Supplement of Atmos. Chem. Phys., 19, 10391–10403, 2019
https://doi.org/10.5194/acp-19-10391-2019-supplement
© Author(s) 2019. This work is distributed under the Creative Commons Attribution 4.0 License.

Supplement of

Alkyl nitrates in the boreal forest: formation via the NO$_3^-$-, OH- and O$_3$-induced oxidation of biogenic volatile organic compounds and ambient lifetimes

Jonathan Liebmann et al.

Correspondence to: John N. Crowley (john.crowley@mpic.de)

The copyright of individual parts of the supplement might differ from the CC BY 4.0 License.
Table S1: Rate coefficients and branching ratios used for the calculations of $P_{\Sigma AN}$

| VOC        | $k$(NO$_3$) at 298 K (molecules cm$^{-3}$ s$^{-1}$) | $\alpha^{NO_3}$ | $k$(OH) at 298 K (molecules cm$^{-3}$ s$^{-1}$) | $\alpha^{RO_2}$ | $k$(O$_3$) at 298 K (molecules cm$^{-3}$ s$^{-1}$) | $\alpha^{O_3}$ |
|------------|---------------------------------------------|----------------|---------------------------------------------|----------------|---------------------------------------------|----------------|
| $\alpha$-pinene | 6.2×10$^{-12}$ 1                        | 0.15 2.5       | 5.3×10$^{-11}$ 1                           | 0.18 6        | 9.6×10$^{-17}$ 1                           | 0.80 1        |
| $\beta$-pinene | 2.5×10$^{-12}$ 1                        | 0.40 2.3       | 7.6×10$^{-11}$ 1                           | 0.24 2        | 1.9×10$^{-17}$ 1                           | 0.30 1        |
| $\Delta$-carene  | 9.1×10$^{-12}$ 1                        | 0.77 3         | 8.8×10$^{-11}$ 2                           | 0.23 2        | 4.9×10$^{-17}$ 1                           | 0.86 1        |
| $d$-limonene  | 1.2×10$^{-11}$ 1                        | 0.67 2.5       | 1.7×10$^{-10}$ 1                           | 0.23 2        | 2.2×10$^{-16}$ 1                           | 0.75 1        |
| isoprene    | 6.5×10$^{-13}$ 1                        | 0.70 1         | 1.0×10$^{-10}$ 1                           | 0.07 4        | 1.28×10$^{-17}$ 1                          | 1.00 1        |
| unattributed | -                                      | 0.70            | -                                          | -             | -                                          | -             |

$\alpha^{NO_3}$: yield of AN in the reaction of the BVOC with NO$_3$ in air.

$\alpha^{RO_2}$: yield of AN in the reaction of the peroxy radical (formed in OH + BVOC + O$_2$) with NO.

$\alpha^{O_3}$ is the yield of peroxy radicals formed in the reaction of each BVOC with O$_3$ in air.

1Task Group on Atmospheric Chemical Kinetic Data Evaluation, (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeil, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J. http://iupac.pole-ether.fr/index.html., 2019.

2Perring, A. E., Pusede, S. E., and Cohen, R. C.: An observational perspective on the atmospheric impacts of alkyl and multifunctional nitrates on ozone and secondary organic aerosol, Chemical Reviews, 113, 5848-5870, doi:10.1021/ cr300520x, 2013.

3Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkler, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C., and Lee, L.: Secondary Organic Aerosol Formation and Organic Nitrate Yield from NO$_3$ Oxidation of Biogenic Hydrocarbons, Environmental Science & Technology, 48, 11944-11953, 10.1021/es502204x, 2014.

4Lockwood, A. L., Shepson, P. B., Fiddler, M. N., and Alaghmand, M.: Isoprene nitrates: preparation, separation, identification, yields, and atmospheric chemistry, Atmos. Chem. Phys., 10, 6169-6178, https://doi.org/10.5194/acp-10-6169-2010, 2010.

5Spittler, M., Barnes, I., Bejan, I., Brockmann, K. J., Benter, T., Wirtz, K.: Reactions of NO$_3$ radicals with limonene and $\alpha$-pinene: Product and SOA formation, Atmospheric Environment, 40, S116, https://doi.org/10.1016/j.atmosenv.2005.09.093, 2006.

6Nozière, B., Barnes, I., and Becker, K.-H.: Product study and mechanisms of the reactions of $\alpha$-pinene and of pinonaldehyde with OH radicals, Journal of Geophysical Research: Atmospheres, 104, 23645-23656, doi:10.1029/1999JD900778, 1999.
Figure S1: Overview of meteorological measurements during IBAIRN. The grey shaded regions represent nighttime.
**Figure S2:** Calculated OH reactivity ($k_{OH}$) and O₃ reactivity ($k_{O3}$) from VOC measurements.

$k_{BVOC}$ (biogenic VOCs) consists of α-pinene, β-pinene, Δ-carene, d-Limonene, isoprene, and camphene.

$k_{OVOC}$ (oxidised VOCs) consists of propanoic acid, butanoic acid, isopentanoic acid, pentanoic acid, hexanoic acid, 1-pentanol, 1-penten-3-ol, cis-3-hexen-1-ol, 1-hexanol.

$k_{VOC}$ (remaining VOCs) consists of benzene, toluene, p/m-xylene, styrene, o-xylene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, hexane, pentanal, hexanal, methacrolein, 4-acetyl-1-methylcyclohexene, nopinone, heptanal, octanal, nonanal, decanal, ethane and propane.
Figure S3: Aerosol surface area during IBAIRN.
Figure S4: Upper: AMS-nitrate versus NOx (5th-22nd Sept 2016). Lower: AMS-nitrate versus the total ANs production rate colour-coded with AMS-organic mass.
**Figure S5:** Campaign averaged relative contribution of the measured organic nitrates as measured by the I-CIMS (assuming equal sensitivity across the mass-range).