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Yields of *β*-Hydroxynitrates and Dihydroxynitrates in Aerosol Formed from OH Radical-Initiated Reactions of Linear Alkenes in the Presence of NO_x

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Yields of *β*-hydroxynitrates and dihydroxynitrates in aerosol formed from OH radical-initiated reactions of linear C_8-C_{17} 1-alkenes and $C_{14}-C_{17}$ internal alkenes in the presence of NO_x were measured using a thermal desorption particle beam mass spectrometer coupled to a high-performance liquid chromatograph (HPLC) with UV−vis detector for identification and quantification. For 1-alkenes, total yields of *β*-hydroxynitrates normalized for OH radical addition to the C═C double bond increased with carbon number, primarily because of enhanced gas-to-particle partitioning, to a plateau of 0.140 ± 0.009 in the $C_{14}-C_{17}$ range, with 1-hydroxy/2-hydroxy isomer fractions of 0.7:0.3. When combined with yields measured by O'Brien et al. (O'Brien, J. M.; Czuba, E.; Hastie, D. R.; Francisco, J. S.; Shepson, P. S. *J. Phys. Chem. A* 1998, *102*, 8903) for reactions of smaller alkenes, the results for both 1-alkenes and internal alkenes indicate that the branching ratios for the formation of *β*-hydroxynitrates from the reactions of NO with *β*-hydroxyperoxy radicals (averaged over both isomers) increase from 0.009 for C_2 up to 0.13−0.15 for C_{14} and larger and are approximately half the values determined by Arey et al. (Arey, J.; Aschmann, S. M.; Kwok, E. S. C.; Atkinson, R. *J. Phys. Chem. A* 2001, *105*, 1020) for the corresponding alkyl peroxy radicals. The range of branching ratios may be higher for individual isomers, but this could not be determined. It is estimated that for 1-alkenes, approximately 60−70% of OH radical addition occurred at the terminal carbon atom. Average yields of dihydroxynitrates normalized for OH radical addition were 0.039 ± 0.006 and 0.006 ± 0.002 for 1-alkenes and internal alkenes, with differences reflecting enhanced decomposition of *β*-hydroxyalkoxy radicals formed from internal alkenes. The addition of NH_3 reduced yields significantly, apparently by altering hydrogen bonding between hydroxy and peroxy groups in hydroxyperoxy radical−NO complexes, whereas adding H_2O had no obvious effect.

Introduction

Alkenes are a major component of the ~1150 Tg of nonmethane volatile organic compounds (NMVOCs) emitted annually to the atmosphere.[1] Most come from biogenic emissions estimated to be approximately 44% isoprene, 11% monoterpenes, and 1% sesquiterpenes and ~10 times greater than global anthropogenic emissions.[1,2] In urban areas, alkenes constitute ~10% of NMVOCs.[3] In the atmosphere, alkenes react with OH radicals, NO_3 radicals, and O_3. The kinetics, products, and mechanisms of these reactions have been studied,[3−5] with results indicating that reactions with OH radicals are the largest atmospheric loss process and lead to the formation of a variety of oxygenated products. Products containing multiple functional groups may condense to form secondary organic aerosol (SOA) and so are of special interest because of the effects of aerosol particles on global climate and human health.[6,7] For example, the formation of SOA from OH radical-initiated reactions of isoprene, monoterpenes, and sesquiterpenes has received considerable attention[8−11] because of the large contribution of terpene photooxidation products to global SOA.[2]

The products of OH radical-initiated reactions of alkenes depend on the concentration of NO_x, which influences the reactions of organic peroxy radical intermediates. In polluted areas, where NO_x concentrations are high, they react primarily with NO, leading to the formation of carbonyls, *β*-hydroxcarbonyls, dihydroxycarbonyls, *β*-hydroxynitrates, and dihydroxynitrates.[3−5] Analyses of the latter two products have focused on the gas phase, primarily because of analytical challenges. *β*-Hydroxynitrates up to C_6 have been measured in the atmosphere[12−15] and up to C_{10} in the laboratory.[16−22] In the most comprehensive laboratory study to date, O'Brien et al.[16] measured yields of *β*-hydroxynitrates from reactions of a series of C_2-C_6 linear alkenes. Yields increased with carbon number from 0.009 to 0.055 and were approximately half those of alkyl nitrates formed from reactions of the corresponding alkanes. Since measurements and modeling indicate that the yields of alkyl nitrates reach a plateau value of ~0.3 at ~C_{15},[23,24] these results suggest that yields of *β*-hydroxynitrates might be as high as ~0.15 for large alkenes. This would be consistent with the yield of 0.18 measured by Nozière et al.[20] via FTIR analysis of the total (gas plus particle phase) organic nitrate products of the reaction of α-pinene, a C_{10} cyclic alkene. To our knowledge, the only identifications of dihydroxynitrates are those of Aschmann et al.[21,22] for the gas-phase products of the reactions of α-pinene and *β*-pinene.

Because of the absence of data on the formation of large, low-volatility *β*-hydroxynitrates and dihydroxynitrates, which could contribute to atmospheric SOA, we recently measured the yields of these compounds in SOA formed from OH radical-initiated reactions of a series of C_8-C_{17} 1-alkenes and $C_{14}-C_{17}$ internal alkenes in the presence of NO_x. Analyses were carried out by coupling a thermal desorption particle beam mass spectrometer to a high-performance liquid chromatograph

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(HPLC) with UV−vis detector,[25] allowing identification and quantification of nitrate-containing products. The results provide new quantitative data as well as insights into the effects of carbon number, the position of the C=C double bond, and also H_2O and NH_3, on the yields of these compounds and the branching ratios of pathways that lead to their formation. In a study presented elsewhere,[26] these results were used with data obtained by us and from the literature on other products, and from reaction rate constants calculated using structure−reactivity methods, to develop and evaluate a quantitative chemical mechanism and model of SOA formation from these reactions.

Experimental Section

Chemicals. The following chemicals, with purities (when available) and suppliers, were used: 1-octene (99%), 1-nonene (96%), 1-decene (96%), 1-undecene (97%), 1-dodecene (95%), 1-tridecene (99%), 1-tetradecene (96%), 1-pentadecene (98%), 1-hexadecene (99.8%), 1-heptadecene (≥97%), 2-ethylhexyl nitrate (97%), chloroform-*d* (99.8 atom % D), and dioctyl sebacate (90%) [Sigma-Aldrich], 7-pentadecene (0.25 cis/0.75 trans) and 8-heptadecene (0.25 cis/0.75 trans) [ChemSampCo], 7-tetradecene (0.30 cis/0.70 trans) [TCI], and NO and NH_3 [Matheson Gas]. The cis/trans fractions were determined by ^{1}H NMR analysis using a Bruker Avance 600 MHz instrument. Methyl nitrite was synthesized[27] and stored in liquid nitrogen.

Environmental Chamber Method. Reactions of C_8−C_{17} 1-alkenes, 7-tetradecene, 7-pentadecene, and 8-heptadecene with OH radicals in the presence of NO_x were performed in a 5900 L PTFE environmental chamber at ~25 °C and atmospheric pressure. The chamber was filled with clean, dry air (<5 ppbv hydrocarbons, <1% RH) and has blacklights covering two walls. Dioctyl sebacate (DOS) particles from an evaporation−condensation apparatus were flushed into the chamber to achieve a seed particle concentration of ~200−400 μg m^{-3}. An alkene, methyl nitrite, and NO were then added to achieve concentrations of 1 (0.5 and 0.3 for 1-heptadecene and 8-heptadecene), 5, and 5 ppmv. NO suppresses O_3 and NO_3 radical formation. Reactions were also performed with 1-tetradecene at 50% RH and with 20 ppmv NH_3 in dry air.

Reactions were initiated by turning on the blacklights to form OH radicals by methyl nitrite photolysis.[28] After 6 min the blacklights were turned off. Typically, ~40−50% of the alkene reacted, NO decreased by 1−2 ppmv, NO_x stayed approximately constant, and SOA formed within 1 min. The average OH radical concentration estimated from the amount of alkene reacted and its OH radical rate constant[29] was ~3×10^7 cm^{-3}.

Particle and Gas Analysis. A thermal desorption particle beam mass spectrometer (TDPBMS) was used to analyze particle composition in real time[30] and by temperature-programmed thermal desorption (TPTD).[31] Aerosol was sampled into an aerodynamic lens to form a particle beam that impacted on a polymer-coated metal vaporizer rod.[32] For real-time analysis, the rod was resistively heated to 160 °C. Particles vaporized upon impact, and the vapor was ionized by 70 eV electrons and analyzed in a quadrupole mass spectrometer. For TPTD analysis, the rod was cooled to −40 °C and particles were collected for 30 min. The rod was allowed to warm to −5 °C and then heated to 200 °C using a 2 °C min^{-1} ramp to desorb and separate compounds by volatility prior to mass analysis.

After a reaction, replicate particle samples were collected for 2 h on Millipore filters (1.0 μm pore size, Fluoropore FALP, 47 mm) at flow rates of ~15 L min^{-1}. In side-by-side tests these filters performed as well as those with 0.45 μm pore size but had a smaller pressure drop and so less effect on sample flow rates during collection. Filters were extracted immediately or stored at −20 °C. Filters were extracted twice in 4 mL of ethyl acetate at room temperature for >10 min. Extracts were combined, dried with N_2, and dissolved in 50 μL of ethyl acetate. Tests using different solvents, sonication, multiple extractions, and filter spiking indicated recovery efficiencies were 90−100%.

Extracts were analyzed using an Agilent 1100 Series HPLC coupled to a UV−vis diode array detector for quantification and the TDPBMS for identification. A 10 μL sample was separated on a 250 mm × 4.6 mm Zorbax 5 μm XDB-C18 column at room temperature and a flow rate of 1 mL min^{-1} using a water/acetonitrile gradient elution method: 50% acetonitrile for 10 min increasing to 100% over 50 min. Absorbance was measured at 210 nm, where the molar absorptivity of alkyl nitrates is ≥20 times that of alcohols, ketones, carboxylic acids, or alkenes.[33] The flow then entered a Collison atomizer to form an aerosol, passed through charcoal diffusion dryers to remove solvent vapor, and the dried particles entered the TDPBMS for real-time analysis.[25] Selected compounds associated with chromatographic peaks were collected, dried, and dissolved in $CDCl_3$ for ^{1}H NMR analysis using a Varian Inova 400 MHz instrument.

Standard curves used for quantification were prepared using β-hydroxynitrates and dihydroxynitrates purified from the SOA extract from the 1-tetradecene reaction. The extract was fractionated using HPLC, and mixtures of β-hydroxynitrate isomers and dihydroxynitrate isomers were collected separately after their UV−vis peaks were detected. Samples were dried under vacuum, weighed in a microbalance, and dissolved in ethyl acetate to create primary standards. Sample purity was verified by HPLC analysis. The calibration curve for β-hydroxynitrates was prepared using the mixture of C_{14} β-hydroxynitrate isomers. The calibration curve for dihydroxynitrates was prepared using 2-ethylhexyl nitrate as a secondary standard because the dihydroxynitrate isomer sample was too small to prepare a dilution series. The molar absorptivities of the dihydroxynitrate and β-hydroxynitrate standards relative to 2-ethylhexyl nitrate were 0.963 and 0.786. The β-hydroxy group affects nitrate UV absorption, whereas more distant groups do not.[34] The molar yield of an organic nitrate in particles was calculated as (moles of compound on filter/sampled air volume)(aerosol mass concentration after reaction/average aerosol mass concentration during sampling)/(moles of alkene reacted per volume of air). The second term accounts for wall losses during sampling and was calculated from scanning mobility particle sizer (SMPS) measurements. Yields of β-hydroxynitrates and dihydroxynitrates measured in replicate experiments were within ±10% of the value.

Aerosol volume concentrations were measured using an SMPS[35] composed of a long differential mobility analyzer, ^{210}Po bipolar charger, TSI model 310 CPC, and software from the McMurry group at the University of Minnesota. Number and volume concentrations were within ±10% of those measured with a TSI 3936L72 SMPS system. SOA volume concentrations were calculated from the difference between seed and SOA plus seed aerosol volume concentrations, without corrections for chamber wall losses since they were negligible for these 6 min experiments. SOA mass concentrations, M_{SOA}, were calculated by multiplying SOA volume concentrations by a particle density of 1.13 g cm^{-3}. This value was determined from a dried SOA filter extract from a 1-tetradecene reaction with no seed aerosol: a microliter syringe was weighed, a measured volume of liquid SOA was drawn into the syringe, and then it was reweighed.

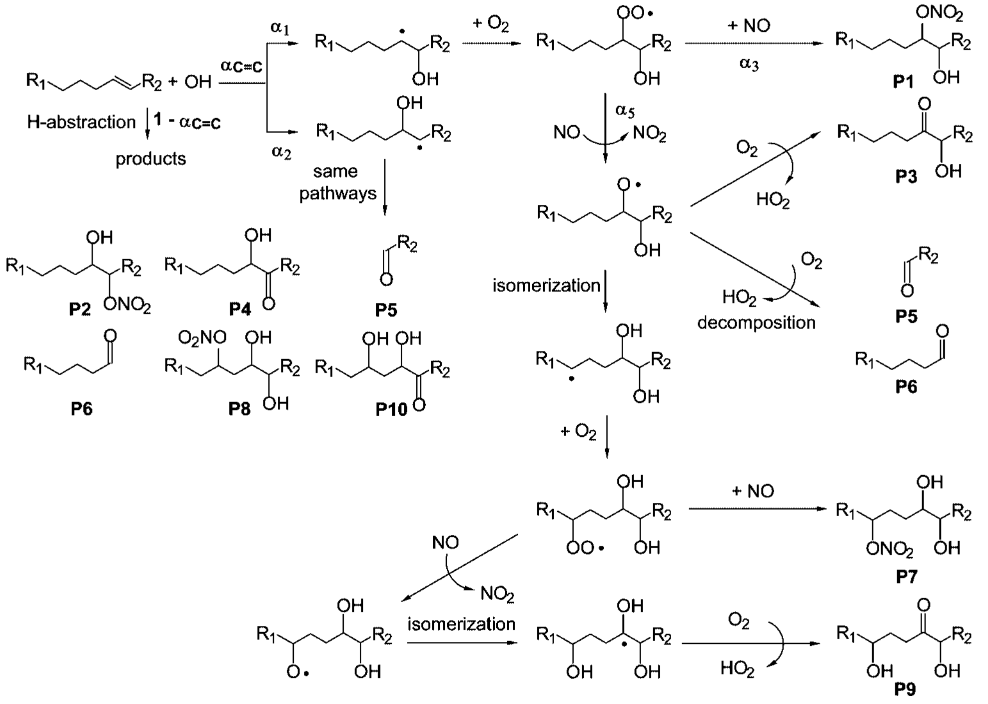

Figure 1. Mechanism of the OH radical-initiated reaction of linear alkenes in the presence of NO_x.

Organic aerosol mass concentrations measured with the SMPS were within ±20% of those determined by weighing dried filter extracts.

Alkenes were collected on Tenax TA and analyzed by gas chromatography with flame ionization detector (GC-FID).[36] Concentrations measured for replicate samples taken at 30 min intervals both before and after reaction agreed to within ±5%, so no corrections were made for wall losses.

Results and Discussion

Reaction Mechanism. The mechanism of OH radical-initiated reactions of linear alkenes in the presence of NO_x[5] is shown in Figure 1, where R_1 represents an alkyl group and R_2 represents an H atom for 1-alkenes and an alkyl group for internal alkenes. Branching ratios are defined as $\alpha_i = r_i/\Sigma r_i$, where r_i is the rate a species reacts by pathway i and the sum is over all pathways by which the species reacts. The sum of the branching ratios for a species is 1. The branching ratios quantified here are $\alpha_{C=C}$ and α_1–α_6. Note that α_4 and α_6 are associated with the portion of the mechanism labeled "same pathways" in Figure 1 and correspond to α_3 and α_5. The reaction is initiated by addition of an OH radical to the C=C double bond or by H-atom abstraction, with branching ratios $\alpha_{C=C}$ and $1 - \alpha_{C=C}$. Products of H-atom abstraction should be similar to those formed from reactions of alkanes.[5,23,37] We focus here on OH radical addition, which dominates for C_8–C_{17} alkenes, although H-atom abstraction is significant. This pathway forms two isomeric β-hydroxyalkyl radicals (one for a symmetrical alkene) with branching ratios α_1 and α_2 ($\alpha_1 + \alpha_2 = \alpha_{C=C}$). The β-hydroxyalkyl radicals react with O_2 to form β-hydroxyperoxy radicals that react with NO, forming β-hydroxynitrates [P1, P2] with branching ratios α_3 and α_4 or β-hydroxyalkoxy radicals with branching ratios $\alpha_5 = 1 - \alpha_3$ and $\alpha_6 = 1 - \alpha_4$. The β-hydroxyalkoxy radicals can react with O_2, decompose, or isomerize. Reaction with O_2 forms α-hydroxycarbonyls [P3, P4] but is unimportant for $C_n > 5$.[38] Decomposition followed by reaction with O_2 creates two aldehydes [P5, P6] (the same for both β-hydroxyalkoxy isomers) that are too volatile to form SOA. Isomerization through a six-membered ring followed by reaction with O_2 forms dihydroxyperoxy radicals that react similarly to β-hydroxyperoxy radicals. The products are dihydroxynitrates [P7, P8] and dihydroxyalkoxy radicals that isomerize and react with O_2 to form dihydroxycarbonyls [P9, P10]. As is shown elsewhere,[26] dihydroxycarbonyls present in particles can isomerize to cyclic hemiacetals that can dehydrate to dihydrofurans, or they can form dimers.

SOA Product Identification. Real-time mass spectra of SOA formed from the reaction of 1-tetradecene are shown in Figure 2A. Peaks at m/z 179, 197, and 199 are characteristic of β-hydroxynitrates and dihydroxynitrates, as verified below. Thermal desorption profiles are shown in Figure 2B. Total ion (TI) signal is proportional to organic mass,[39] and m/z 46 identifies organic nitrates. The overlap of TI and m/z 46 profiles at low temperature suggests the most volatile products are organic nitrates, consistent with the expectation that aldehydes are too volatile to form SOA. The most volatile organic nitrates are β-hydroxynitrates, assigned to the peak at 50 °C. Dihydroxynitrates are assigned to the peak at 70 °C.

This assignment is consistent with results of HPLC analysis shown in Figures 3 and 4. Structures of β-hydroxynitrates and dihydroxynitrates are designated using the following notation: (1) hydroxy and nitrooxy groups are designated H and N, (2) the location of a group on the alkyl chain is designated by a number placed before the letter, and (3) the length of the alkyl chain is designated by a number following the letter C. For example, 1,2-dihydroxy-4-nitrooxytetradecane is designated $1,2H4NC_{14}$.

The predominant fragmentation channel for compounds having adjacent functional groups, as do the β-hydroxynitrates and dihydroxynitrates, is scission of the C–C bond between the two groups. For $1N2HC_{14}$, $7H8NC_{14}$, $7H8NC_{15}$, $7N8HC_{15}$, $8H9NC_{17}$, and $8N9HC_{17}$, this leads to peaks at m/z 199, 115, 115, 129, 129, 143 from $RCHOH^+$ ions and neutral aldehyde and NO_2 coproducts. For small carbon chains, $RCHOH^+$ ions can lose H_2O, as occurs for all these ions except m/z 199. For $7H8NC_{14}$, $7H8NC_{15}$, $7N8HC_{15}$, $8H9NC_{17}$, and $8N9HC_{17}$ this

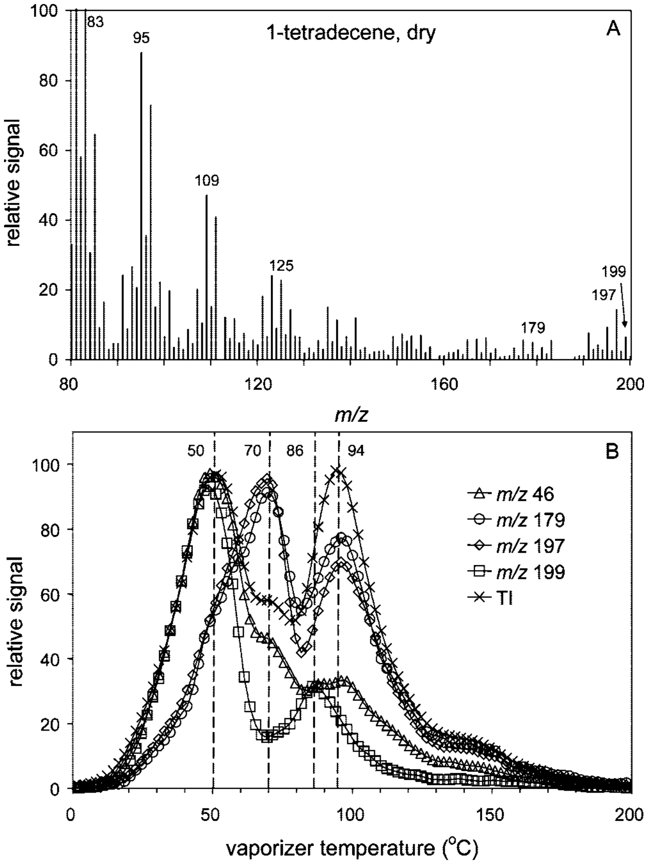

Figure 2. (A) Real-time TDPBMS mass spectra and (B) thermal desorption profiles for SOA formed from the OH radical-initiated reaction of 1-tetradecene in dry air in the presence of NO_x. Thermal desorption profiles were smoothed and normalized to peak values.

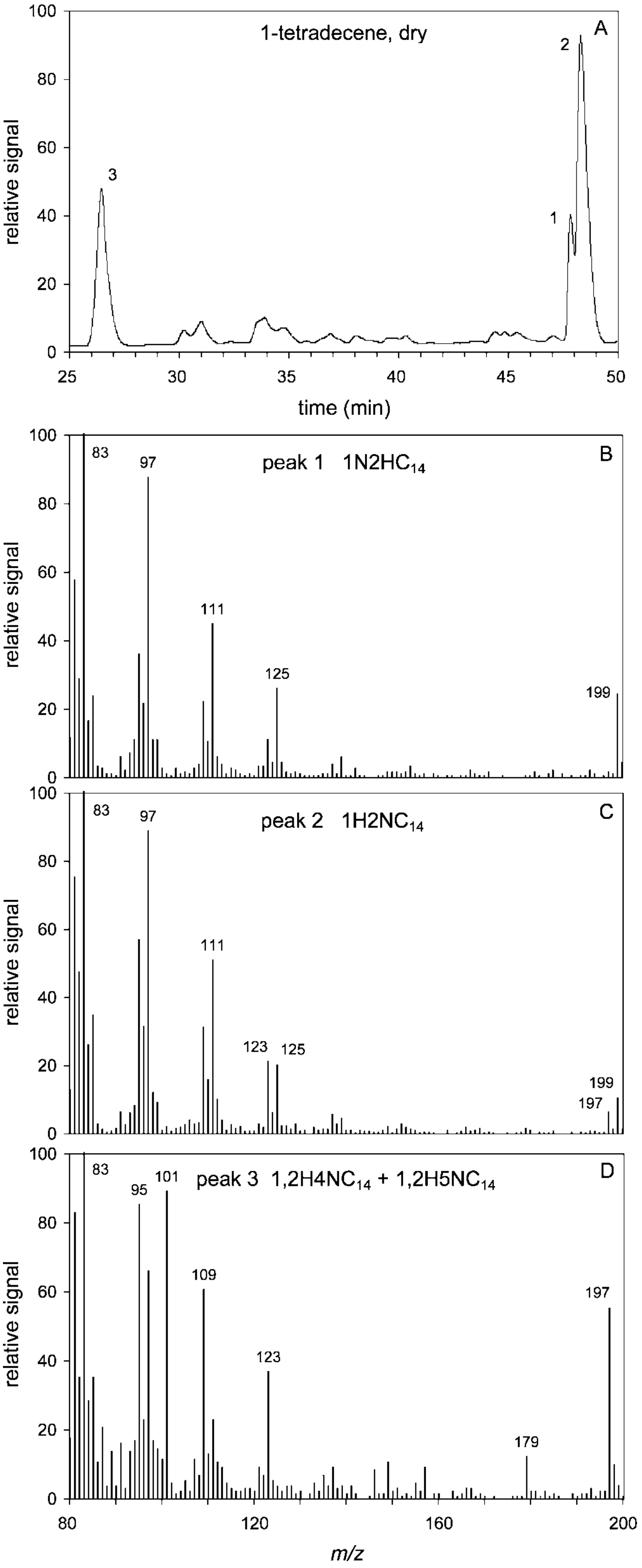

Figure 3. (A) HPLC-UV chromatogram and HPLC−TDPBMS mass spectra of (B and C) β-hydroxynitrate isomers and (D) dihydroxynitrates formed from the OH radical-initiated reaction of 1-tetradecene in dry air the presence of NO_x.

gives ions at m/z 97, 97, 111, 111, and 125. This is observed in mass spectra of 1,2-dihydroxytetradecane and 7-hydroxytetradecane, which have peaks at m/z 199 and m/z 129, 115, 111, and 97, respectively.[40] For the 1,2H4NC$_{14}$ and 1,2H5NC$_{14}$ dihydroxynitrates, scission forms an unstable m/z 260 ion that loses HNO_3 or $HNO_3 + H_2O$ to form m/z 197 and 179 ions. For 1H2NC$_{14}$, scission forms RCO^+ at m/z 197 and $CH_3OH + NO_2$. These product assignments are consistent with results of ^{1}H NMR analyses of β-hydroxynitrates and dihydroxynitrates formed from the 1-tetradecene reaction presented in Supporting Information Table S2.

β-Hydroxynitrate Yields. Measured molar yields (moles of product formed/mole of alkene reacted) of β-hydroxynitrates are presented in Figure 5 and Supporting Information Table S1. Losses by secondary reactions with OH radicals were estimated at ≤5% using a model that accounted for decreased reactivity in particles and so were neglected. Yields of both β-hydroxynitrate isomers are reported for reactions of 1-alkenes, but total yields are reported for internal alkenes because isomers could not be resolved. Also presented are yields normalized for the fraction of the OH radical reaction that occurred by addition to the C=C double bond, $\alpha_{C=C} = k_{add}/(k_{add} + k_{abs})$, where k_{add} and k_{abs} are the rate constants for OH radical addition and H-atom abstraction, respectively, with their sum being equal to the total rate constant. Values of $\alpha_{C=C}$ were calculated using equations for k_{abs}[41] and k_{add}[42] developed by Atkinson and co-workers from measured rate constant data. For 1-alkenes, $k_{abs} = 2.47 + 1.4(\mathrm{CN} - 5)$ and $k_{add} = 28 + 9[1 - \exp(-0.35(\mathrm{CN} - 3))]$, where CN is the carbon number and k values are in units of 10^{-12} cm^3 molecule^{-1} s^{-1}. For cis and trans internal alkenes, $k_{abs} = 4.93 + 1.4(\mathrm{CN} - 8)$, $k_{add}(\mathrm{cis}) = 56.4$, and $k_{add}(\mathrm{trans}) = 64$ and were used with the measured fractions of cis and trans isomers to calculate weighted values of $\alpha_{C=C}$. In general, $\alpha_{C=C}$ increases with increased alkyl group substitution at the C=C double bond and decreases with increasing carbon number.

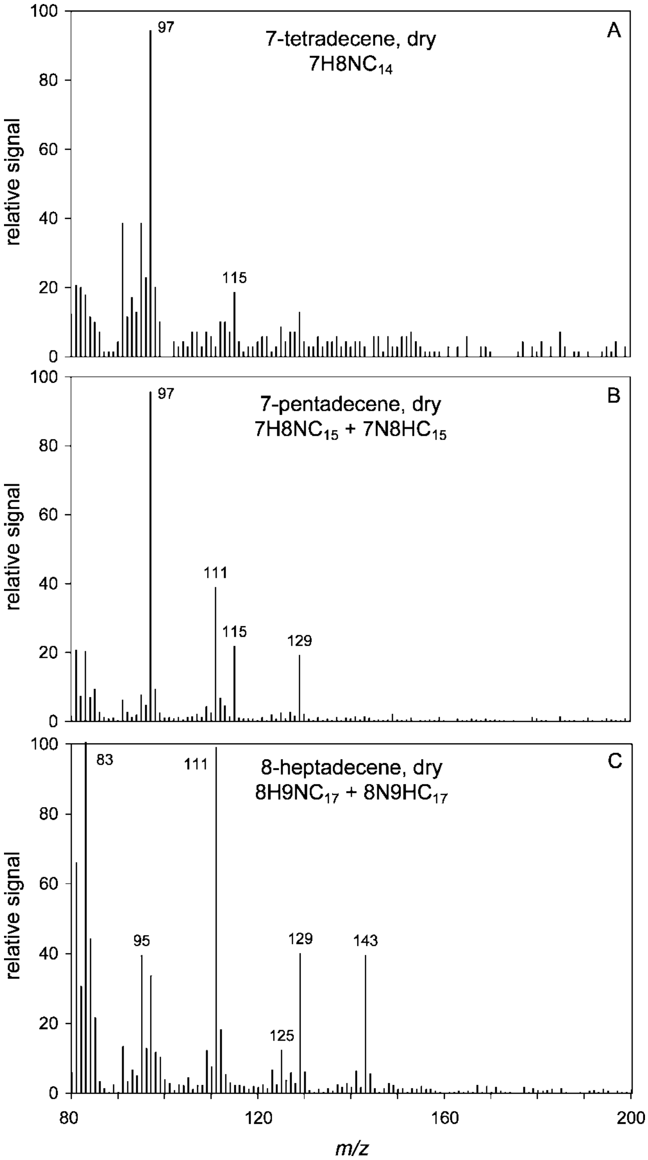

Figure 4. HPLC−TDPBMS mass spectra of β-hydroxynitrates formed from the OH radical-initiated reactions of (A) 7-tetradecene, (B) 7-pentadecene, and (C) 8-heptadecene in dry air in the presence of NO_x.

Total β-hydroxynitrate yields measured for reactions of 1-alkenes and internal alkenes without and with normalization for OH addition are shown in Figure 5. Normalization reduces scatter caused by differences in the relative reactivity of the C═C double bond. Yields increase with carbon number and for 1-alkenes reach a plateau at C_{14}−C_{17}, where the average OH addition-normalized yield is 0.133 ± 0.002. Stated uncertainties here and throughout the text are one standard deviation. Yields for internal alkenes may reach a plateau at about C_{17}, where the OH addition-normalized yield is 0.150, but this could not be verified because C_{16} or C_{18} internal alkenes were not available for experiments. Also shown in Figure 5 are total yields of β-hydroxynitrates formed from reactions of C_2−C_4 and C_6 1-alkenes and *cis*-2-butene, measured using gas chromatography.[16] Note that C_2−C_6 β-hydroxynitrates are gas-phase products, whereas C_8−C_{17} β-hydroxynitrates could be in the gas and/or particle phases. Yields reported here are for particulate C_8−C_{17} β-hydroxynitrates and can be affected by gas−particle partitioning.

The solid curve in Figure 5B was calculated using a scaled version of an equation developed by Arey et al.[23] from measurements of yields of C_2−C_8 secondary alkyl nitrates formed from reactions of *n*-alkanes with OH radicals in the presence of NO_x. Results of computational studies[24] are consistent with the form of this equation. They predict alkyl nitrate yields increase with carbon number to a plateau at ~C_{15} because the internal energy generated by formation of the alkyl peroxy radical−NO intermediate is distributed among more vibrational modes, increasing stability and thereby nitrate formation. The scaling factor used for the curve in Figure 5B was 0.455, chosen to reduce the yield calculated for a C_{15} β-hydroxynitrate from 0.292, the value for a C_{15} secondary alkyl nitrate, to 0.133, the average total OH addition-normalized β-hydroxynitrate yield at the plateau. Previous studies of $C_n \leq 8$ alkenes noted that β-hydroxynitrate yields are about half those of alkyl nitrates.[16,43] Quantum chemical calculations indicate yields are lower for β-hydroxynitrates because hydrogen bonding between hydroxy and peroxy groups weakens the O−O bond in the β-hydroxyperoxy radical−NO intermediate, enhancing formation of a β-hydroxyalkoxy radical and NO_2.[16]

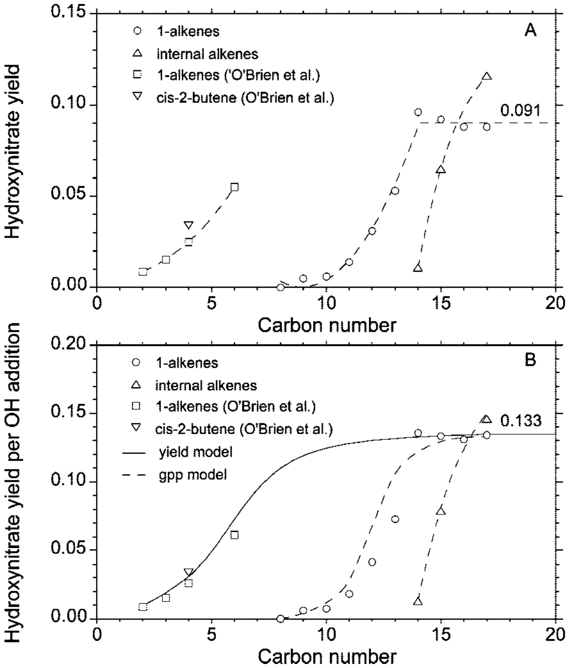

Figure 5. Molar yields of β-hydroxynitrates formed from the OH radical-initiated reaction of linear alkenes in dry air in the presence of NO_x (A) without and (B) with normalization for the fraction of the OH radical reaction that occurred by addition to the double bond. In panel A, the dashed curves were drawn to aid the eye. In panel B, the solid line (yield model) is a scaled version of an equation from Arey et al. (ref 23) for secondary alkyl nitrate yields, the dashed curve through the yields for 1-alkenes (gpp model) is calculated using gas−particle partitioning theory, and the dashed curve though the yields for internal alkenes was drawn to aid the eye.

Comparison of measured and modeled β-hydroxynitrate yields (Figure 5) indicates the increase in measured yields with increasing carbon number is primarily due to enhanced gas-to-particle partitioning. This conclusion is also consistent with yields that have been corrected for gas−particle partitioning, shown by the dashed curve in Figure 5B. Values were calculated by multiplying the plateau value of 0.133 by the fraction of each β-hydroxynitrate estimated to be in the particle phase using gas−particle partitioning theory[44] and β-hydroxynitrate vapor pressures assumed to be the same as those of 1,2-dialkynitrates.[45] Yields measured for reactions of internal alkenes are shifted to higher carbon numbers because functional groups located away from the ends of a molecule have less effect on vapor pressure.

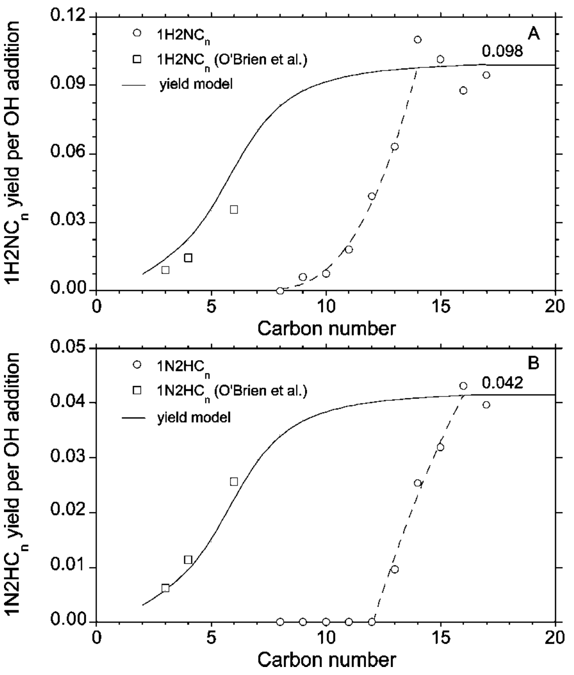

Figure 6. Molar yields of β-hydroxynitrate isomers formed from the OH radical-initiated reaction of 1-alkenes in the presence of NO_x, with normalization for the fraction of the OH radical reaction that occurred by addition to the double bond. The solid curves (yield model) are scaled versions of an equation from Arey et al. (ref 23) for secondary alkyl nitrate yields, and the dashed curves were drawn to aid the eye.

The shift in the two curves is ~2−3 carbon numbers, which suggests that the yield measured for the C_{17} internal alkene should, like the corresponding C_{14} or C_{15} 1-alkenes, be close to a plateau. The OH addition-normalized yields measured for the β-hydroxynitrate isomers, 1H2NC$_n$ and 1N2HC$_n$, formed from reactions of 1-alkenes are shown in Figure 6 with model curves adjusted to match average plateau values at C_{15}. Yields are much larger for 1H2NC$_n$ than 1N2HC$_n$ isomers; a 1H2NC$_n$ isomer was first detected at C_9 and a 1N2HC$_n$ isomer at C_{13}. Yields increase with increasing carbon number reaching plateaus at C_{14} for 1H2NC$_n$ isomers and C_{16} for 1N2HC$_n$ isomers. Average OH addition-normalized yields for 1H2NC$_n$ and 1N2HC$_n$ isomers are 0.098 ± 0.009 and 0.042 ± 0.002 within the C_{14}−C_{17} and C_{16}−C_{17} plateau regions, corresponding to fractions of 0.70 and 0.30 of the total yield of 0.140 ± 0.009. Fractions measured for C_3, C_4, and C_6 1-alkenes were 0.59 and 0.41.[16] The value of 0.140 does not include yields for the 1N2HC$_{14}$ and 1N2HC$_{15}$ isomers, which are impacted by gas−particle partitioning, and so is more accurate than the value of 0.133 obtained from the total OH addition-normalized yields (Figure 5B).

Branching Ratios. From Figure 1 and the discussion above, it can be seen that the OH addition-normalized yields of the 1H2NC$_n$ [P1] and 1N2HC$_n$ [P2] isomers are equal to $Y_{P1}/\alpha_{C=C} = (\alpha_1/\alpha_{C=C})(\alpha_3)$ and $Y_{P2}/\alpha_{C=C} = (\alpha_2/\alpha_{C=C})(\alpha_4)$, where Y is the measured yield. The fraction of OH radical addition reactions that occur at the first and second carbon atoms, $\alpha_1/\alpha_{C=C}$ and $\alpha_2/\alpha_{C=C}$, can therefore be calculated from our reported OH-normalized yields, if the branching ratios for the formation of these compounds from the reactions of NO with 1-hydroxy-2-peroxy radicals, α_3, and 1-peroxy-2-hydroxy radicals, α_4, are known. Here, we estimate these values using two plausible sets of values for α_3 and α_4 and isomer yield data for $C_n \geq 16$, where gas−particle partitioning is not important.

In the first case, we assume that $\alpha_3 = \alpha_4$. Since $(\alpha_1/\alpha_{C=C}) + (\alpha_2/\alpha_{C=C}) = 1$, then $\alpha_3 = \alpha_4 = 0.14$, the sum of the OH addition-normalized isomer yields, and $(\alpha_1/\alpha_{C=C}) = 0.098/0.14 = 0.70$ and $(\alpha_2/\alpha_{C=C}) = 0.042/0.14 = 0.30$. These values agree well with values of 0.65 and 0.35 measured by Cvetanovic for 1-propene.[46] For the internal alkenes studied here, OH radical addition should not depend on the alkyl groups attached to the double-bonded carbon atoms so that $(\alpha_1/\alpha_{C=C}) = (\alpha_2/\alpha_{C=C}) = 0.5$ and $\alpha_3 = \alpha_4 = 0.15$, the sum of OH addition-normalized yields measured for the reaction of 8-heptadecene. In this case, then, the branching ratios for the formation of β-hydroxynitrates from reactions of NO with β-hydroxyperoxy radicals appear to be similar for 1-alkenes and internal alkenes at their plateaus (assuming for reasons discussed above that the value for 8-heptadecene is close to the plateau) and ~0.13−0.15.

In the second case, we assume that $\alpha_3/\alpha_4 = 1.5$, the ratio measured recently by Cassanelli et al.[47] for the formation of alkyl nitrates from reactions of NO with pentyl peroxy radical isomers. These results indicate that the branching ratio for 1-hydroxy-2-peroxy radicals, α_3, could be ~1.5 times the value for 1-peroxy-2-hydroxy radicals, α_4, although β-hydroxyperoxy radicals may not necessarily behave the same as alkyl peroxy radicals, due to the presence of the hydroxy group. Combining the equations $\alpha_3/\alpha_4 = 1.5$, $Y_{P1}/\alpha_{C=C} = 0.098 = (\alpha_1/\alpha_{C=C})(\alpha_3)$, $Y_{P2}/\alpha_{C=C} = 0.042 = (\alpha_2/\alpha_{C=C})(\alpha_4)$, and $(\alpha_1/\alpha_{C=C}) + (\alpha_2/\alpha_{C=C}) = 1$ then gives for reactions of 1-alkenes, $\alpha_1/\alpha_{C=C} = 0.62$, $\alpha_2/\alpha_{C=C} = 0.38$, $\alpha_3 = 0.16$, and $\alpha_4 = 0.11$. The value of α_3 for reactions of internal alkenes should therefore be ~0.16 in this case. The agreement between these values and those noted above for 1-propene[46] and 8-heptadecene is again good, indicating that both sets of branching ratios are consistent with the experimental results and that it is not possible to identify differences in the branching ratios for nitrate formation from reactions of NO with primary and secondary peroxy groups in β-hydroxyperoxy radicals. It is worth noting that values of $\alpha_3/\alpha_4 \sim 2$ have been suggested,[48] although the measurements were less precise than those of Cassanelli et al.[47] The resulting branching ratios are $\alpha_1/\alpha_{C=C} = 0.54$, $\alpha_2/\alpha_{C=C} = 0.46$, $\alpha_3 = 0.18$, and $\alpha_4 = 0.09$, which do not agree as well with the measurements.

Dihydroxynitrate Yields. Total yields of dihydroxynitrates in particles are given in Supporting Information Table S1; the isomers could not be resolved. Unlike β-hydroxynitrate yields, dihydroxynitrate yields are independent of carbon number. This is probably because the additional hydroxy group leads to almost complete gas-to-particle partitioning. Yields without and with normalization for OH addition were 0.029 ± 0.005 and 0.039 ± 0.006 for the C_{10}−C_{17} 1-alkenes and 0.005 ± 0.002 and 0.006 ± 0.002 for the internal alkenes. The lower yields for internal alkenes reflect the higher rates of decomposition relative to isomerization for the β-hydroxyalkoxy radicals.[38]

Effects of Humidity and Ammonia on β-Hydroxynitrate and Dihydroxynitrate Yields. As mentioned above, it is thought that the lower branching ratios for nitrate formation from reactions of NO with β-hydroxyperoxy radicals compared to alkyl peroxy radicals are due to hydrogen bonding between hydroxy and peroxy groups.[16] This effect was further investigated here by comparing yields of β-hydroxynitrates and dihydroxynitrates formed from reactions of 1-tetradecene in dry air with those formed at 50% RH and in dry air with 20 ppmv of NH_3. H_2O and NH_3 are both capable of hydrogen bonding and so could affect yields.

Results are given in Table 1. They show that H_2O did not affect the yields of β-hydroxynitrates but may have reduced those of dihydroxynitrates (the difference is within uncertainties).

TABLE 1: Effects of Experimental Conditions on Molar Yields of β-Hydroxynitrates and Dihydroxynitrates Formed from OH Radical-Initiated Reactions of 1-Tetradecene in the Presence of NO_x

condition[a]	$1H2NC_{14}$	$1N2HC_{14}$	dihydroxynitrates[b]
dry	0.078	0.018	0.033
H_2O	0.082	0.018	0.023
NH_3	0.018	0.004	0.010

[a] Dry = <1% RH; H_2O = 50% RH; NH_3 = 20 ppmv NH_3. [b] Dihydroxynitrate isomers are $1,2H4NC_{14}$ and $1,2H5NC_{14}$.

The absence of an effect is consistent with results of computations that predict that at 300 K and 50% RH ~1% of β-hydroxyperoxy radicals exist as complexes with H_2O.[49] The additional hydroxy group in dihydroxyperoxy radicals might enhance complex formation with H_2O sufficiently to reduce the yields. Conversely, NH_3 had a large impact on yields, reducing those of β-hydroxynitrates and dihydroxynitrates by ~70−80%. The greater effect of NH_3 probably results from stronger hydrogen bonding weakening the O−O bond. According to calculations,[49] log K_{eq} for forming complexes of H_2O with various peroxy radicals at 300 K is a linear function of the binding energy of the complex, BE (kcal mol^{-1}), with slope ~0.5. If this relationship holds in general, then the fraction of β-hydroxyperoxy radicals present as complexes, *F*, with a species C is approximately given by eq 1 with [C] in ppmv.

$$\log F = 0.5\mathrm{BE} + \log[\mathrm{C}] - 9.5 \qquad (1)$$

This equation is used here to estimate the minimum binding energy for a β-hydroxyperoxy radical−NH_3 complex. From our results, the minimum value of *F* at 20 ppmv NH_3 is ~0.75 if the branching ratio for β-hydroxynitrate formation from the reaction of NO with a complex is zero. Otherwise, *F* and BE are higher. Substituting these values into eq 1 gives BE ~16 kcal mol^{-1}, compared to ~6.4 kcal mol^{-1} for the H_2O complex. In the atmosphere, NH_3 concentrations can range from tens of parts-per-billion by volume in polluted air to tens of parts-per-trillion by volume in clean air.[50] Under these conditions, calculated binding energies of ~22−28 kcal mol^{-1}, which are unlikely, are required to achieve a similar fraction of complexes, suggesting ammonia does not effect these reactions.

Conclusions

The results presented here represent the first measurements to date of the yields of β-hydroxynitrates and dihydroxynitrates in SOA, in this case formed from OH radical-initiated reactions of linear alkenes in the presence of NO_x. The yields depend on the structure of the parent alkene, which influences a number of important aspects of the reaction mechanism. These include the rates at which OH radicals abstract H atoms and add to the C=C double bond, the C atom to which the OH radical adds, branching ratios for the reactions of organic peroxy radicals with NO, and rates of decomposition and isomerization of alkoxy radicals, as well as gas−particle partitioning of products. The yields can also be impacted by the presence of species such as NH_3, which can form hydrogen bonds with organic peroxy radicals. Reactions were carried out with C_8−C_{17} alkenes in order to form at least some products that were sufficiently large that gas-to-particle partitioning was essentially complete (and therefore yields measured in aerosol were the same as total yields) and that reaction branching ratios did not depend on carbon number. For 1-alkenes, a plateau was reached at C_{14}−C_{17} for the yields of β-hydroxynitrates normalized for OH radical addition to the C=C double bond, corresponding to branching ratios for their formation from reactions of NO with β-hydroxyperoxy radicals (averaged over both isomers) of 0.13−0.15. A similar value was obtained for internal alkenes, but with less data. A simple model developed previously[23] to describe the carbon number dependence of this branching ratio for reactions of alkyl peroxy radicals with NO also works well for these reactions after scaling by a factor of 0.455 to match the plateau value. The lower branching ratios for β-hydroxyperoxy radicals apparently result from hydrogen bonding between the hydroxy and peroxy groups. This branching ratio equation can be used with structure−reactivity calculations[41,42] of OH radical addition and abstraction to estimate yields of β-hydroxynitrates from the reactions of alkenes. For example, for C_{10} monoterpenes and C_{15} sesquiterpenes, major atmospheric alkene emissions whose OH radical reactions are dominated by addition, β-hydroxynitrate yields should be close to 0.14, consistent with a total organic nitrate yield of 0.18 measured for the α-pinene reaction.[20]

Yields of dihydroxynitrates were highly dependent on the structure of the parent alkene, most likely because of differences in rates of decomposition of β-hydroxyalkoxy radicals and possibly branching ratios for the reactions of dihydroxyperoxy radicals with NO. Partitioning to the aerosol phase appeared to be complete over the C_{10}−C_{17} carbon number range where analysis was possible, reflecting the lower volatility of these compounds compared to β-hydroxynitrates. As is shown elsewhere,[26] the dihydroxynitrate yields measured here can be used with the β-hydroxynitrate yields, carbonyl yields from the literature, and structure−reactivity calculations for OH radical reactions and β-hydroxyalkoxy radical isomerization and decomposition to develop a quantitative chemical mechanism and model of SOA formation from these reactions.

It is also worth emphasizing that the yields reported here were measured by coupling a TDPBMS to an HPLC with UV−vis detector via an atomizer. For these experiments, it was therefore possible to analyze SOA in three different ways with the TDPBMS: in real time, by TPTD, and following HPLC separation. Products were therefore separated according to their temporal behavior during formation, volatility, and solvent−column interactions. All of this information can aid in product identification, which is difficult in SOA studies because of the general lack of authentic standards of potential products. Here, authentic standards were synthesized by HPLC purification of SOA samples, followed by ^1H NMR analysis to verify their identity. The use of the same particle mass spectrometer for all analyses also has the advantage that it is easier to identify possible artifacts that can occur during off-line analysis, since the mass spectra can be directly compared. We have recently used this approach with a high-resolution time-of-flight Aerodyne aerosol mass spectrometer (AMS), which further enhances analytical capabilities by providing elemental analysis, to aid in the creation of a database of multifunctional organic nitrate mass spectra. Given the variety of particle mass spectrometers currently in use, this may be an approach for others to consider.

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Supporting Information Available: Molar yields of β-hydroxynitrates and dihydroxynitrates in aerosol formed from reactions of 1-alkenes and internal alkenes (Table S1) and results of ^{1}H NMR analyses of β-hydroxynitrates and dihydroxynitrates (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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