α-Pinene Organic Nitrate Synthesis, Formation, and Simulation

by

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To my husband Bret

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ABSTRACT

α-Pinene Organic Nitrate Synthesis, Formation, and Simulation

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α-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 ~50 Tg yr^{-1}, α-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 α-pinene is reaction with the hydroxyl radical (OH) during the daytime. One important product of OH and α-pinene reactions is β-hydroxynitrates ($HOC_{10}H_{16}ONO_2$), which represent a terminating step in the α-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 α-pinene β-hydroxynitrates are presented in this work. The synthesis

standard supported a series of photochemical reaction chamber studies that reacted pure α-pinene with OH in a high NO_x environment. The results from these experiments were analyzed to identify for the first time individual α-pinene hydroxynitrate isomers, calculate formation yields, and determine the relative branching ratios of the precursor peroxy radical RO_2 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 α-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.