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Airborne observations of total $RONO_2$: new constraints on the yield and lifetime of isoprene nitrates

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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 (ΣANs), NO_2, total peroxy nitrates (ΣPNs), HNO_3, CH_2O, 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 ΣANs over a wide range of land surface types and in the lower free troposphere. ΣANs were a significant, 12–20%, fraction of NO_y throughout the experimental domain and ΣANs were more abundant when isoprene was high. We use the observed hydrocarbon species to calculate the relative contributions of ΣAN precursors to their production. These calculations indicate that isoprene represents at least three quarters of the ΣAN source in the summertime continental boundary layer of the US. An observed correlation between

ΣANs and CH_2O 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.

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