NO_3-initiated oxidation of isoprene: Gas-particle partitioning and SOA yields of organonitrate products in varied chemical regimes

Bellamy Brownwood,[1] Juliane L. Fry,[1] Thorston Hohaus,[2] Avtandil Turdziladze,[2] Epameinondas Tsiligiannis[3], Mattias Hallquist[3], Hendrik Fuchs[2], Anna Novelli[2], and the whole SAPHIR NO3Isop chamber experiment team

[1]Chemistry and Environmental Studies, Reed College, Portland, OR, USA; [2]Institute of Energy and Climate Research (IEK-8), Forschungszentrum Jülich, Germany; [3]Department of Chemistry and Molecular Biology, University of Gothenburg, Sweden

Abstract

Four weeks of experiments in July and August 2018 in the Forschungszentrum Jülich SAPHIR Chamber measured the products and reactions progression of NO_3-initiated oxidation of isoprene under varying conditions, focusing on the initial peroxy radical (RO_2) lifetime and fate. Experiments were conducted with and without NH_4SO_4 and organic seed aerosol, under humid and dry conditions, with or without OH scavenger, and with varying ratios of NO_2 to isoprene and of O_3 to NO_3. Under seeded conditions, organic nitrates were a major product, and nitrate aerosol was formed.

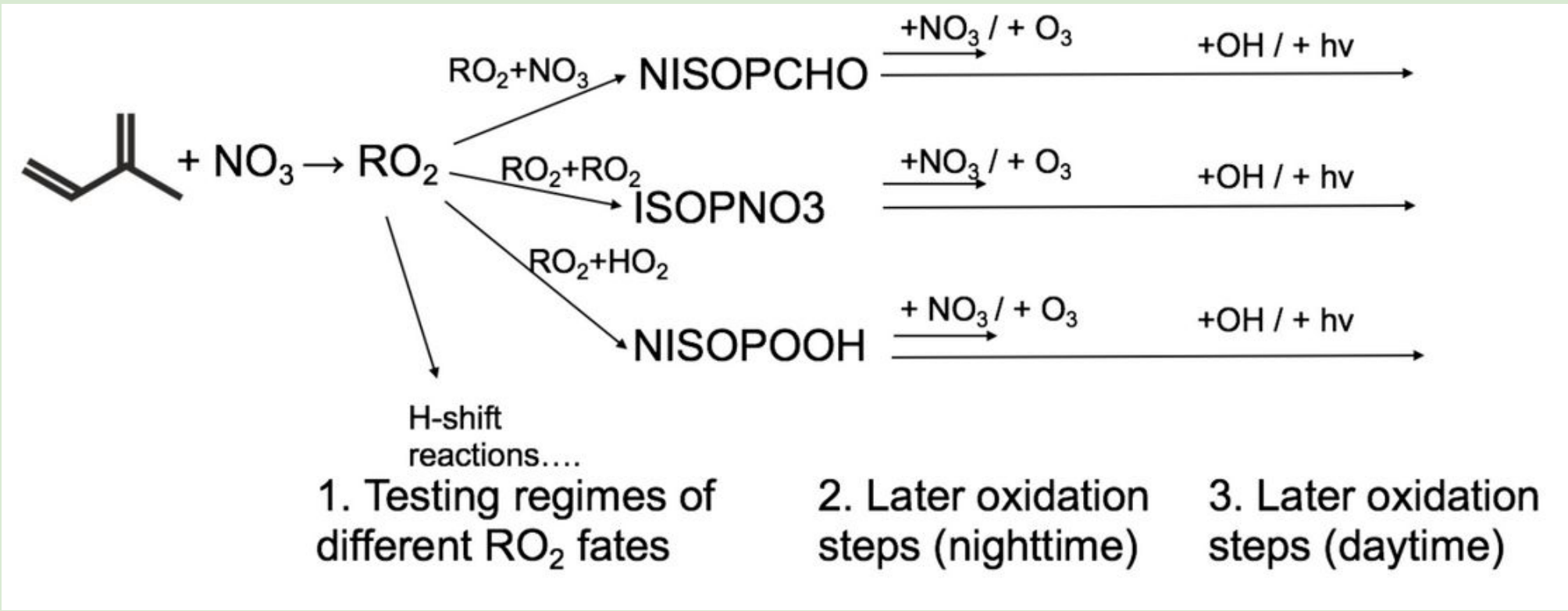


Figure 1: Reaction scheme.

Methodology & Instrumentation

Experiments were run in the SAPHIR Chamber, a 270 m^3 Teflon reaction chamber. Gas-phase organonitrate products were measured by a thermal dissociation-cavity ringdown (TD-CRDS) instrument (Reed College), and particle-phase organonitrate products were monitored by an AMS (IEK-8) with organic and inorganic nitrates split using the NO+ / NO_2+ ratio. Total organic aerosol for absorptive partitioning calculations was obtained from SMPS volume data, assuming a density or 1.4 g cm^{-3}. Theoretical partitioning coefficients were determined using absorptive partitioning theory and vapor pressures estimated from group contribution methods (Pankow & Asher 2008).

SAPHIR Chamber, Forschungszentrum Jülich

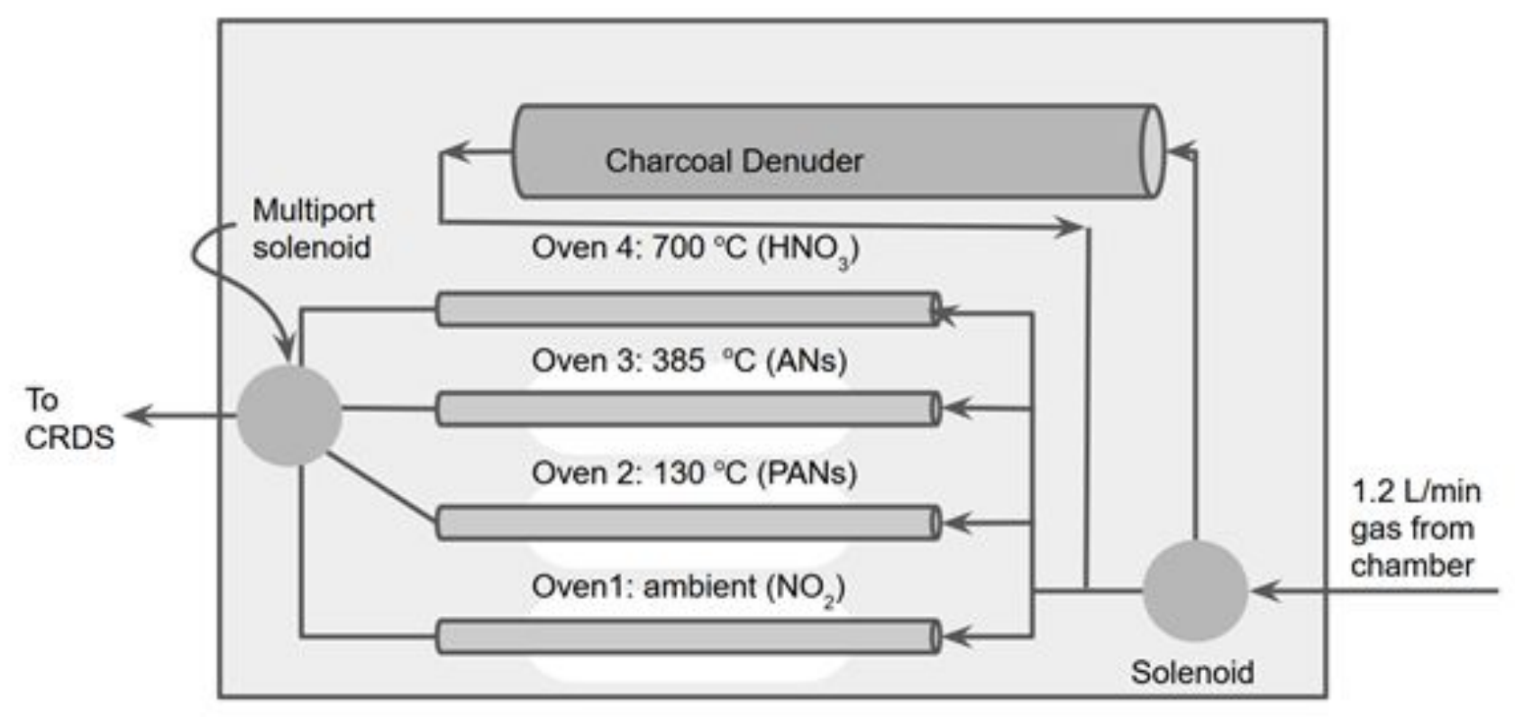


Figure 2: Reed's homebuilt thermal dissociation - cavity ringdown spectrometer (TD-CRDS) (CRDS: Los Gatos Research, λ= 405 nm) measures NO_2, PANs, ANs, and HNO_3 in both aerosol-only and gas + aerosol phase using a charcoal denuder to remove gas phase components. Oven temperatures were set based on thermal dissociation of NO_3 + Δ-carene (at a concentration of 230 ppb) used to produce PANs and ANs; and separate experiments with direct sampling of isobutyl nitrate and HNO_3.

Organonitrate Yields

Table 1: Observed organonitrate yields do not appear to depend on RO_2 regime or whether the experiment was unseeded (through 13 August) or seeded (remaining, shaded experiments).

Experiment Date	Reaction Pathway	Total Isoprene Measured (ppb)	Alkyl Nitrate Buildup (ppb)	Molar Alkyl Nitrate Yield (%)
3 Aug	Humid night to day	5.57	2.13	38.29
6	Humid night to day	5.15	Before roof open: 2.8 ± 0.1 After roof open: 1.39 ± 0.02	B: 54.81 A: 26.86
7	RO_2 isomerization	6.83	1.9 ± 0.15	27.18
8	$RO_2 + RO_2$	30.5	11.1 ± 0.3	36.44
9	$RO_2 + HO_2$	8.01	3.3 ± 0.2	40.99
10	$RO_2 + RO_2$	4.46	1.75 ± 0.08	39.26
12	dry medium NO_3 + photolysis	9.09	Before roof open: 3.9 ± 0.2 After roof open: 2.5 ± 0.2	B: 43.30 A: 27.38
13	$RO_2 + RO_2$	21.7	10.5 ± 0.14	48.30
14 Aug 2018	$RO_2 + RO_2$	28.9	9.23 ± 0.09	31.94
15	$RO_2 + RO_2$	17.5	8.39 ± 0.09	48.10
16	humid AS seed lower isop	7.98	2.7 ± 0.2	33.32
18	B-carene seed humid	7.60	2.1 ± 0.1	27.32
19	N_2O_5 from trap	6.82	6.04 ± 0.06	88.57
20	AS seed with org coating	11.2	3.55 ± 0.08	31.63
21	$RO_2 + HO_2$	10.5	4.3 ± 0.2	40.59

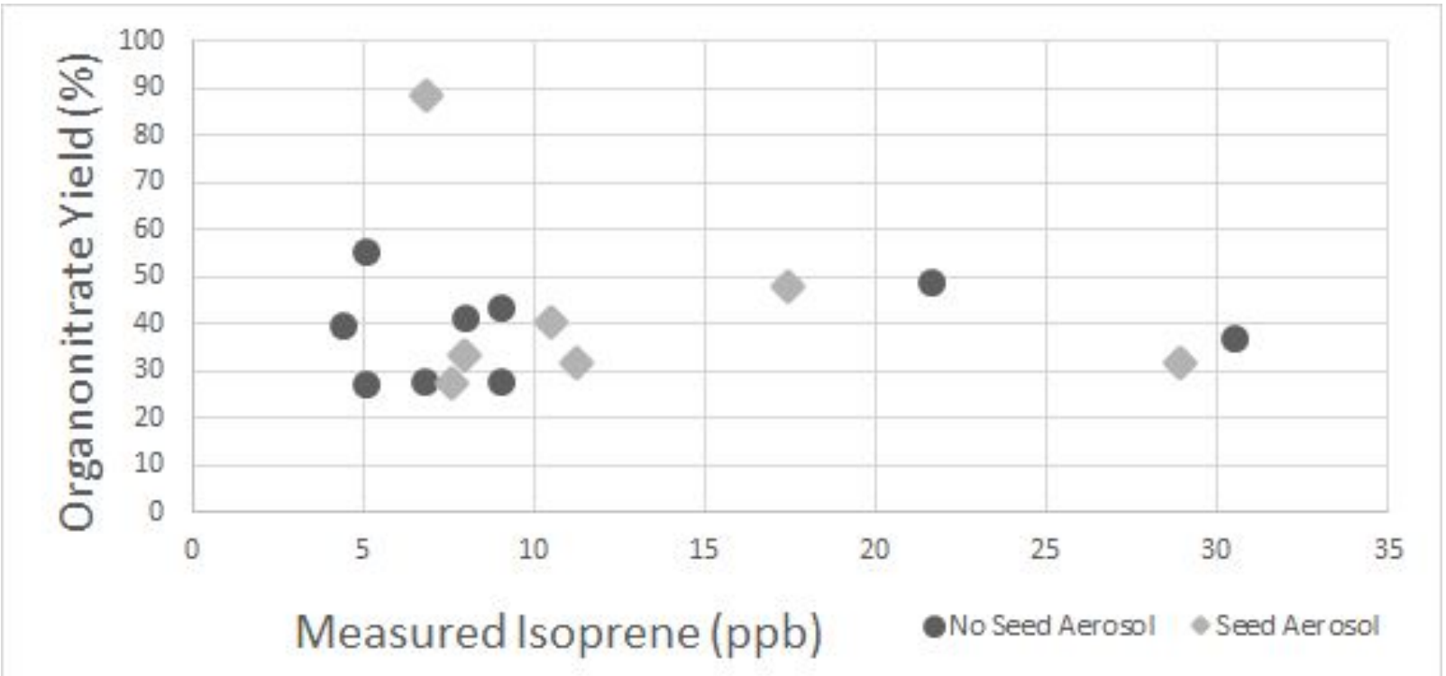


Figure 3: Molar alkyl nitrate yield as a function of isoprene reacted.
Yield is ~ 40%, independent of RO_2 regime, [isoprene], and seed state.

Organonitrate (alkyl nitrate) yields are calculated from net observed alkyl nitrate production (TD-CRDS) divided by the summation of isoprene peaks measured by the VOCUS PTR (Ralf Tillmann, FZJ IEK-8). Isoprene was always added to the chamber already containing oxidants so this measurement can be assumed to be a lower limit on the amount of isoprene reacted to form ANs, and these yields therefore an upper limit. We note that the highest apparent yield was observed in an experiment in which NO_3 was supplied by N_2O_5 thermal dissociation, a more rapid source of NO_3 that would result in faster isoprene reactivity and greater suppression of the inferred Δisoprene.

Gas-Particle Partitioning

$$K_p = \frac{C_{aero}}{C_{gas} \times M_t}$$

Experimental

Table 2: Observed average gas/aerosol partitioning coefficient based on total gas-phase organonitrate concentration (C_{gas}) measured by TD-CRDS, total aerosol-phase organic nitrate concentration (C_{aero}) measured by AMS (Total NO3 = upper limit, OrganicNO3, based on NO^+:NO_2^+ ratio = lower limit), and total background aerosol (M_t) measured by SMPS and converted to μg m^{-3} assuming a density of 1.4 g cm^{-3}.

Date	Experiment	Regime	K_p ($m^3 \mu g^{-1}$) NO3 UPPER LIMIT	K_p ($m^3 \mu g^{-1}$) OrgNO3 LOWER LIMIT
14 Aug 2018	High NO_3	$RO_2 + RO_2$	$1.6 \pm 0.2 \times 10^{-3}$	$1.0 \pm 0.1 \times 10^{-3}$
15 Aug 2018	High NO_3	$RO_2 + RO_2$	$1.3 \pm 0.1 \times 10^{-3}$	$6.0 \pm 0.9 \times 10^{-4}$
16 Aug 2018	Photolysis	$RO_2 + RO_2$	Roof closed: 2.85×10^{-3} Roof opened: $2.5 \pm 0.3 \times 10^{-3}$	Roof closed: 1.08×10^{-3} Roof opened: $1.7 \pm 0.2 \times 10^{-3}$
18 Aug 2018	Organic seed & photolysis	$RO_2 + RO_2$	Roof closed: 4.25×10^{-3} Roof opened: $3.4 \pm 0.9 \times 10^{-3}$	Roof closed: 2.02×10^{-3} Roof opened: $2.5 \pm 0.3 \times 10^{-3}$
19 Aug 2018	N_2O_5 source		5.66×10^{-4} No Bkgd subt: $1.2 \pm 0.1 \times 10^{-3}$	3.7×10^{-4} No bkgd subt: $9 \pm 1 \times 10^{-4}$
20 Aug 2018	Organic seed & NO_3		$2.9 \pm 0.3 \times 10^{-3}$	$2.2 \pm 0.2 \times 10^{-3}$
21 Aug 2018	NO_3 & HO_x	$RO_2 + HO_2$	$1.0 \pm 0.2 \times 10^{-3}$	$4.4 \pm 0.7 \times 10^{-4}$
22 Aug 2018	Plant emissions	Isomerization, then $RO_2 + RO_2$	$8.5 \pm 1.2 \times 10^{-4}$	$7.65 \pm 1.1 \times 10^{-4}$
23 Aug 2018			$3.3 \pm 0.7 \times 10^{-3}$	$1.4 \pm 0.3 \times 10^{-3}$

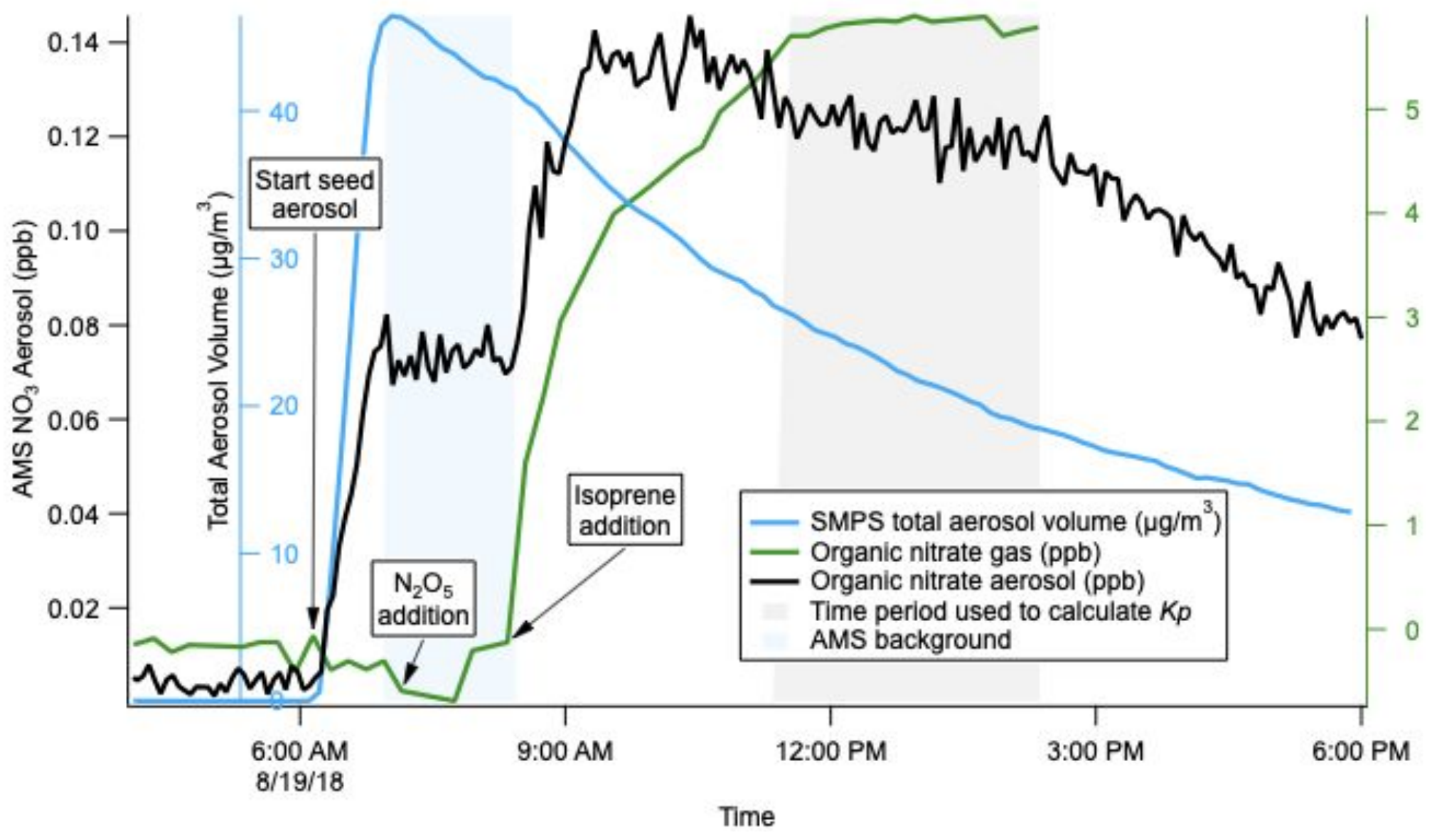


Figure 4: Representative data used to calculate the gas/aerosol partitioning of organonitrates. Gas- and aerosol- phase nitrates, and total aerosol volume, were averaged for the shaded period to determine the empirical average K_p, listed in Table 2 for each experiment.

Theoretical

$$K_{p,i}(\text{theoretical}) = \frac{760\, RT f_{om}}{MW_{om} 10^6 \zeta_i p^{\circ}_{L,i}}$$

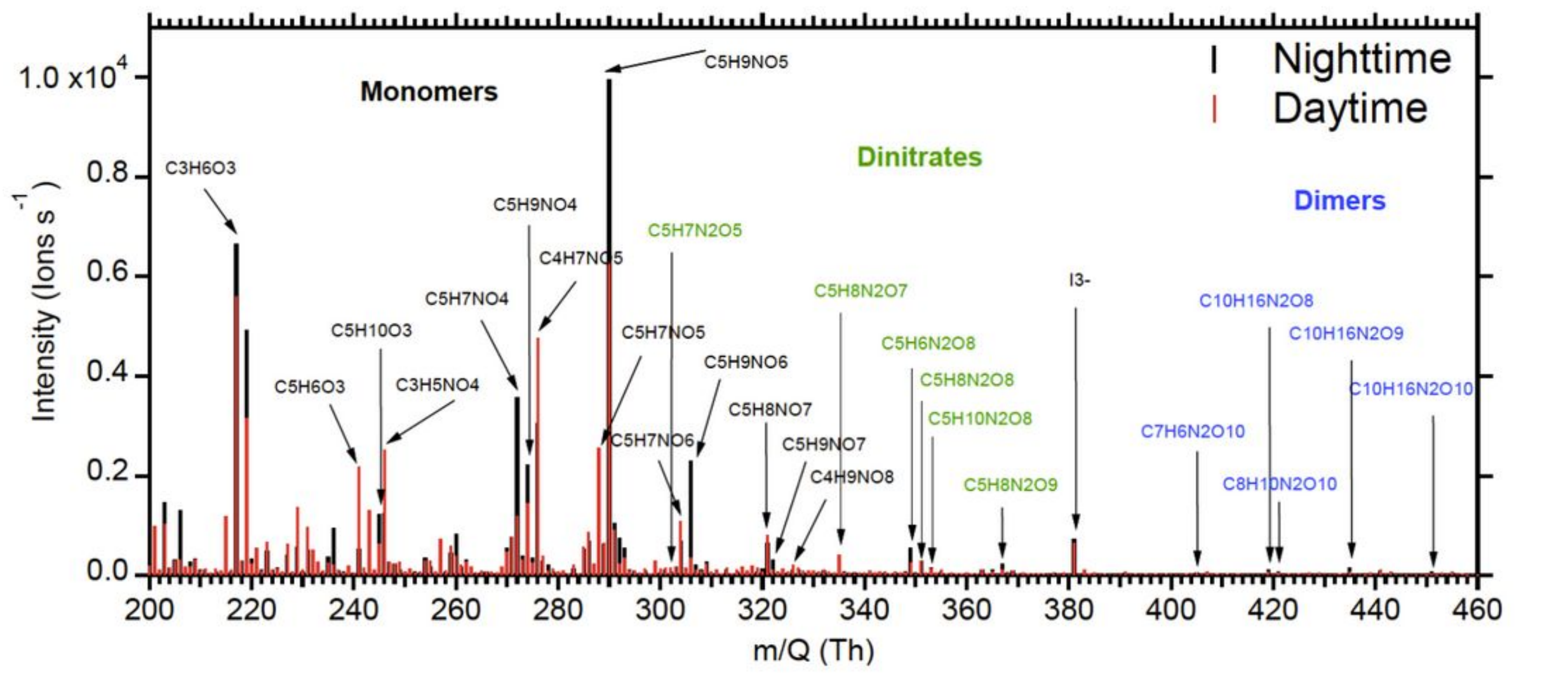
Table 3: Theoretical gas/aerosol partitioning coefficients for relevant compounds calculated based on vapor pressures determined via group contribution method at 295K (Pankow & Asher, 2008).

Number of Functional Groups							
C	NO3	OH	C=O	OOH	R-O-O-R	Product, MW (amu)	Theoretical K_p ($m^3 \mu g^{-1}$)
5	1	--	1	--		ICN, 145[a]	5.26×10^{-7}
5	1	1	--	--		IHN, 147[a]	9.85×10^{-6}
5	1	2	--	--		IDHN, 161[a]	1.47×10^{-3}
5	1	1	1	--		IHCN, 163[a]	7.68×10^{-5}
5	1	--	--	1		INP, 163[a]	1.60×10^{-5}
5	1	1	--	1		IHPN, 179[a]	2.38×10^{-3}
5	1	2	1	--		179	1.14×10^{-2}
5	1	1	1	1		195	1.88×10^{-2}
5	2	2	--	--		IDHDN, 226[c]	1.71×10^{-1}
10	2	1	--	--	1	$C_{10}H_{16}N_2O_9$, 308	2.67×10^{-1}

[a]Schwantes et al (2015), [b]Ng et al (2008), and [c]Rollins et al (2009).

How do theoretical and experimental compare?

In I^- CIMS measurements of individual nitrates (example in Figure 5), mononitrates appear to be the dominant products, with dinitrates and dimers also observed. Compared to theoretical K_p's (Table 3) for the major observed mononitrate ($C_5H_9NO_5$: 1.60×10^{-5}) , dinitrate ($C_5H_6N_2O_8$: 1.71×10^{-1}), and dimer ($C_{10}H_{16}N_2O_9$: 2.67×10^{-1}), we see that the empirically observed averaged K_p's (Table 2) ranging from 10^{-4} – 10^{-3} suggest a substantially more volatile mix of organonitrates than the CIMS data, possibly indicating differential sensitivities to the classes of nitrates, or partitioning that is not driven by absorptive partitioning..



Monomers: C_5 fragments **Dinitrates**: C_5 with 2 NO_3 groups **Dimers**: C_{10} fragments

Figure 5: Representative I- CIMS data from 12. August experiment. Gas-phase fragments detected include many nitrates.

Major Results

- Alkyl nitrates yields are independent of chemical regime and seeding, ~ 40%
- Observed gas/aerosol partitioning of organonitrates shows a higher average volatility than inferred from CIMS speciated nitrate measurements.
- Partitioning coefficients indicate product primarily consists of monomers.

Acknowledgements

Funding for this research came from the European Commission (EC) under the European Union's Horizon 2020 research and innovation program (Eurochamp 2020 grant agreement No.730997). BB and JLF also gratefully acknowledge a Reed College Opportunity Grant and the Dreyfus Foundation for travel support.

Contacts for questions and comments: Bellamy Brownwood (bellamybrownowod@gmail.com), Julie Fry (fry@reed.edu)