Nighttime to daytime transition of the oxidation products of isoprene by NO_3 radicals

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Motivation on NO_3 + isoprene studies

- ✓ Biogenic volatile organic compounds (BVOC) emissions are 1 order of magnitude higher than the anthropogenic ones.
  - ✓ **Isoprene** represents about **50%** of the total BVOC emissions.
- ✓ **NO_3** can be the **major oxidant** during **nighttime**.
  - ✓ NO_3-induced oxidation of BVOC has been **poorly studied** compared to OH and O_3 oxidation.
- ✓ **Better representation of organonitrates formation** is essential for properly describing isoprene's effect on NO_x, HO_x as well as ozone formation.
- ✓ Contribution of organonitrates to secondary organic aerosol (SOA).

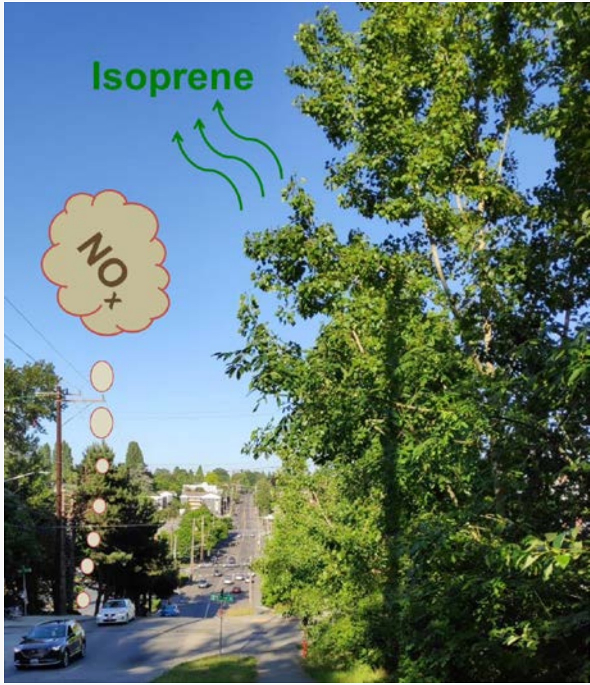


Photo: E. Tsiligiannis

NO_3 formation

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M$$

Guenther et al., 2012; Goldstein & Galbally, 2007; Wennberg et al., 2018; Lee et al., 2016; Fry et al., 2018

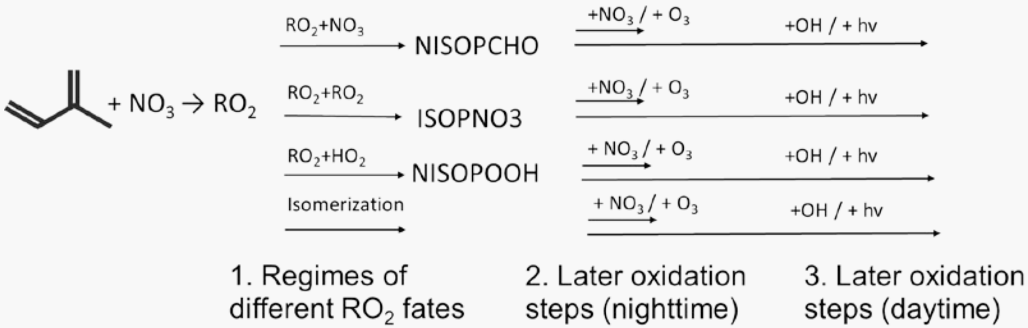
Experimental set up & conditions

Photo: E. Tsiligiannis

Atmospheric simulation chamber **SAPHIR** at **Forschungszentrum Jülich**, Germany (Aug. 2018)

- Volume: 270 m^3, surface: 320 m^2
- FEP double wall
- Ambient pressure & temperature
- Shutter system for simulating dark conditions or daytime by exposuring to sunlight

Rohrer et al., 2005



Various chemical conditons in order to change the **fate** of the **peroxy radicals** initially formed by NO_3+isoprene

- ➢ High/low RO_2 or HO_2
- ➢ Without or with seed particles
  - ➢ $(NH_4)_2SO_4$ with or without organic coating (β-caryophyllene)
- ➢ Nighttime to daytime transition
  - ➢ Photolysis
  - ➢ Photolysis + OH radicals

❑ Isoprene injections
❑ NO_3 formation by NO_2/O_3 injections

Focus on this study

Instrumentation

Gas & particle phase measurements by **I^-** Chemical Ionization Mass spectrometer **(CIMS)**

Photo: E. Tsiligiannis

Resolution:
~ 4000 M/ΔM

Mass Range:
0 – 1000 Th

Detection limits:

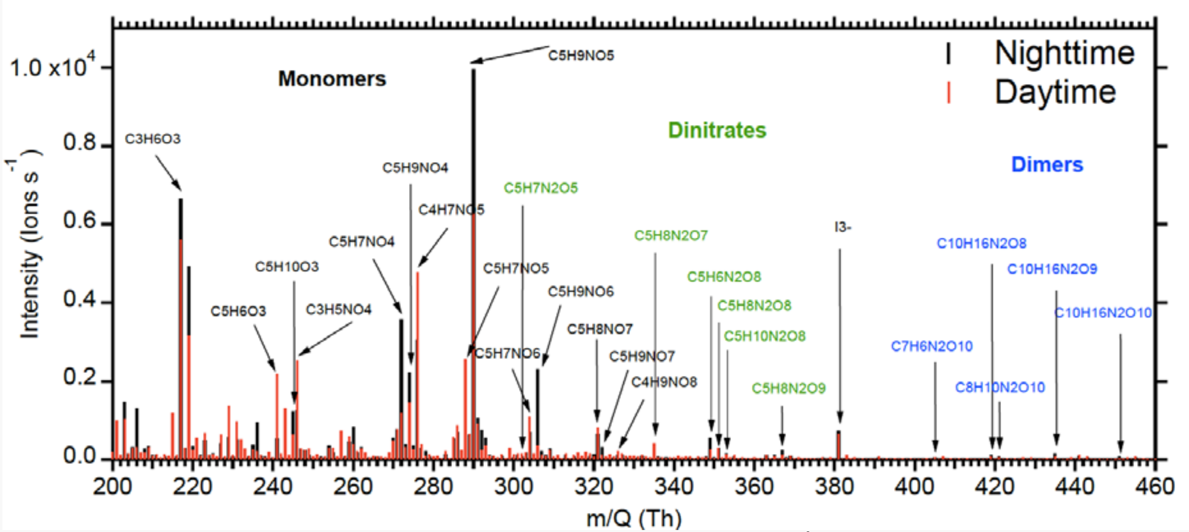
Gas-Phase: e.g, 4 pptv formic acid (1s, Bertram et al., 2011), 0.4 pptv malonic acid (15s, Lee et al., 2014)
Aerosol, FIGAERO: e.g, 4 ng m^{-3} formic acid and 2 ng m^{-3} C_9 pinene acid (Lopez-Hilfiker et al., 2014)

Experiments

- Gas phase measurements of Organonitrates
- Effect of OH oxidation on the nighttime products

Conditions	Aug. 12	Aug. 12
	Nighttime → Photolysis	**Nighttime → Photolysis + OH oxidation**
Max Isoprene (ppbv)	3	2.5
O_3 (ppbv)	70-115	80-115
NO_2 (ppbv)	4-12	2-5
CO (ppbv)	120000	20
Seed aerosol	No	$(NH_4)_2SO_4$
Max $J(NO_2)/10^{-3}$ s^{-1}	4.8	4.8
T (°C)	14-36	20-28
H_2O (%)	0	1.6

Mass spectra overview

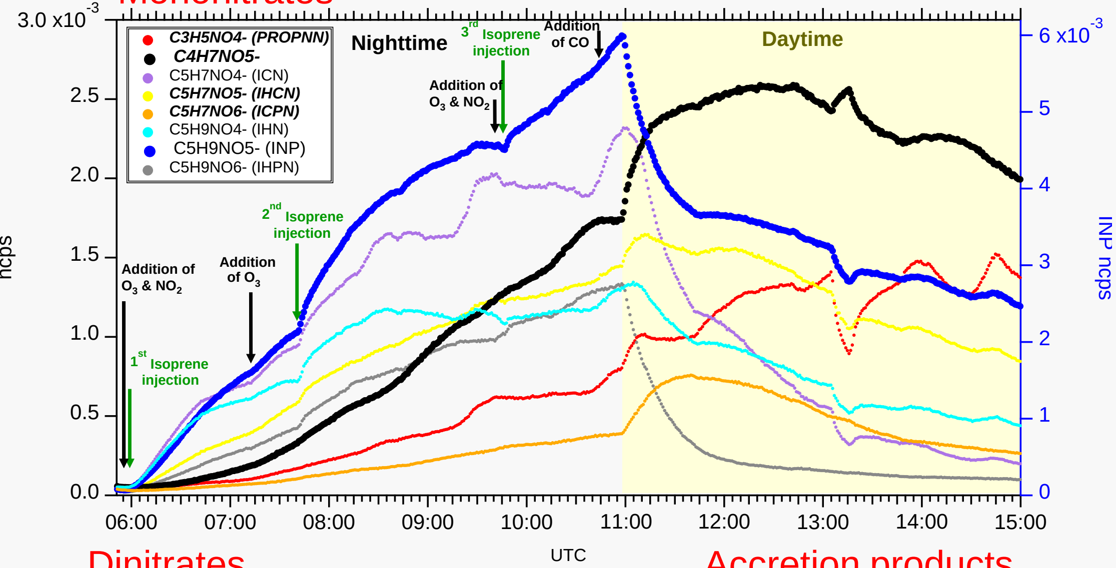


Representative I- CIMS data. Experiment 12th of August at dry & medium NO_3 conditions without seeds. CO was used as OH scavenger during the "daytime" mode.

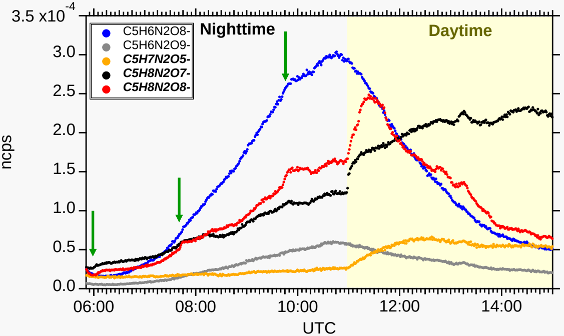
- **Monomers:** $C_5H_9NO_{4,5,6}$, $C_5H_7NO_{4,5,6}$, $C_4H_7NO_5$ (major compounds)
- **Dinitrates:** $C_4H_6N_2O_7$, $C_5H_{8,10}N_2O_8$, $C_5H_{8,10}N_2O_9$ → Probably formed by 1st gen. organonitrates + NO_3
- **Dimers:** $C_{10}H_{16}N_2O_{8,9,10}$ → RO_2 + RO_2

Product time evolution – exp. Aug 12th

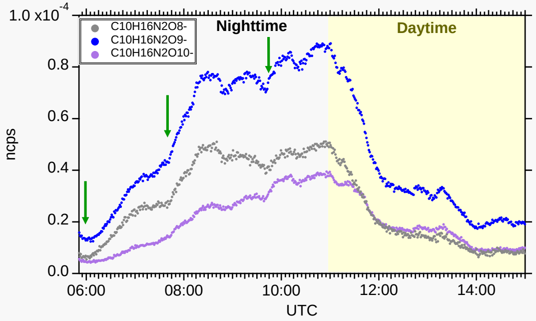
Mononitrates



Dinitrates



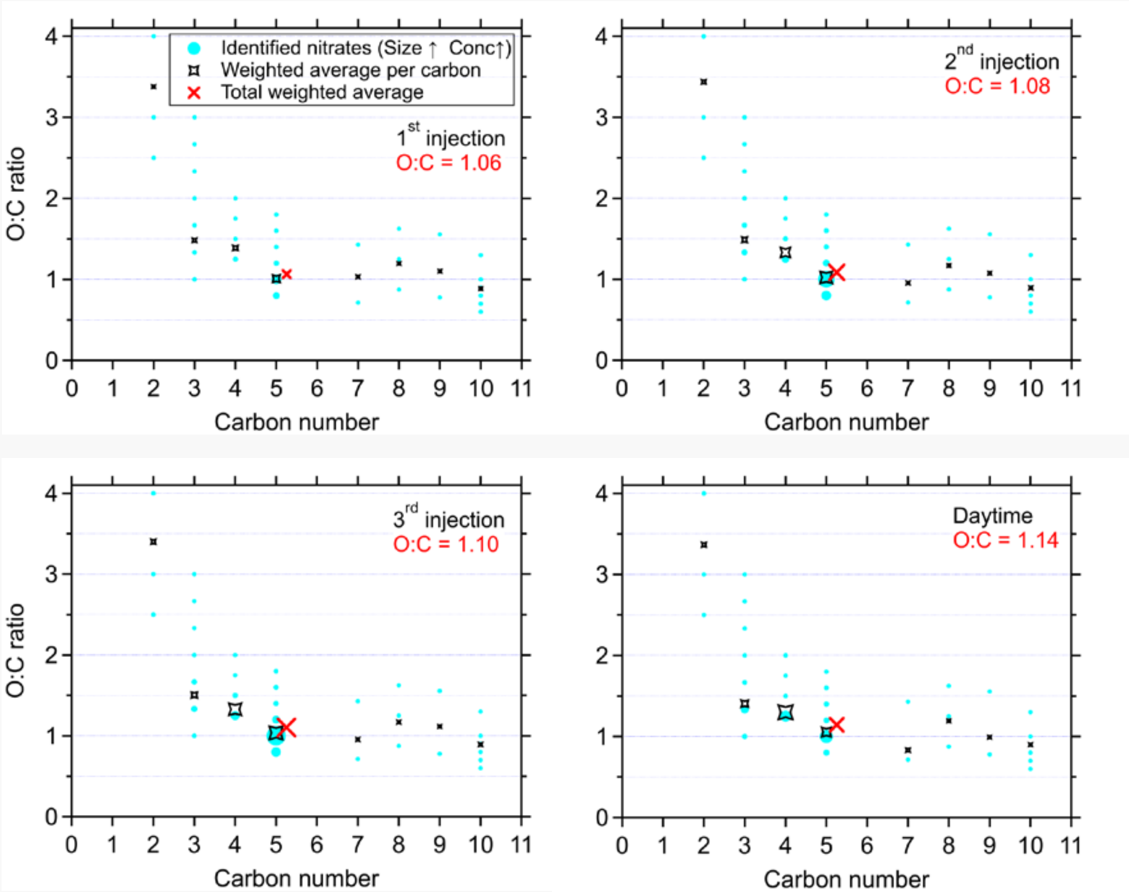
Accretion products



	(M) : (D) : (A)
1st injection	10 : 0.72 : 0.29
2nd injection	10 : 0.68 : 0.17
3rd injection	10 : 0.72 : 0.19
Daytime	10 : 0.79 : 0:18

- ✓ 36 mononitrates, 20 dinitrates & 15 accretion products have been identified.
- ✓ Mononitrates are the dominant signal.
- ✓ Dinitrates increase relative to mononitrates with time.
- ✓ Accretion products decrease relative to mononitrates with time.

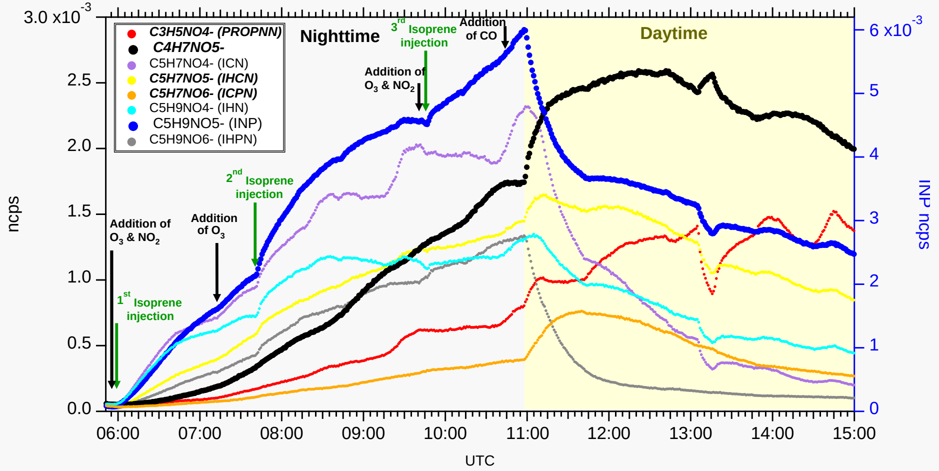
O:C ratio time evolution – exp. Aug 12th

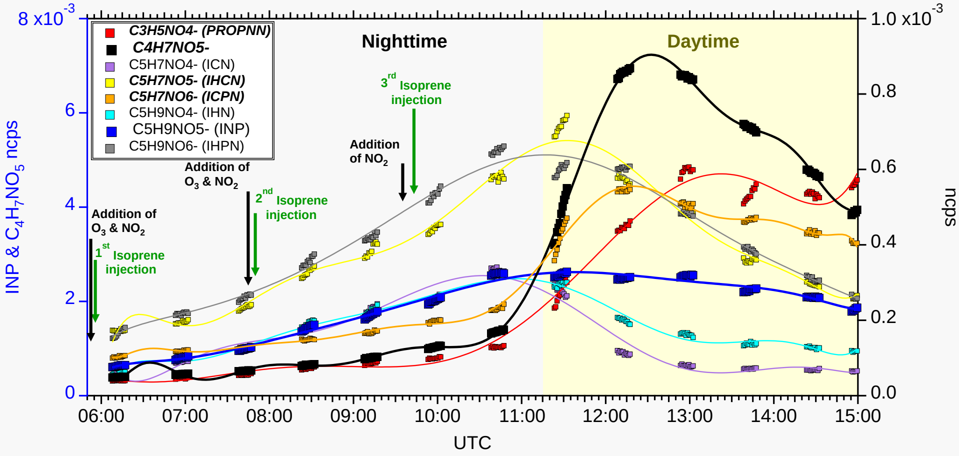


- ✓ O:C ratio increases (1.06 to 1.14) with time & after a new isoprene injection.
- ✓ O:C ratio of C_4 & C_5 compounds increase with addition of NO_3 + isoprene.
- ✓ O:C ratio of C_5 compounds decreases during daytime while O:C ratio of C_4 compounds increases during daytime.

Photolysis effect

Photolysis + OH radicals effect





Mononitrates

- ✓ Most of the mononitrates are photolyzed rapidly during daytime.
- ✓ The major $C_4H_7NO_5$ products are enhanced further under the presence of both photolysis and OH chemistry.
- ✓ Less sharp reduction of compounds with chemical formula $C_5H_9NO_5$ under the presence of OH chemistry. Likely consumed by photolysis but formed by OH oxidation.

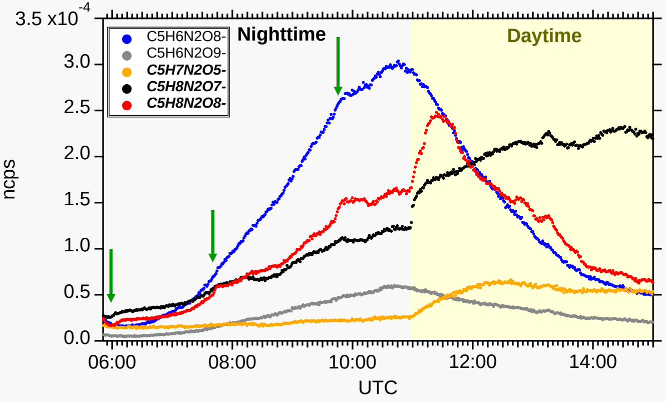
Potential formation pathways of $C_4H_7NO_5$ compounds:

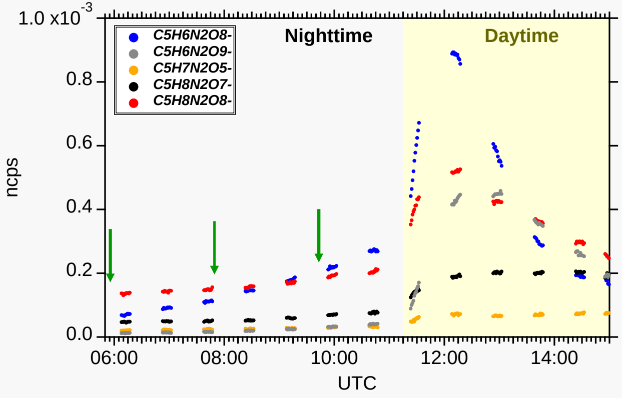
$$C_5H_9NO_4 + NO_3 \rightarrow \cdots \rightarrow C_4H_7NO_5$$

$$C_5H_9NO_5 + OH \rightarrow \cdots \rightarrow C_4H_7NO_5$$

Photolysis effect

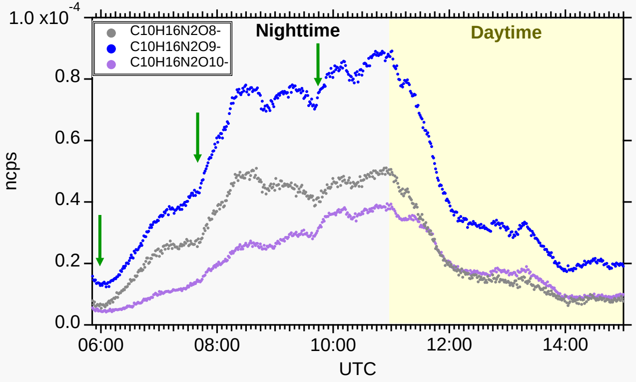
Photolysis + OH radicals effect

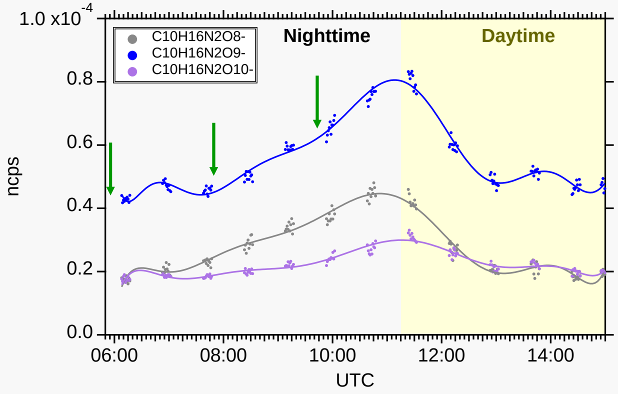




Dinitrates

- ✓ The major dinitrate ($C_5H_6N_2O_8$) get photolyzed.
- ✓ All the major dinitrates increase under the presence of OH radicals.





Accretion products

- ✓ Sharp reduction during photolysis.
- ✓ Less pronounced reduction with both photolysis and OH chemistry.
- ✓ Possible a day-time source from OH oxidation.

Conclusions

- **Mononitrates**, **dinitrates** & **accretion nitrated compounds** were characterized.
- **O:C ratio increases** (1.06 to 1.14 at the given experiment) with time and after a new isoprene injection.
- Most of the **nighttime products** are **photolyzed** during **daytime**.
- Products with the chemical formula $\mathbf{C_4H_7NO_5}$ become the **dominant** ones during **daytime conditions** and **enhanced** further via **OH chemistry**.
- $\mathbf{C_5H_9NO_5}$ products are **photolyzed** during **daytime** but partly **compensated** by formation from **OH chemistry**.

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UNIVERSITY of WASHINGTON

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MERGE

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