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Airborne observations of total RONO₂: new

constraints on the yield and lifetime of isoprene nitrates

A. E. Perring¹, T. H. Bertram^{1,*}, P. J. Wooldridge¹, A. Fried², B. G. Heikes³, J. Dibb⁴, J. D. Crounse⁵, P. O. Wennberg^{6,7}, N. J. Blake⁸, D. R. Blake⁸, W. H. Brune⁹, H. B. Singh¹⁰, and R. C. Cohen^{1,11} ¹Department of Chemistry, University of California Berkeley, Berkeley, CA, USA ²National Center for Atmospheric Research, Earth Observing Laboratory, Boulder, CO, USA ³Graduate School of Oceanography, University of Rhode Island, Narragansett, RI, USA ⁴Climate Change Research Institute, University of New Hampshire, Durham, NH, USA ⁵Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA ⁶Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA ⁷ Division of Environmental Science and Engineering, California Institute of Technology, Pasadena, CA, USA

⁸Department of Chemistry, University of California Irvine, Irvine, CA, USA
⁹Department of Meteorology, Pennsylvania State University, University Park, PA, USA

¹⁰NASA Ames Research Center, Moffett Field, CA, USA

¹¹Department of Earth and Planetary Sciences, University of California Berkeley, Berkeley, CA, USA

*now at: Department of Atmospheric Sciences, University of Washington, Seattle, WA, USA

Abstract. Formation of isoprene nitrates (INs) is an important free radical chain termination step ending production of ozone and possibly affecting formation of secondary organic aerosol. Isoprene nitrates also represent a potentially large, unmeasured contribution to OH reactivity and are a major pathway for the removal of nitrogen oxides from the atmosphere. Current assessments indicate that formation rates of isoprene nitrates are uncertain to a factor of 2–3 and the subsequent fate of isoprene nitrates remains largely unconstrained by laboratory, field or modeling studies. Measurements of total alkyl and multifunctional nitrates (Σ ANs), NO₂, total peroxy nitrates (Σ PNs), HNO₃, CH₂O, isoprene and other VOC were obtained from the NASA DC-8 aircraft during summer 2004 over the continental US during the INTEX-NA campaign. These observations represent the first characterization of Σ ANs over a wide range of land surface types and in the lower free troposphere. ΣANs were a significant, 12–20%, fraction of NO_v throughout the experimental domain and Σ ANs were more abundant when isoprene was high. We use the observed hydrocarbon species to calculate the relative contributions of Σ AN precursors to their production. These calculations indicate that isoprene represents at least three quarters of the Σ AN source in the summertime continental boundary layer of the US. An observed correlation between

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03 | ACP, 12 Mar 2009: Comparison of tropospheric gas-phase chemistry schemes for use within global models ΣANs and CH₂O is used to place constraints on nitrate yields from isoprene oxidation, atmospheric lifetimes of the resulting nitrates and recycling efficiencies of nitrates during subsequent oxidation. We find reasonable fits to the data using sets of production rates, lifetimes and recycling efficiencies of INs as follows (4.4%, 16 h, 97%), (8%, 2.5 h, 79%) and (12%, 95 min, 67%). The analysis indicates that the lifetime of ΣANs as a pool of compounds is considerably longer than the lifetime of the individual isoprene nitrates to reaction with OH, implying that the organic nitrate functionality is at least partially maintained through a second oxidation cycle.

■ Final Revised Paper (PDF, 699 KB) ■ Discussion Paper (ACPD)

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