after lights until the measurements stopped. For hydroxy nitrates from 1-octene, data after 10 min is averaged. The time lag for hydroxy nitrates from 1-octene arises from wall and sample line equilibration. This suggests that the measured yield is likely a lower limit.

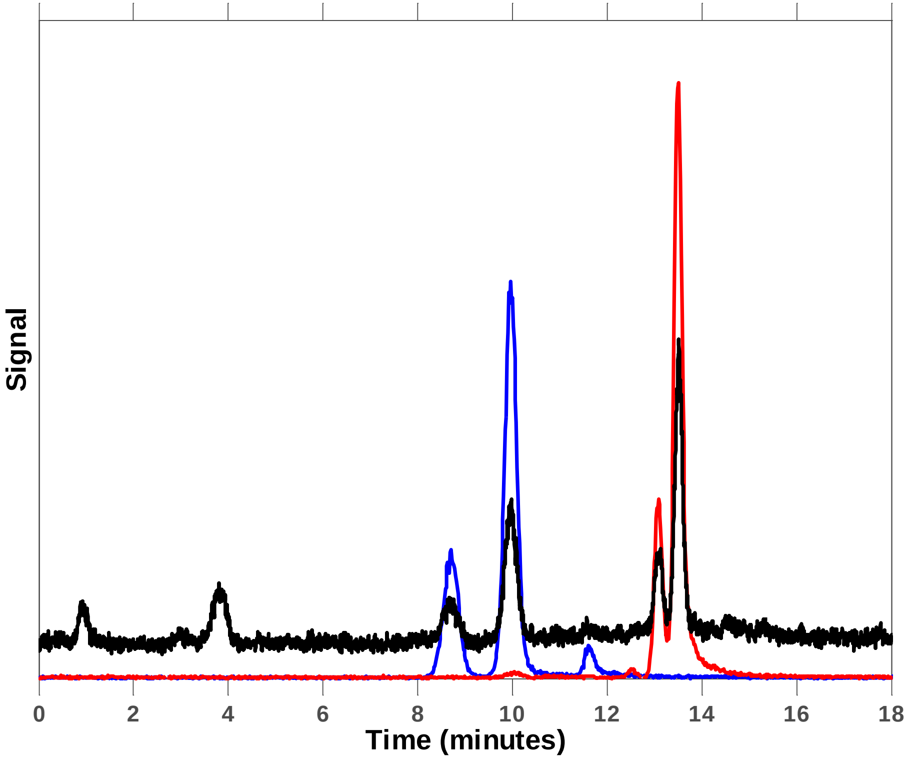

Fig. 3. An example GC-CIMS/TD-LIF chromatogram is shown. Absolute amounts of hydroxy nitrate are measured by integrating the alkyl nitrate peaks (black line, elevated baseline) which co-elute with the individual hydroxy nitrates observed by CIMS, e.g. hydroxy nitrates from 1-butene at 220 m/z (blue) and from 1-hexene at 248 m/z. Absolute sensitivities are determined by integrating individual peaks for CIMS signal and TD-LIF signal and dividing.

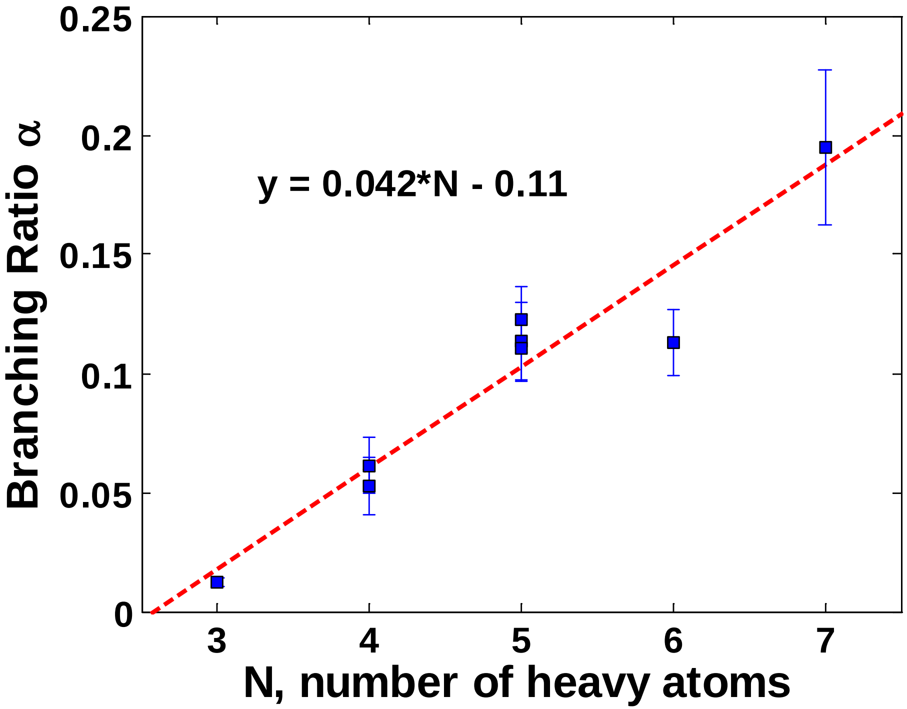

Fig. 4. The hydroxy nitrate branching ratios after OH and O_2 addition plotted against the number of heavy atoms (not including the peroxy radical moiety) derived from a subset of alkenes in this study. Data is taken from Table 3 and normalized by f_a to account for abstraction chemistry (see text for more details). An OLS fit is shown in the dotted red line, with a slope of 0.042 ± 0.008 and an intercept of −0.11 ± 0.04.

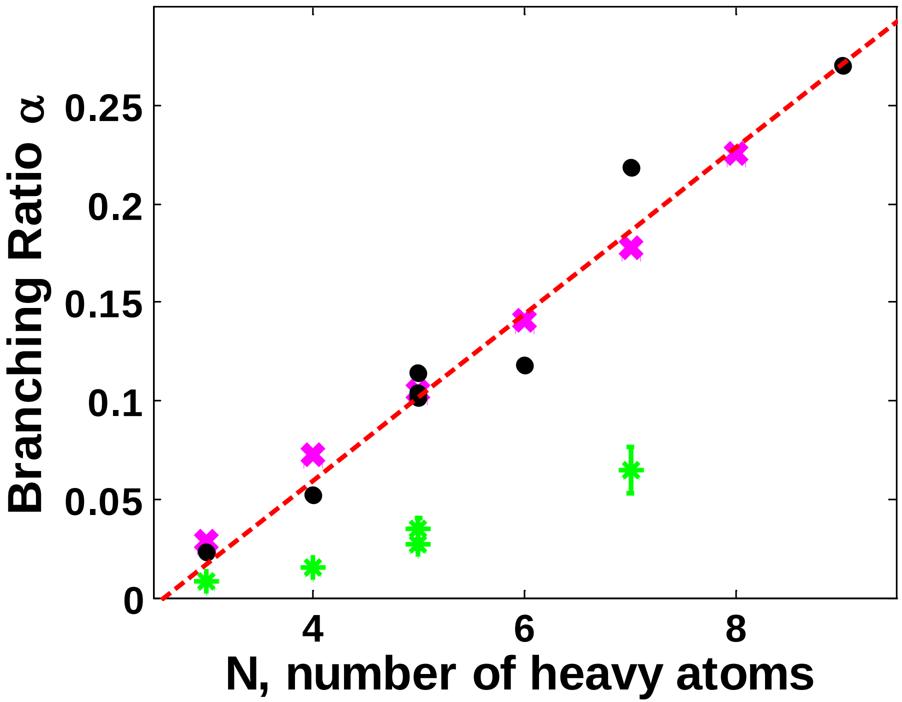

Fig. 5. The isomer-averaged branching ratios, α, derived in this study (black circles, data from Table 4), compared to similar carbon numbered *n*-alkanes (Arey et al., 2001; pink exes) and previously published nitrate branching ratios (O'Brien et al., 1998; green stars). Alkene nitrate yields from O'Brien et al., 1998 have been normalized by f_a to account for H-abstraction in the same fashion as this study. The OLS fit derived from Fig. 4 is shown for hydroxy nitrate branching ratios (red dotted line) from all measured alkenes yields a slope of 0.042 ± 0.008 and intercept of −0.11 ± 0.04 (errors are 2σ). This fit agrees well with Arey et al., 2001, who calculated a slope of 0.0381 ± 0.0016 and an intercept of −0.073 ± 0.009 for alkanes.

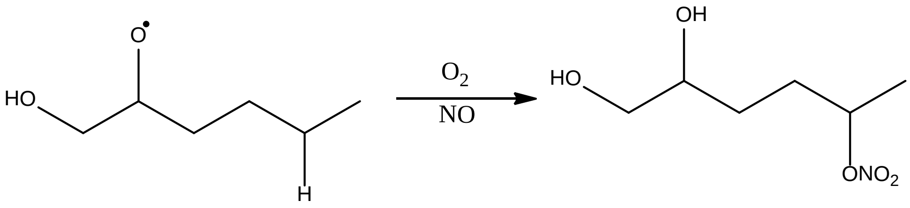

Fig. 6. Alkoxy H-shift isomerization leading to dihydroxy nitrate formation for 1-hexene.

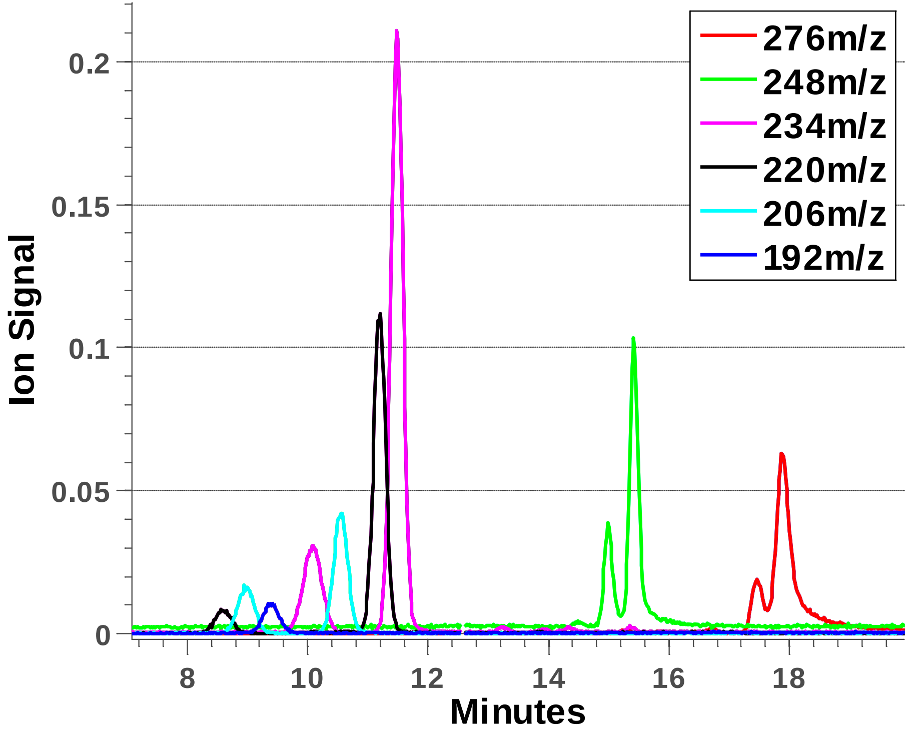

Fig. 7. An example chromatographic separation of hydroxy nitrates formed from a set of alkenes. 192 m/z = ethene hydroxy nitrate, 206 m/z = propene hydroxy nitrate; 220 m/z = methylpropene hydroxy nitrate; 234 m/z = 2-methyl 2-butene hydroxy nitrate; 248 m/z = 1-hexene hydroxy nitrate; 276 m/z = 1-octene hydroxy nitrate. Isomer distributions were determined based on integrating peak areas from chromatograms. The later eluting peaks are prone to tailing and co-elution. In such cases, Gaussian peaks were fit to deconvolute co-eluting isomers and the trailing tail residual was assigned to the later eluting peak. This approach is consistent with the fact that the wider and larger peak elutes later in all cases for these hydroxy nitrates.

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