Kinetic and mechanistic studies of the atmospheric chemistry of isoprene-4,1-hydroxynitrate

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Isoprene hydroxynitrates are intermediates generated in both the OH and NO_3 initiated oxidation of isoprene. Laboratory measurements suggest that the subsequent reactions of these compounds may be responsible for a substantial amount of the secondary organic aerosol (SOA) generated in the NO_3 + isoprene reaction [1]. This chemistry may also have a significant impact on NOx levels.

In this work, isoprene-4,1-hydroxynitrate was synthesized and its gas phase reactions with OH and Cl were studied in a photochemical reactor with analysis by long path FTIR spectroscopy and GC-FID. Mixtures containing the isoprene hydroxynitrate, air, and either chlorine or methyl nitrite and nitric oxide were photolyzed at room temperature and 1 atm. The rate coefficients for the reactions of isoprene-4,1-hydroxynitrate with OH and Cl were investigated using the relative rate technique using propene, 2-methyl-2-butene and 1-pentene as the reference compounds. Yields of formaldehyde and hydroxyacetaldehyde were also measured from the reaction between OH and isoprene-4,1-hydroxynitrate.

The measured rate coefficients for the reaction of OH and Cl with isoprene-4,1-hydroxynitrate are $(3.7\pm0.4) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} and $(5.1\pm0.5) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. The rate coefficient for reaction with OH is significantly lower than the indirect measurement reported by Paulot et al [1]. There are no previous measurements of the Cl + isoprene-4,1-hydroxynitrate rate coefficient for comparison. Product yields measured in the OH-initiated reaction are $Y_{Formaldehyde} = 0.88$ and $Y_{Hydroxyacetaldehyde} < 0.10$. The mechanistic implications of these measurements will be discussed.

References

(1) Paulot, F.; Crounse, J. D.; Kjaergaard, H. G.; Kroll, J. H.; Seinfeld, J. H.; Wennberg, P. O., *Atmos. Chem. Phys.* **2009,** *9*, 1479-1501.