Introduction

Production of organic nitrates represents an important sink for NOx [1]. Waterparticle soluble hydrotlyte nitrates are formed during the atmospheric oxidation of isocyclic volatile organic compounds (BVOCs) by OH radicals in the presence of NOx. 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 aldehydes and ketones products such as pinonaldehyde, formaldehyde, and acetone. Reported yields for total α-pinene/NOx hydrolyte (APN) production range from 1% to 18% [4], i.e., two conflicting and divergent sets of data with no overlap.

Objectives of this project:
- Synthesis α-pinene hydrotlyte nitrate isomers.
- Identify and detect α-pinene nitrates in photochemical reaction chamber experiments.
- Quantify the yields and RO₂/NOx branching ratios of individual first generation hydrolyte nitrates produced from α-pinene and OH
- Determine the rate constants for the reaction of OH radical with α-pinene hydrotlyte nitrate atmospheric pressure and 298K ± 2K.
- Calculate their atmospheric lifetimes

α-Pinene Nitrates Yields

A series of six experiments were conducted. The total and individual α-

pinene nitrate yields were determined using a GC-MS 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/NOx irradiation chamber experiment. A typical chromatogram from an isopropyl nitrate α-pinene/NOx irradiation is shown in Figure 3. According to our synthesized α-pinene nitrate standards, these 4 synthesized α-pinene nitrate yields were all identified, as peaks A-D in Figure 3.

![Figure 3. GC-MS chromatogram of an α-pinene/NOx yield experiment.](image)

The ketone corresponds to the APN produced in the yield experiment.

Each APN concentration was corrected for the OH consumption using the method described by Aisikuron et al. [7]. For each individual nitrate we have the following reactions accounting for individual isomer APN production.

\[
\begin{align*}
{\text{OH}} + \text{α-pinene} & \rightarrow \text{RO}_2^- + \text{HO}_2 \quad (1) \\
\text{RO}_2^- + \text{NO} & \rightarrow \text{RO}_2 + \text{NO}_2 \quad (2a) \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \quad (2b)
\end{align*}
\]

Here, x is the fractional yield of the appropriate precursor peroxidicaldehyde. Assuming steady state in RO₂ and where "R" represents the reaction rate, \(R_1\), \(R_2\), and \(R_3\) are the unimolecular reactions. Equation 1 then describes the α-

pinene decay rate.

\[
\frac{d[\text{α-pinene}]}{dt} = -R_1 - R_2 - R_3
\]

Thus, if we plot \(\text{RO}_2^- + \text{NO} = \alpha [\text{α-pinene}]\), the slope is \(k_{\text{RO}_2^- + \text{NO}}\). Knowing the branching ratio, \(k_{\text{RO}_2^- + \text{NO}}/k_{\text{α-pinene}}\) can be determined. If we plot \(\text{RO} + \text{NO}_2\) vs. \(\alpha [\text{α-pinene}]\), 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. Plot of the total α-pinene nitrate yield, total APN vs. basis of α-pinene over time. The data plotted are from multiple experiments.](image)

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α-Pinene Nitrates Yields

OH Rate Constant

The data obtained from the OH radical reactions with the α-pinene hydrotlyte nitrates is plotted in accordance with equation 1 V. The relative rate plots for APN-A and APN-B are shown in Figure 6 (isoline and benzene as a reference compound, respectively).

\[
\frac{\text{APN-A}}{\text{APN-B}} = \frac{k_{\text{APN-A}}}{k_{\text{APN-B}}} \quad (\text{V})
\]

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

- \(k_{\text{APN-A}} = 6.5 (0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\)
- \(k_{\text{APN-B}} = 1.2 (0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\)

These values can be compared with the calculated values from the EPA website) of \(6.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) and \(1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

![Figure 5. OH rate constant data for two α-pinene hydrotlyte nitrates. The top one is APN-A, the bottom one is APN-B.](image)

Figure 5. OH rate constant data for two α-pinene hydrotlyte nitrates. The top one is APN-A, the bottom one is APN-B.

Conclusions

Four α-pinene hydrotlyte 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 \(15.0 ± 0.7\). The individual nitrate yields for APN-A is \(2.7 ± 0.3\), APN-B is \(4.8 ± 0.5\), APN-C is \(2.2 ± 0.3\), and APN-D is \(3.1 ± 0.5\). The atmospheric lifetime of these nitrate is 1.0-10 days, making it possible for them to contribute to NOx and atmospheric transport of nitrogen. Furthermore, they may contribute significantly to atmospheric nitrate. However, in the future, we intend to measure the free RO₂ yield from reaction with the α-pinene nitrate.

APN Lifetimes

The lifetimes of the APNs in the atmospheric triggering OH reactions during the daytime (1) can be expressed as Equation III

\[
\frac{1}{\tau} = \alpha \frac{1}{\tau_{\text{OH}}}
\]

On the basis of the rate coefficients determined in this study, the atmospheric lifetime of α-pinene nitrate, assuming an ambient 24-hour average OH concentration of 1.0×10⁷ 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, and in that case, we estimate that \(\alpha = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). These lifetime values do not consider dry deposition, which is likely to be significant for these compounds.

References