Reactions of Unsaturated and Saturated Organic Aerosol Particles with NO_3 Radicals

Lin Wang, Aiko Matsunaga, Christen Strollo, Janet Arey, Roger Atkinson, and Paul Ziemann

Air Pollution Research Center

UNIVERSITY OF CALIFORNIA
RIVERSIDE

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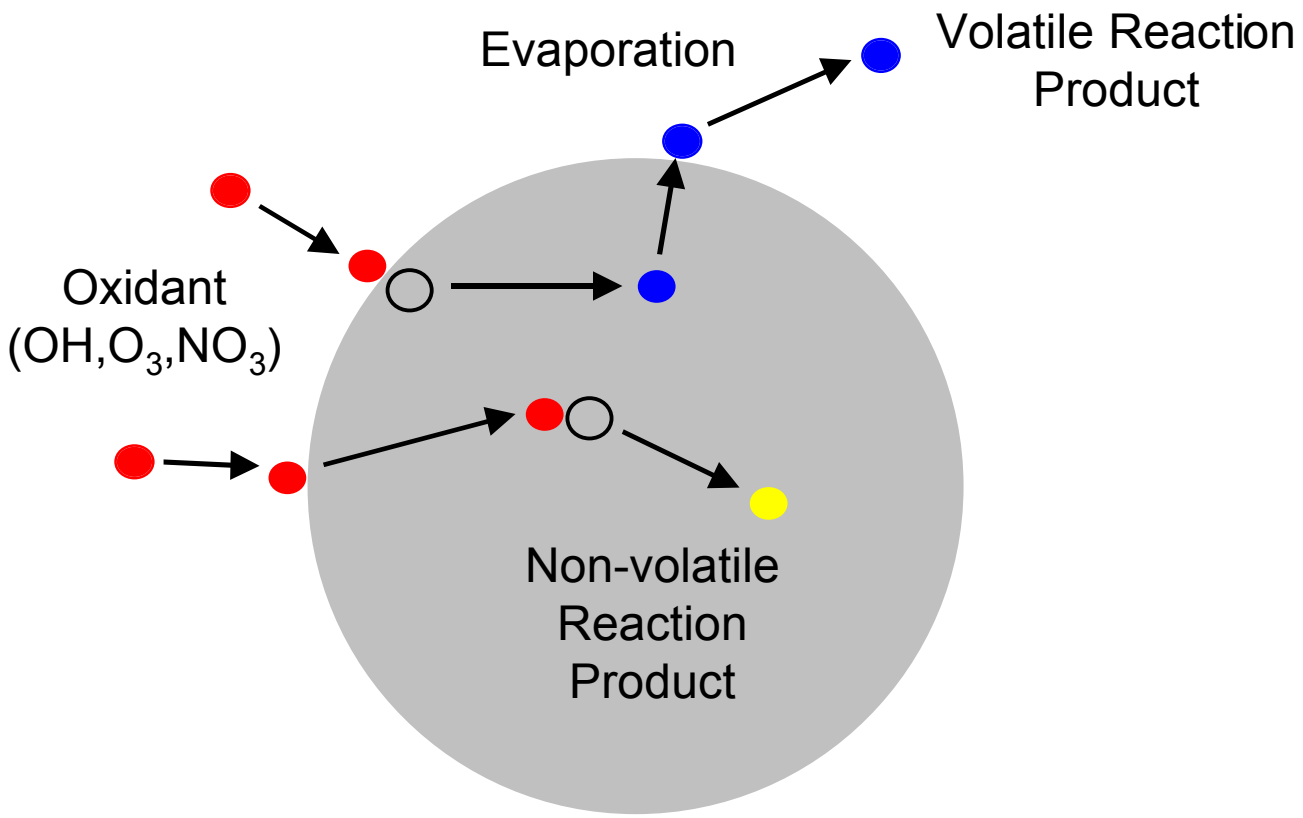
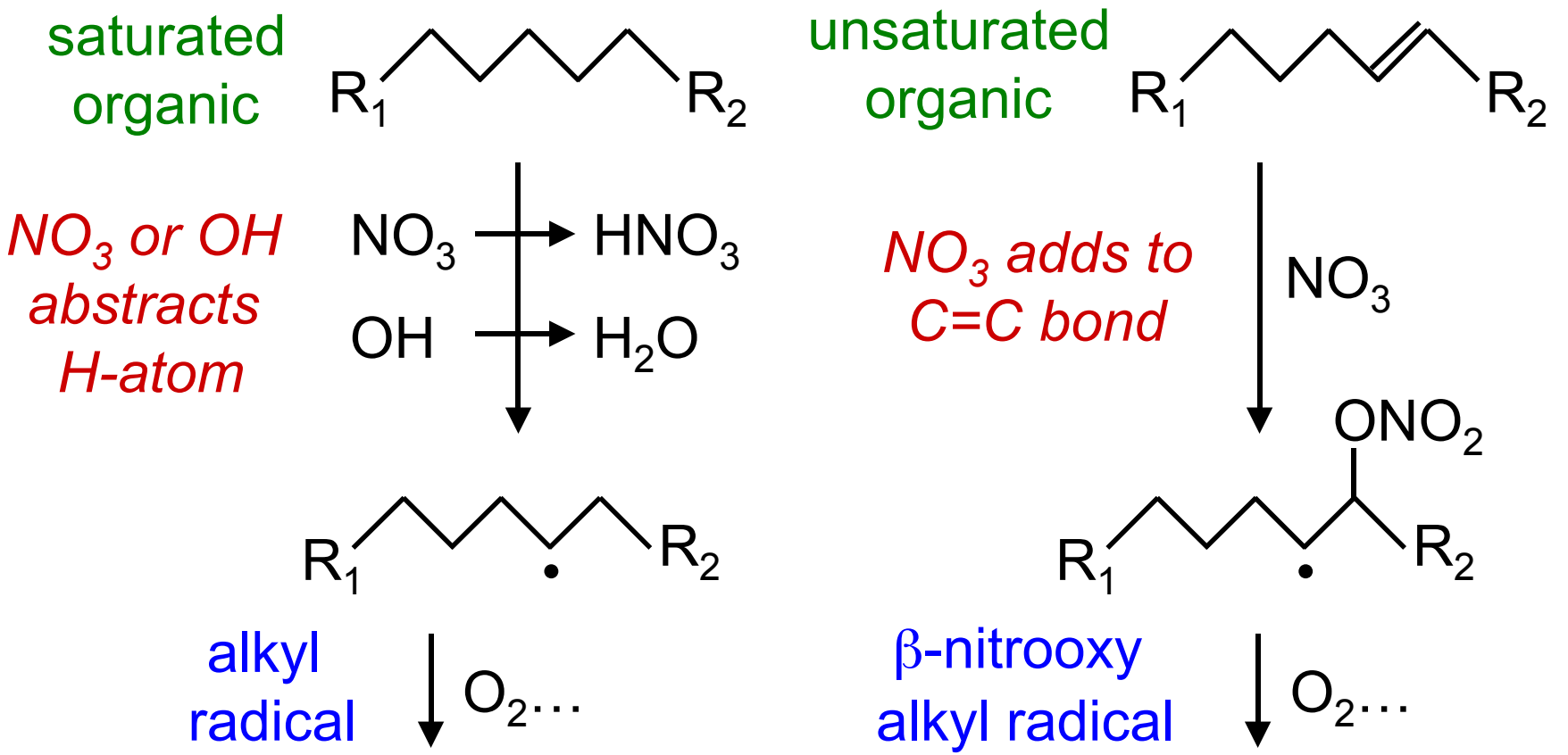
Heterogeneous Oxidation of Organic Particles



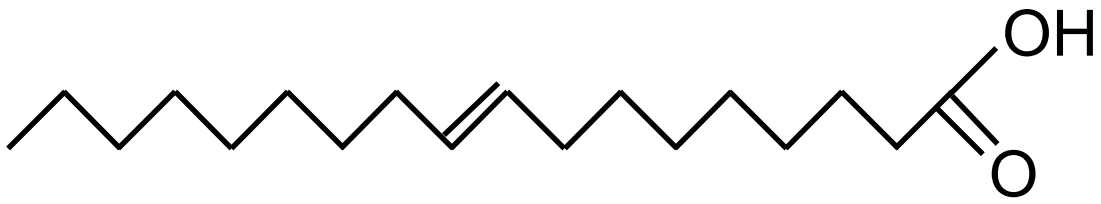
Radical-Initiated Reactions of Organics



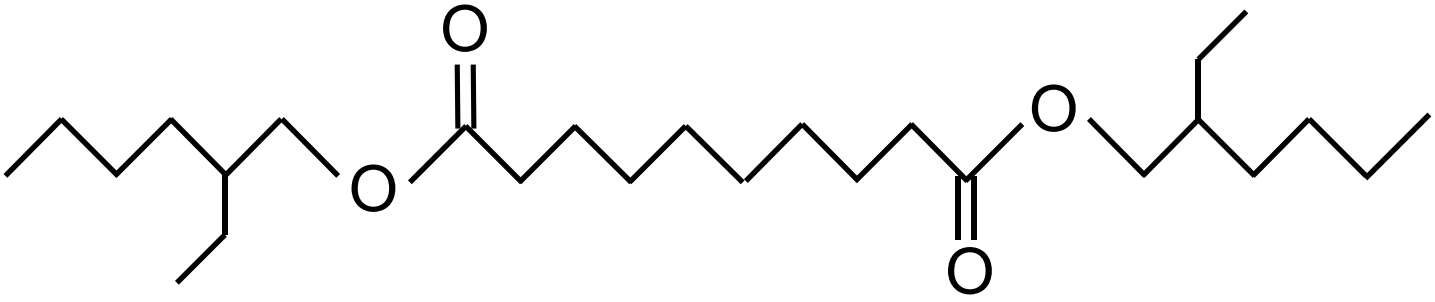
Functional groups located anywhere. Complex mixture

Functional groups localized near C=C bond. Additional -NO_3 compared to H-atom abstraction

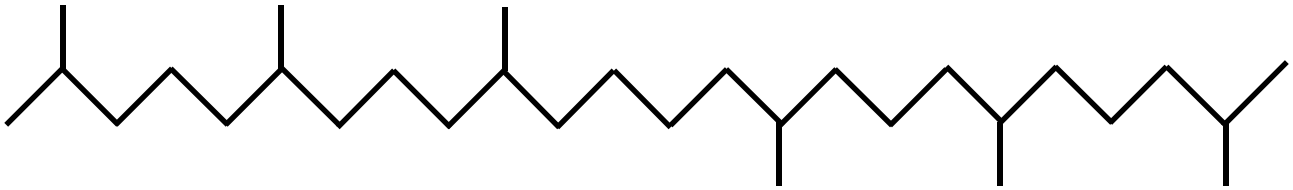
Investigated Compounds



oleic acid

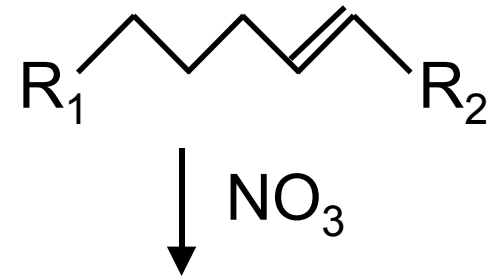


DOS



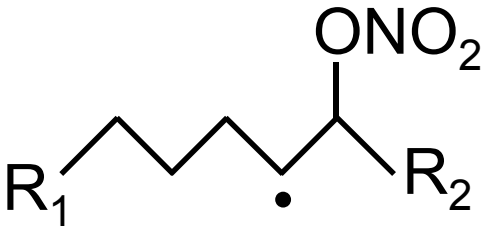
squalane

Mechanism of Oleic Acid + NO_3 Reaction

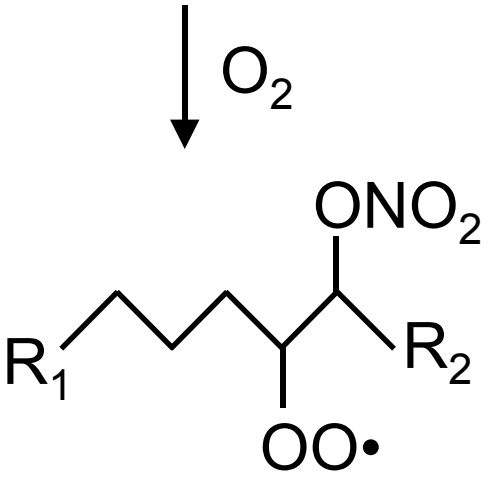


oleic acid (OA)

$R_1 = CH_3(CH_2)_4$
$R_2 = (CH_2)_7C(O)OH$

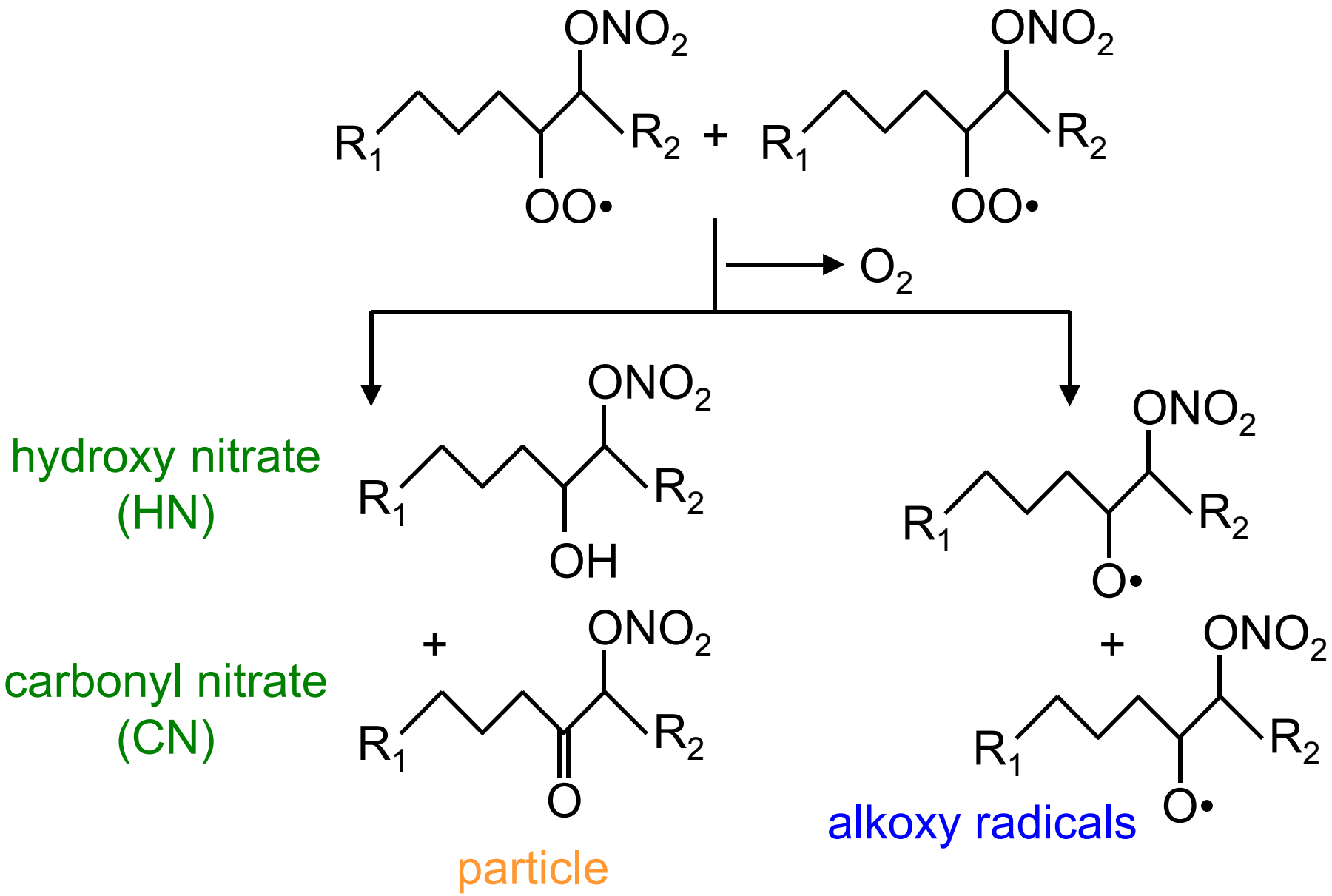


alkyl radical

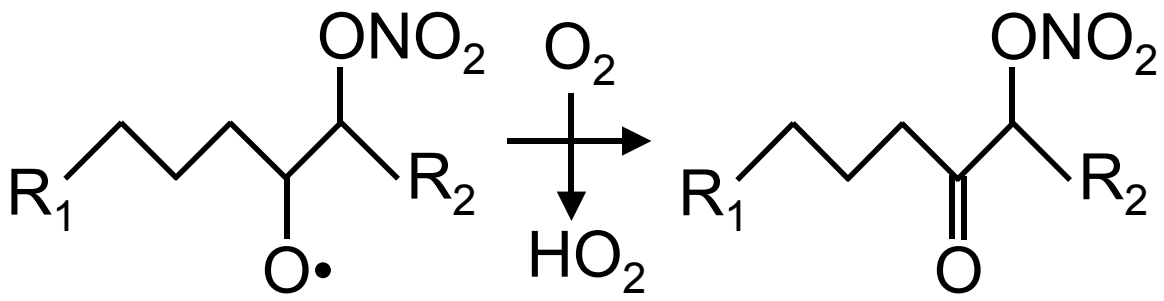


alkyl peroxy radical

Reactions of Alkyl Peroxy Radicals



Reactions of Alkoxy Radicals



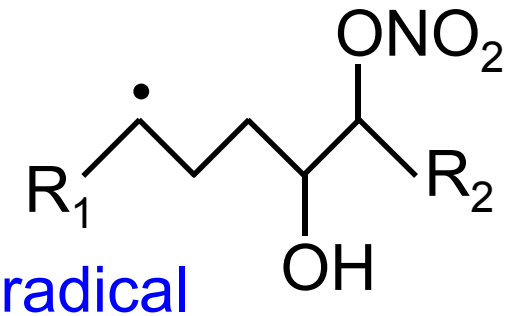
carbonyl nitrate

particle

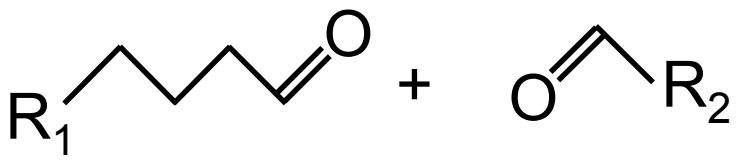
isomerization

decomposition

NO_2



alkyl radical



$CH_3(CH_2)_7CHO$ + $OHC(CH_2)_7C(O)OH$

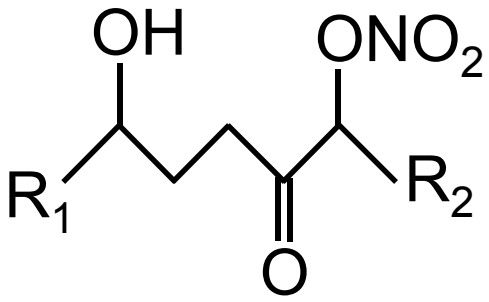
nonanal

gas

9-oxononanoic acid (9-ONA)

particle

O_2 …

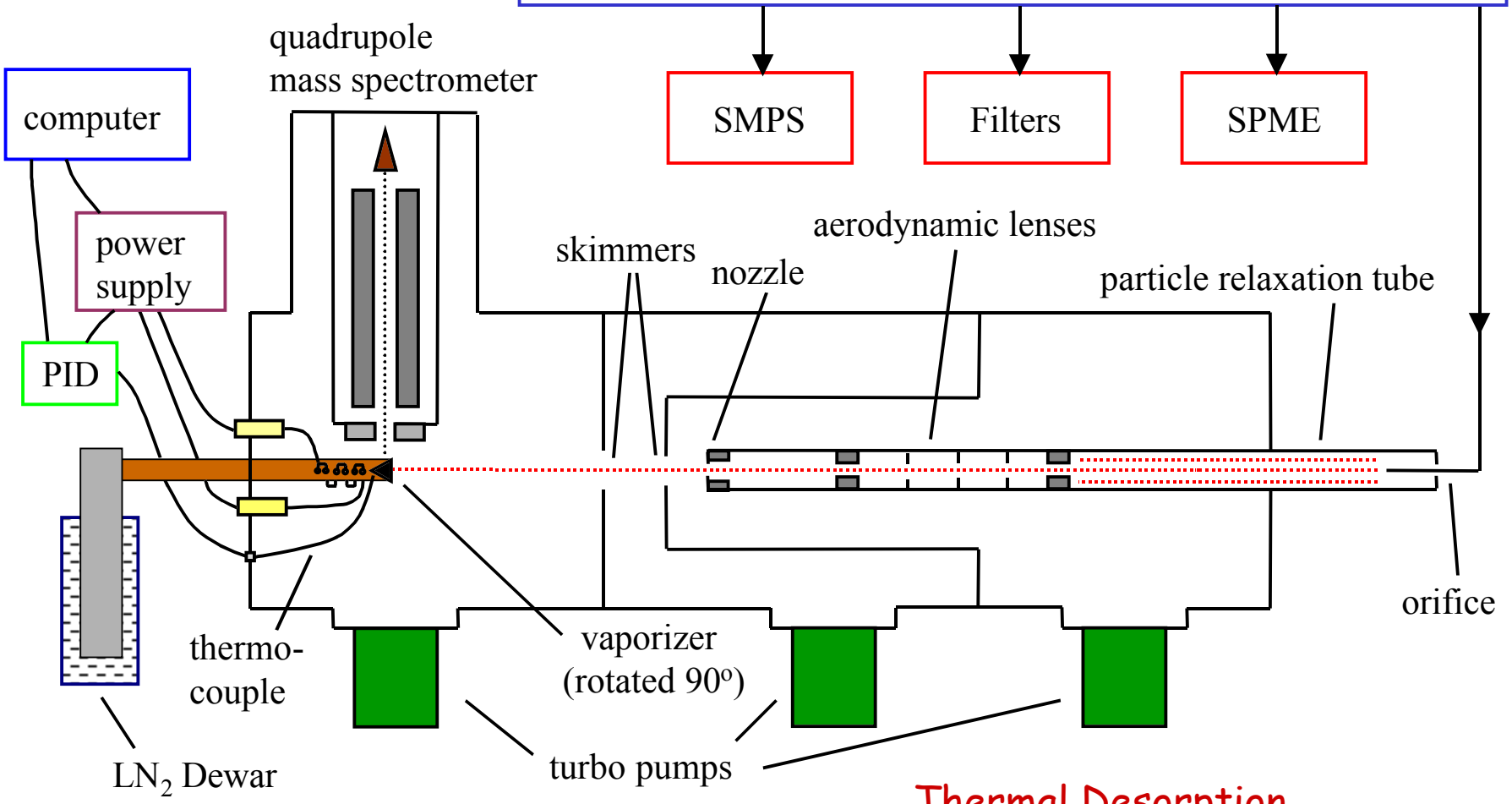


hydroxycarbonyl nitrate (HCN)

particle

Experimental Apparatus

6000 L Teflon film environmental chamber
Oleic Acid, DOS, or Squalane particles: D_p~0.2 µm, ~1 mg m^{-3}
5 ppmv $N_2O_5 \longleftrightarrow NO_2 + NO_3$
1 ppmv methacrolein ($CH_2=C(CH_3)CHO$)
10 ppmv NO to stop reaction: $NO_3 + NO_2 \longrightarrow 2NO_2$)

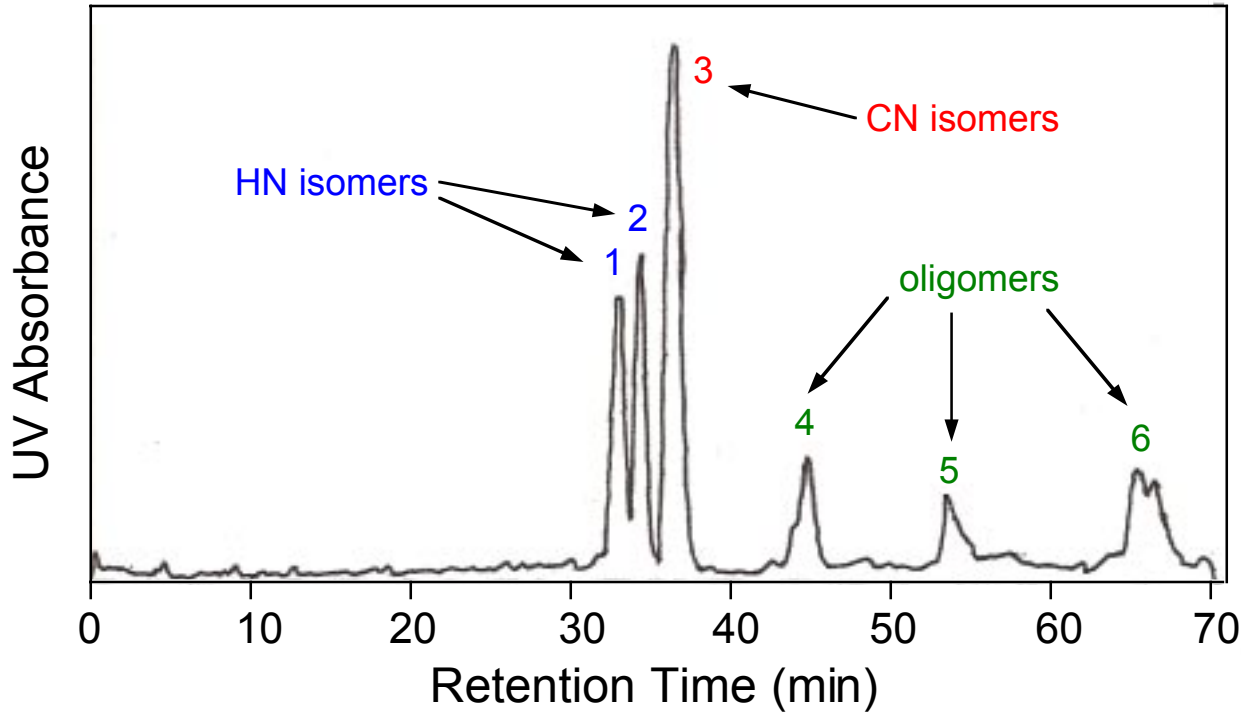


Thermal Desorption
Particle Beam Mass Spectrometer (TDPBMS)

Experimental Methods

- Particles generated by evaporation-condensation and reacted in chamber with N_2O_5 as NO_3 source. Methacrolein added as a reference compound and decay measured by GC-FID to determine NO_3 concentration for kinetics. When particles ~60-100% reacted, NO added to remove N_2O_5.
- Particles analyzed in real-time and by temperature-programmed thermal desorption with TDPBMS.
- Filter samples separated by HPLC and analyzed with UV and TDPBMS detection to identify and quantify products, and by high resolution ESI-APCI-MS for identification.
- Particle size distribution measured by scanning mobility particle sizer (SMPS).
- Gas-phase aldehydes collected/derivatized on solid-phase micro-extraction (SPME) fibers and quantified by GC-FID.

HPLC Analysis of Oleic Acid + NO_3 Reaction Products



- HN and CN concentrations measured using authentic standards
- HN:CN yields = 0.41:0.59[1]
- HN:CN yields = 0.48:0.52[2]

[1]Calculated from peaks 1-3

[2]Calculated from peaks 1-3 + 4-6 (weighted using ESI-APCI-MS signals)

HPLC/ESI-APCI-MS of Oleic Acid + NO_3 Products

Peak	Molecular Formula	Predicted Mass	Measured Mass	Δ Mass (ppm)
1.	HN+H-HNO_3-$2H_2O$	263.2375	263.2384	3.5
	HN+H-HNO_3-H_2O	281.2481	281.2487	2.3
	HN+H-HNO_3	299.2586	299.2591	1.6
	HN+Na	384.2362	384.2366	1.0
2.	Identical to Peak 1			
3.	CN+H-HNO_3-H_2O	279.2324	279.2325	0.3
	CN+H-HNO_3	297.2430	297.2431	0.4
	CN+Na	382.2206	382.2209	0.9
	CN+K	398.1945	398.1947	0.5
4.	HN+H-HNO_3-$2H_2O$	263.2375	263.2359	6.0
	HN+H-HNO_3-H_2O	281.2481	281.2473	2.7
	HN+H-HNO_3	299.2586	299.2576	3.4
	CN+Na	382.2206	382.2197	2.2

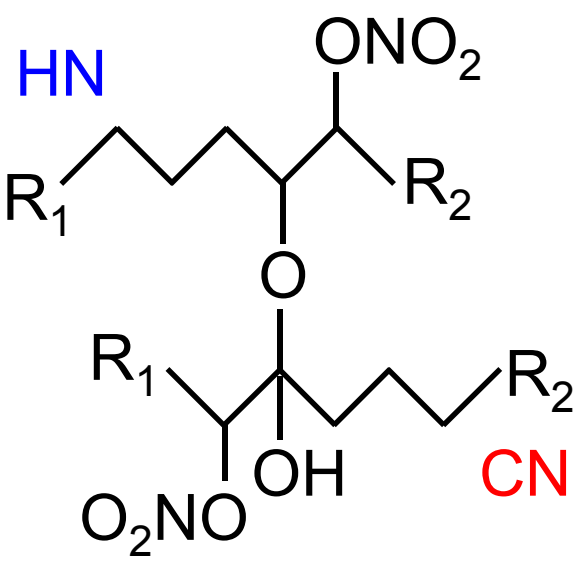
HN: $C_{18}H_{35}NO_6$: $CH_3(CH_2)_7CH(ONO_2)CH(OH)(CH_2)_7C(O)OH$ 361.2464

CN: $C_{18}H_{33}NO_6$: $CH_3(CH_2)_7CH(ONO_2)C(O)(CH_2)_7C(O)OH$ 359.2308

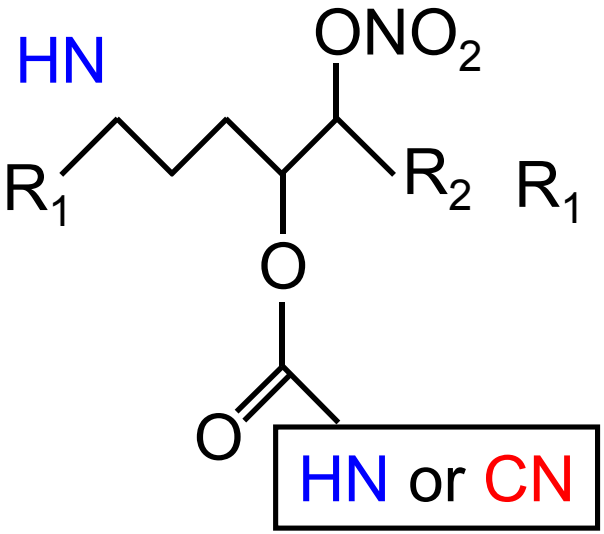
HPLC/ESI-APCI-MS of Oleic Acid + NO_3 Products

Peak	Molecular Formula	Predicted Mass	Measured Mass	Δ Mass (ppm)
6.	HN+H-HNO_3-H_2O	281.2481	281.2473	1.5
	HN+H-HNO_3	299.2586	299.2570	5.4
	HN+Na	382.2206	382.2201	1.2
	HN+H-HNO_3	297.2430	297.2427	0.9
	HN+CN+-H_2O+Na	725.4564	725.4543	2.9
	HN+CN+Na	743.4670	743.4641	3.8
	HN+CN-H_2O+K	741.4304	741.4287	2.3
	HN+CN+K	759.4409	759.4412	0.3
	HN+2CN-2H_2O+Na	1066.6767	1066.6729	3.6
	HN+2CN-2H_2O+K	1082.6506	1082.6504	0.2
	HN+2CN-H_2O+K	1100.6612	1100.6651	3.6
	2HN+CN-H_2O+Na	1068.6923	1068.6859	6.0
	2HN+CN-H_2O+K	1102.6768	1102.6709	5.4
	2HN+CN-2H_2O+K	1084.6662	1084.6711	4.5
	3HN-2H_2O+K	1086.6818	1086.6869	4.7
	2HN+2CN-2H_2O+Na	1427.9230	1427.9161	4.8
	2HN+2CN-2H_2O+K	1443.8970	1443.8958	0.8

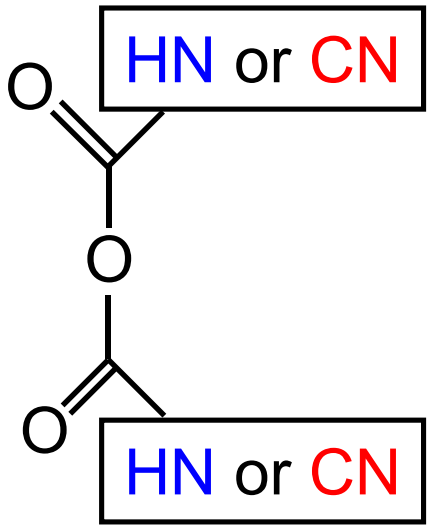
Possible Oligomer Linkages



hemiacetal



ester

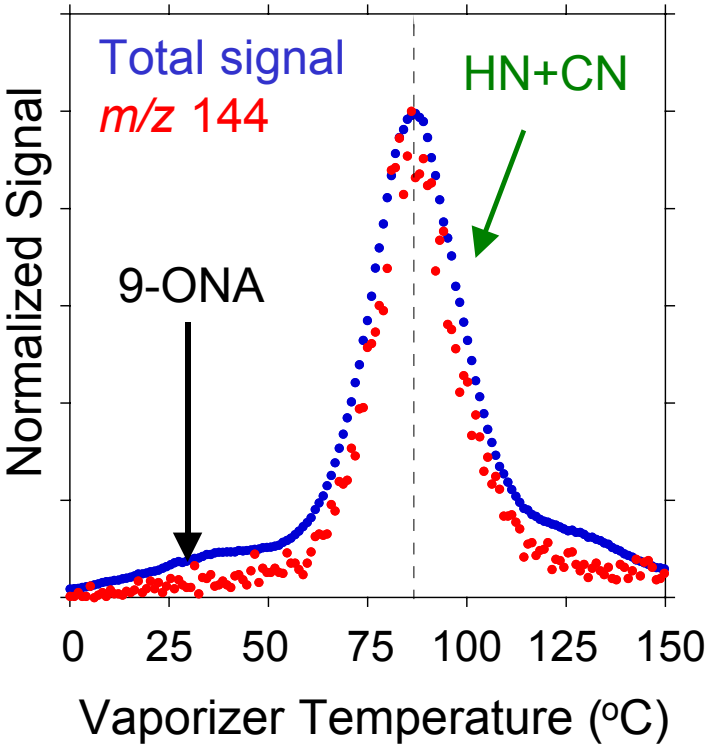


anhydride

Volatilization of Oleic Acid + NO_3 Reaction Products

Thermal desorption profile from oleic acid + NO_3

m/z 144 characteristic of 9-ONA
Should desorb ~28°C if present



- Gas-phase nonanal yield = 2%
- No 9-oxononanoic acid detected in particles by TDPBMS
- Measured relative mass change

$$\Delta m = [V_f \rho_f / V_i \rho_i - 1] = 1.27$$

- Predicted relative mass change, assuming no volatilization and equal HN and CN yields

$$\Delta m = \frac{MW_{HN} + MW_{CN}}{2 \times MW_{OA}} = 1.28$$

Conclusions: Products and Mechanism of the Reaction of Oleic Acid with NO_3 Radicals

- The primary products of the reaction of oleic acid + NO_3 are the hydroxy nitrate and carbonyl nitrate (2 isomers each)
- The hydroxy nitrate and carbonyl nitrate are both formed with yields of ~0.5, indicating that the major reaction pathway for β-nitrooxy peroxy radicals is the formation an alcohol + carbonyl pair (the Russell mechanism)
- The formation of volatile products is negligible (~0.02 yield)
- The hydroxy nitrate and carbonyl nitrate can react in the particles to form oligomers, apparently through some combination of hemiacetal, ester, and anhydride linkages

Heterogeneous Kinetics

- Near-surface reaction

  Plot $[I/I_o]^{1/2}-1$ vs. $P_{NO3}t$

  $\gamma_{NS} = [-slope][V/S][8RTM_o/c]$

- Bulk reaction (fast NO_3 diffusion)

  Plot $\ln[I/I_o]$ vs. $P_{NO3}t$

  $\gamma_B = [-slope][V/S][4RTM_o/c]$

γ = reactive uptake coefficient

I/I_o = organic signal ratio P_{NO3} = NO_3 pressure

V/S = particle volume/surface area t = time

M_o = pure organic concentration R = gas constant

c = NO_3 gas mean thermal speed T = temperature

Heterogeneous Kinetics

- Near-surface reaction

$$k_{NS} = \gamma c/[4RTH(DM_o)^{1/2}]$$

- Bulk reaction

$$k_B = \gamma c/[4RTHM_o(V/S)]$$

For liquid organics 1 and 2, assuming same H and D:

- Near-surface reaction

$$k_1/k_2 = [\gamma_1/\gamma_2][M_{o2}/M_{o1}]^{1/2}$$

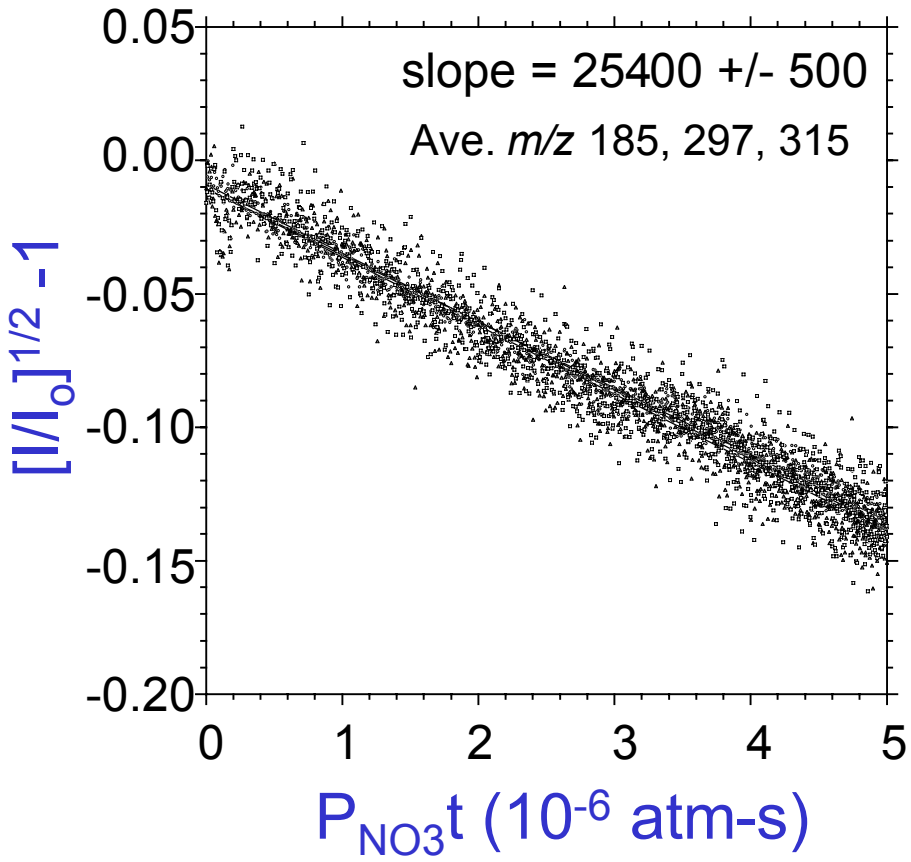
- Bulk reaction

$$k_1/k_2 = [\gamma_1/\gamma_2][M_{o2}/M_{o1}]$$

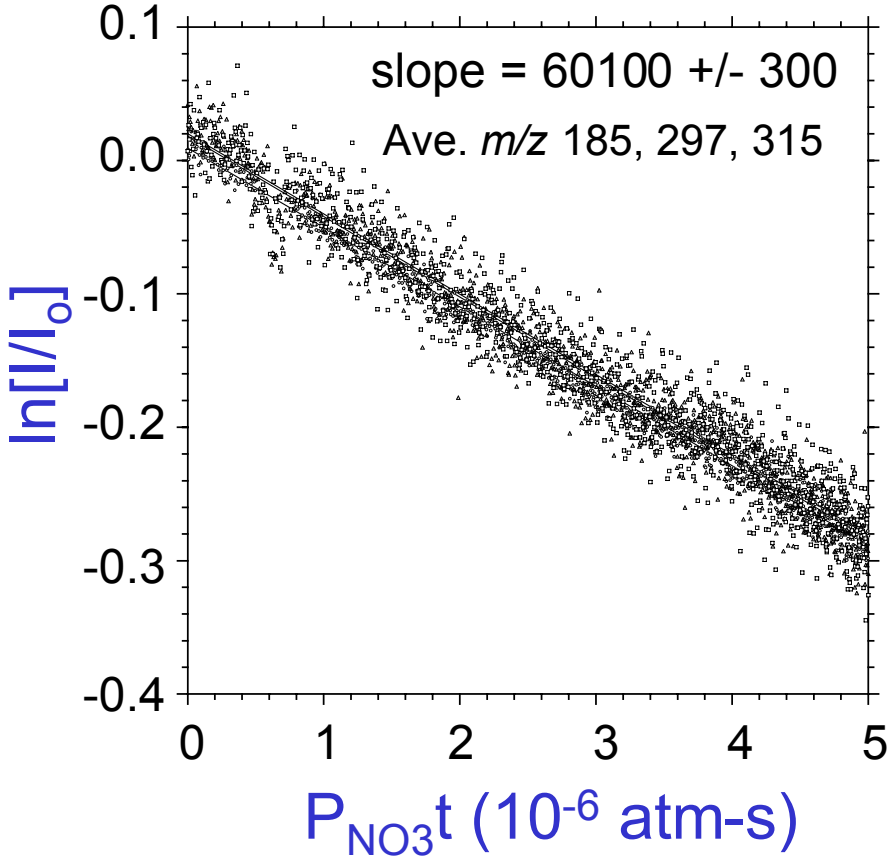
k = rate constant for NO_3 + organic in particle
H = Henry's law constant of NO_3 in organic

DOS + NO_3 Kinetics Plots

Near-surface reaction



Bulk reaction



Uptake Coefficients and Rate Constants

	γ_{NS}	γ_B	k_{NS}/k_{C16}	k_B/k_{C16}	k/k_{C16}[1]
DOS	6.0×10^{-3}	7.1×10^{-3}	8.5	4.4	2.7
Squalane	4.2×10^{-3}	4.6×10^{-3}	4.7	3.0	3.6

C_{16} (film)[2] $\gamma = 2.6 \times 10^{-3}$

C_{18} (SAM)[3] $\gamma = 8.8 \times 10^{-4}$

[1]Ratio calculated using estimation method for NO_3 gas phase rate constants: Aschmann and Atkinson. *Atmos. Environ*. 29, 2311-2316 (1995)

[2]Measured for hexadecane film: Moise et al. *J. Geophys. Res*. 107, D2, 4014, 10.1029/2001JD000334, (2002)

[3]Measured for C_{18} self-assembled monolayer: Knopf et al. *Geophys. Res. Lett*. 33, doi: 10.1029/2006GL026884, (2006)

Conclusions: Kinetics of the Reaction of Saturated Organic Compounds with NO_3 Radicals

- Reactive uptake coefficients measured for the reactions of DOS (C_{26} diester) and squalane (C_{30} branched alkane) liquid aerosol particles with NO_3 radicals are ~2-8 times larger than those measured by others for a C_{16} liquid alkane film and a self-assembled C_{18} alkyl monolayer.

- The larger reactive uptake coefficients are consistent with larger condensed-phase reaction rate constants for DOS and squalane, which are explained at least in part by the greater number of CH_2 groups and higher chain branching.