

## 2.095 Mechanistic Study of the Reactions of NO<sub>3</sub> Radicals with C<sub>3</sub>-C<sub>6</sub> Alkenes.

Early Career Scientist

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Abstract:

The reactions of the nitrate radical, NO<sub>3</sub>, with unsaturated volatile organic compounds (VOCs) are important tropospheric nighttime oxidative processes. The reactions act as sinks for VOCs and contribute to the partitioning and removal of NO<sub>x</sub> from the atmosphere. In the case of larger alkenes (especially biogenic compounds, e.g. isoprene and terpenes), the reactions can lead to the formation of secondary organic aerosols (SOA). The reactions are initiated by NO<sub>3</sub> radical addition to the C=C double bonds that after addition of O<sub>2</sub> form nitrooxy substituted peroxy radicals. These peroxy radicals lead to substituted alkoxy radicals that will either decompose or isomerise in the atmosphere depending on the structure of the parent alkene (in some cases reaction with O<sub>2</sub> is also significant). Depending on the degree of alkyl substitution of the parent alkene the products formed may retain the nitrate group or release NO<sub>2</sub>.

The reactions of several C<sub>3</sub>-C<sub>6</sub> linear and branched alkenes with NO<sub>3</sub> radicals were studied using an environmental chamber coupled to an FTIR spectrometer at NCAR, investigating the end-products formed in the reactions. The focus of this study has been on developing predictive capability for the peroxy and in particular the alkoxy radicals formed in the alkene oxidation processes. Specifically, the structure-activity relationships of the alkoxy radicals formed in the NO<sub>3</sub> reactions with an array of alkene species will be useful in predicting product distributions for the NO<sub>3</sub> radical reacting with larger alkenes, such as terpenes. The products formed in the reaction of NO<sub>3</sub> radicals with trans-2-butene were quantified, and the fate of the nitrooxy alkoxy radical CH<sub>3</sub>CH(O•)CH(ONO<sub>2</sub>)CH<sub>3</sub> was determined. Our results are compared with previous findings for the species studied, when available, and are also compared with current structure-activity relationships and chemical mechanisms.