α-Pinene Nitrates: Synthesis, Identification and Yields

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Introduction

Production of organic nitrates represents an important sink for NO_x [1]. Water/particle soluble hydroxy nitrates are formed during the atmospheric photodegradation of biogenic volatile organic compounds (BVOCs) by OH radicals in the presence of NO. This includes the highly reactive isoprene, monoterpenes, and sesquiterpenes. Global α-pinene emissions amount to 50-60 Tg yr^{-1} [2]. Previous laboratory studies focused on the formation yields of one or more key α-pinene aldehyde and ketone products such as pinonaldehyde, formaldehyde, and acetone. Reported yields for total α-pinene β-hydroxy nitrates (APN) production range from <1% [3] to 18 ± 9% [4], i.e. two conflicting and divergent sets of data with no overlap.

Objectives of this project:

• Synthesize α-pinene hydroxy nitrate isomers.
• Identify and detect α-pinene nitrates in photochemical reaction chamber experiments.
• Quantify the yields and RO_2+NO branching ratios of individual first generation hydroxy nitrates produced from α-pinene and OH-oxidation in the presence of NO_x.
• Determine the rate constants for the reaction of OH radical with α-pinene hydroxy nitrates at atmospheric pressure and 296 ±2 K.
• Calculate their atmospheric lifetimes.

Experiment Details

Synthesis

Four α-pinene hydroxy nitrates were synthesized [5,6], using an array of synthetic approaches. Figures 1 and 2 show the α-pinene hydroxy nitrates synthesis chemistry and the four synthesized α-pinene hydroxy nitrates structure.

• Nitration of α-pinene diol by 65% HNO_3 in acetic anhydride.
• Nitration of α-pinene epoxide by fuming HNO_3 in diethyl ether.
• α-Pinene hydroxy nitrates were also prepared using reactions between α-pinene epoxide with $NbCl_5$ followed by silver nitrate.

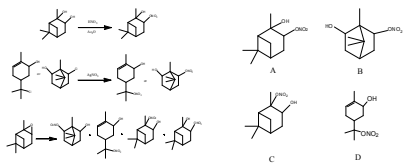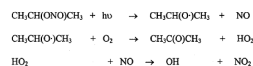**Figure 1. α-pinene hydroxy nitrate synthesis chemistry**

Figure 2. α-pinene hydroxy nitrate isomers

Photochemical Reaction Chamber Experiments

Mixtures of α-pinene, NO, and isopropyl nitrite were irradiated in a 5500 liter PFA photochemical reaction chamber. The organic nitrates were separated and detected using a GC-TSD. OH radicals were produced from the photolysis of isopropyl nitrite, as shown below.

$$CH_3CH(ONO)CH_3 + h\nu \rightarrow CH_3CH(O \cdot)CH_3 + NO$$
$$CH_3CH(O \cdot)CH_3 + O_2 \rightarrow CH_3C(O)CH_3 + HO_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$

OH Rate Constant Experiments

OH rate constants were measured relative to benzene and toluene, as the reference compounds.

α-Pinene Nitrate Yields

A series of six experiments were conducted. The total and individual α-pinene nitrate yields were determined using a GC-TSD and the photochemical reaction chamber. The GC peak assignments were conducted by comparing chromatograms from the total synthesized α-pinene nitrates (APN) standards with those from an α-pinene/NO_x irradiation chamber experiment. A typical chromatogram from an isopropyl nitrite/α-pinene/NO irradiation is shown in Figure 3. According to our synthesized α-pinene nitrate standard, these 4 synthesized α-pinene nitrates were all identified, as peaks A- D in Figure 3.

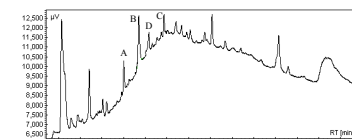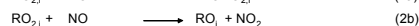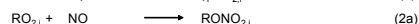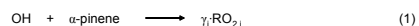**Figure 3. GC-TSD chromatogram of an α-pinene/NO_x yield experiment. The letters correspond to the APNs produced in the yield experiment.**

Each APN concentration was corrected for the OH consumption using the method described by Atkinson et al. [1982]. For any individual nitrate, APN_i, we have the following reactions accounting for individual isomeric APN production.

$$OH + \text{α-pinene} \rightarrow \gamma_i \cdot RO_{2,i} \quad (1)$$
$$RO_{2,i} + NO \rightarrow RONO_{2,i} \quad (2a)$$
$$RO_{2,i} + NO \rightarrow RO_i + NO_2 \quad (2b)$$

Here γ_i is the fractional yield of the appropriate precursor peroxy radical. Assuming steady state in $RO_{2,i}$ and where "R" represents the reaction rate, $R_1 \cdot \gamma_i = R_2$ and $R_1 = k_1[OH][\text{α-pinene}]$. Equation I then describes the α-pinene decay rate.

$$-d[\text{α-pinene}]/dt = R_2/\gamma_i = k_2[RO_{2,i}][NO]/\gamma_i \quad (I)$$

$$d[RONO_{2,i}]/dt = R_{2a} = k_{2a}[RO_{2,i}][NO] \quad (II)$$

Thus, if we plot Δ[$RONO_{2,i}$] vs. -Δ[α-pinene], the slope = $k_{2a}[RO_{2,i}][NO]/(k_2[RO_{2,i}][NO]/\gamma_i) = \gamma_i \cdot k_{2a}/k_2$. If γ_i is known, the branching ratio, $\alpha_i = k_{2a}/k_2$, for $RONO_{2,i}$ formation, can be determined. If we plot Δ∑[$RONO_{2,i}$] vs. -Δ[α-pinene], the slope is equal to the overall yield of α-pinene nitrate. For the nitrates we identified, the results for all experiments are shown in Figure 4, revealing a slope of 0.13 ±0.007. However, it is likely (See Fig. 3) that there are unidentified nitrates, and thus this value represents a lower limit to the overall yield.
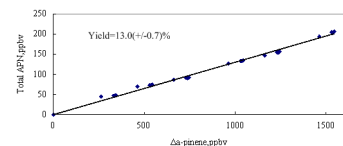

Figure 4. Plot of the total α-pinene nitrate yield. Total [APN] vs. loss of α-pinene over time. The data plotted are from multiple experiments.

Reaction Mechanism

The degradation of α-pinene is initiated primarily by OH radicals by addition to the >C=C< bond, yielding initially the OH-pinene adduct radicals (Figure 5). This leads to P1OH, a secondary radical, or P2OH, a tertiary radical, depending on the addition site [8,9]. The P1OH or P2OH adduct will react rapidly with O_2, forming the corresponding peroxyl radical R1 or R2. For atmospheric conditions with sufficient NO present, R1 or R2 will quickly react to form a peroxynitrite that will in part isomerize to nitrates APN-A or APN-C.

In the case of addition the double bond to give the tertiary radical P2OH, the strain of the nearby four-membered ring is then relieved by either of the two familiar pathways: migration of the isopropyl group, which could involve an isomerization of the chemically activated P2OH to its isomer P3OH, followed by rapid reaction with O_2, forming the corresponding peroxyl radical R3.

Peroxyl radical R3 will quickly react with NO to produce APN-B; or it can promptly open the strained four-membered ring, forming 6-hydroxymethen-8-yl radical P4OH, which reacts with O_2 to form 6-hydroxymethen-8-peroxyl radicals, R4. The resulting 6-hydroxymethen-8-yl radical will then yield the nitrate APN-D.
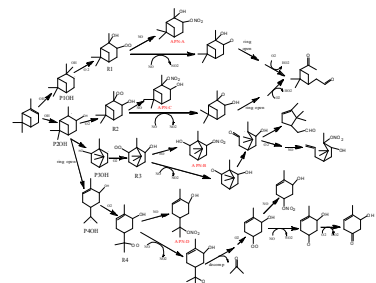

Figure 5. Schematic of the OH-initiated degradation of α-pinene to first generation products in the presence of NO_x

APN Lifetimes

The lifetimes of the APNs in the atmosphere undergoing OH reactions during the daytime (τ) can be expressed as Equation III.

$$\tau = \frac{1}{k_{OH}[OH]} \quad (III)$$

On the basis of the rate coefficients determined in this study, the atmospheric lifetimes of α-pinene nitrates, assuming an ambient 24 h average OH concentration of 1×10^6 molecules cm^{-3}, are 1.9 days for APN-A and 9.6 days for APN-B, respectively. However, for APN-D there is still a double bond. In that case we estimate that k_{OH}=9.9x 10^{-11} cm^3 $molecules^{-1}s^{-1}$, τ_{APN-D}=0.1 day. These lifetime values do not consider dry deposition, which is likely to be significant for these compounds.

OH Rate Constant

The data obtained from the OH radical reactions with the α-pinene hydroxy nitrates are plotted in accordance with equation IV. Typical relative rate plots for APN-A and APN-B are shown in Figure 6 (toluene and benzene as a reference compound, respectively).

$$(1/t) \cdot \ln\left(\frac{APN_0}{APN_t}\right) = (1/t) \cdot \frac{k_{APN}}{k_{RC}} \ln\left(\frac{RC_0}{RC_t}\right) + k_{wl} \quad (IV)$$

From the slopes in Figure 6 and the known reference compound rate constants, we find:

$k_{OH(APN-A)} = 6.6 (\pm 0.3) \times 10^{-12}$ cm^3 $molecules^{-1}$ s^{-1}

$k_{OH(APN-B)} = 1.2 (\pm 0.1) \times 10^{-12}$ cm^3 $molecules^{-1}$ s^{-1}

These values can be compared with the calculated values from the (EPA website) of 6.5×10^{-12} cm^3 $molecules^{-1}s^{-1}$ and 1.0×10^{-12} cm^3 $molecules^{-1}s^{-1}$.

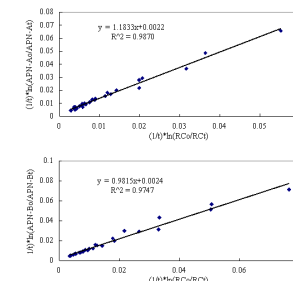**Figure 6. OH rate constant data for two α-pinene hydroxy nitrate isomers. The top one =APN-A, The bottom one =APN-B.**

Conclusions

Four α-pinene hydroxy nitrates are first identified in the smog chamber experiment with a molecular mass of 215. The total yield for the four compounds identified was found to be 13.0 ± 0.7%. The individual nitrate yields for APN-A is 2.7 ± 0.3%, APN-B is 4.9 ± 0.5%, APN-C is 2.2 ± 0.3%, and APN-D is 3.1 ± 0.5%. The atmospheric lifetime of these nitrates are on the order of 2-10 days, making it possible for them to contribute to NO_y and atmospheric transport of nitrogen. Furthermore, they may contribute significantly to aerosol mass. In the future, we intend to measure the free NO_2 yield from OH reaction with the α-pinene nitrates.

References

1. Shepson, P.B.,"Organic Nitrates".Wiley-Blackwell, 1 edition. 2007. 269-289.
2. Guenther, A.B. et al., *Atmospheric Chemistry and Physics* 6, 3181-3210 (2006).
3. Aschmann, S.M. et al., *Journal of Geophysical Research* 107, 4191-4197 (2002).
4. Nozière, B. et al., *Journal of Geophysical Research* 104, 23,645–23,656 (1999).
5. Wängberg, I. et al., *Environ. Sci. Technol.* 31, 2130–2135 (1997).
6. Rollins, A. W. et al., *Atmos. Meas. Tech.* 3, 301–310 (2010).
7. Atkinson, R. et al, *Journal of Physical Chemistry* 86, 4563–4569 (1982).
8. Peeters, J. et al., *Physical Chemistry Chemical Physics* 3, 5489–5504 (2001).
9. Vereecken, L. et al., *Physical Chemistry Chemical Physics* 9, 5241-5248 (2007).