

# $\alpha$ -Pinene Organic Nitrate Synthesis, Formation, and Simulation

by

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To my husband Bret

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## ABSTRACT

$\alpha$ -Pinene Organic Nitrate Synthesis, Formation, and Simulation

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$\alpha$ -Pinene ( $C_{10}H_{16}$ ), a hydrocarbon emitted by vegetation, is the dominant monoterpene in the Earth's atmosphere. With estimated annual global carbon emissions of  $\sim 50 \text{ Tg yr}^{-1}$ ,  $\alpha$ -pinene emissions are comparable to anthropogenic hydrocarbon emissions - making its atmospheric oxidation products and reaction pathways a significant component of tropospheric chemistry. The major oxidation pathway of  $\alpha$ -pinene is reaction with the hydroxyl radical (OH) during the daytime. One important product of OH and  $\alpha$ -pinene reactions is  $\beta$ -hydroxynitrates ( $HOC_{10}H_{16}ONO_2$ ), which represent a terminating step in the  $\alpha$ -pinene reaction pathway. The formation of these hydroxynitrates prevents the production of  $NO_2$ , a tropospheric ozone precursor, effectively suppressing ozone while sequestering  $NO_x$ . With organic nitrates from BVOCs estimated to account for 10-20% of tropospheric ozone generation, organic nitrate chemistry is an important source in the accounting of global ozone concentrations. Results from the first-known organic synthesis of  $\alpha$ -pinene  $\beta$ -hydroxynitrates are presented in this work. The synthesis

standard supported a series of photochemical reaction chamber studies that reacted pure  $\alpha$ -pinene with OH in a high NO<sub>x</sub> environment. The results from these experiments were analyzed to identify for the first time individual  $\alpha$ -pinene hydroxynitrate isomers, calculate formation yields, and determine the relative branching ratios of the precursor peroxy radical RO<sub>2</sub> reacting with NO. A chemistry model was also created to simulate the reaction chamber experimental conditions to compare how well the currently accepted reaction mechanism for the production of these  $\alpha$ -pinene hydroxynitrates matches experimental results. Lastly, a new portable comprehensive GCxGC (or “two-dimensional GC”) was deployed to evaluate its usefulness in gas-phase atmospheric chemistry applications.