Effects of NO_x on the Volatility of Secondary Organic Aerosol from Isoprene Photooxidation

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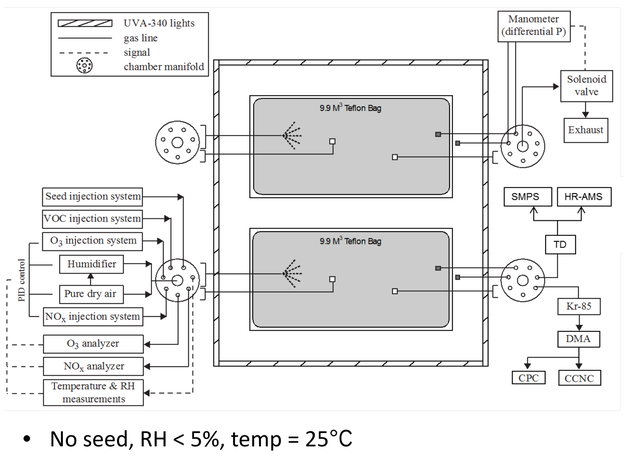
Background

- SOA contributes substantial fraction to total OA
- Isoprene is the most abundant NMHC, even small SOA yields lead to substantial contribution to total SOA
- SOA formation highly dependent on RO2 fate (RO2+NO/NO2/HO2/RO2)
- Volatility is a key property of organic aerosol, but no systematic investigation on volatility of isoprene SOA under different NO_x conditions

PNNL Chamber Facility



- No seed, RH < 5%, temp = 25°C
- Thermal Denuder (TD): 60cm long, 11.4mm ID, RT=12s

30/50/70/100/150/200/180/130/110/85/65/40°C

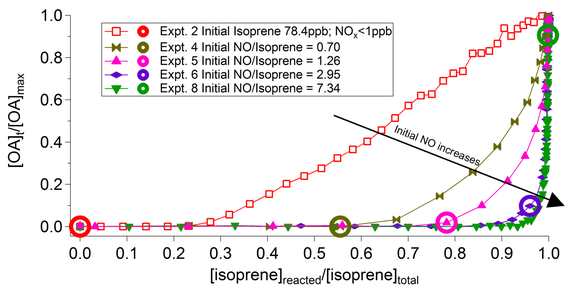
Experimental Conditions and Results

Expt.	$[Isoprene]_0$ (ppb)	$[NO]_0$ (ppb)	[OH] ($10^6 molec^{-1}*cm^3$)	SOA ($\mu g/m^3$)	SOA Yield (%)
1	45.5	<1	1.04	6.3±0.2[a]	5.0±0.1[a]
2	78.4	<1	0.82	14.7±0.3	6.7±0.2
3	144.7	<1	0.44	30.2±1.4[a]	7.5±0.4[a]
4	97.7	68.1	4.64	19.7±0.4	7.2±0.2
5	91.4	114.8	4.40	19.7±0.8	7.7±0.3
6	114.6	338.2	3.58	27.0±1.0	8.5±0.3
7	105.5	466.2	3.35	10.9±1.5	3.7±0.5
8	100.6	738.1	2.72	4.2±0.4	1.5±0.2

a) Not wall loss corrected

b) Both SOA mass concentration and SOA yield correspond to aerosol growth at equivalent OH exposures of approximately $2*10^7$ molecule*hour*cm^{-3}.

Effect of NO_x on growth curve

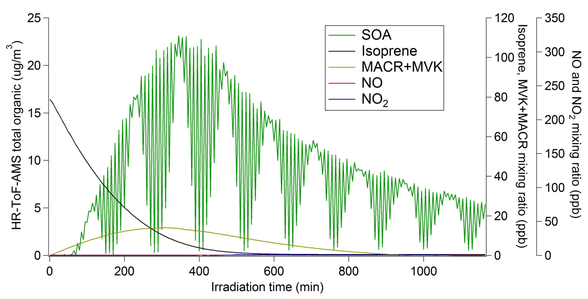


The vertical section becomes more pronounced as the initial NO concentration increases.

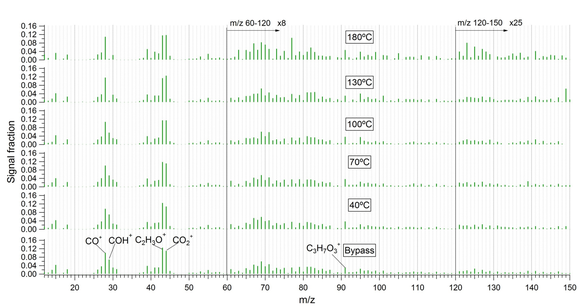
- Higher generation products
- Reactions between high generation products
- Rapid loss of SOA mass in HO2-dominant experiments

Results

HO_2-dominant Experiment
Expt.2 $[NO_x]$ < 1ppb

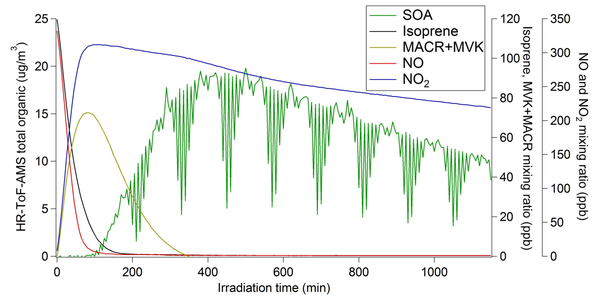


Fast onset; Fast decay rate; Low MACR+MVK yield

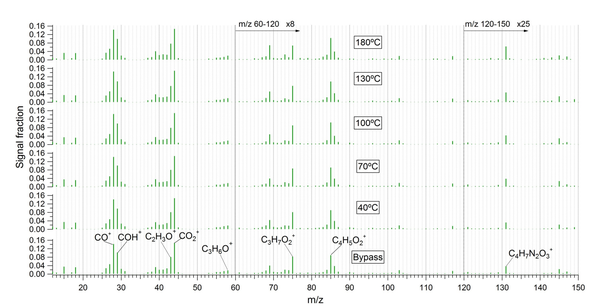


Lower f_CO_2^+; Evenly distributed between *m/z* 60 and 100

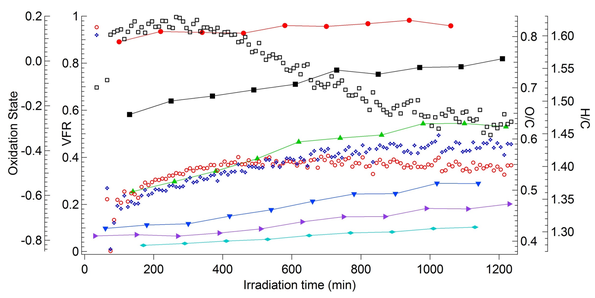
Mixed Experiment
Expt. 6 Initial NO/Isoprene = 2.95



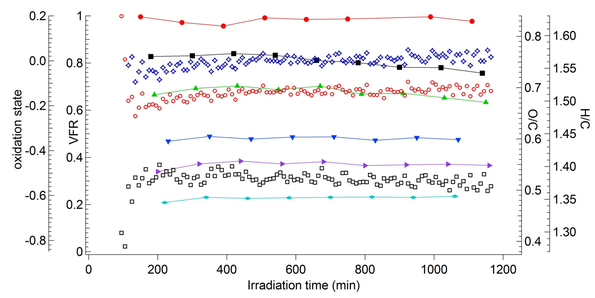
Slow onset; Slow decay rate; High MACR+MVK yield



Higher f_CO_2^+; $C_3H_6O^+$ (*m/z*58), $C_3H_7O_2^+$ (*m/z*75), $C_4H_5O_2^+$ (*m/z*85)

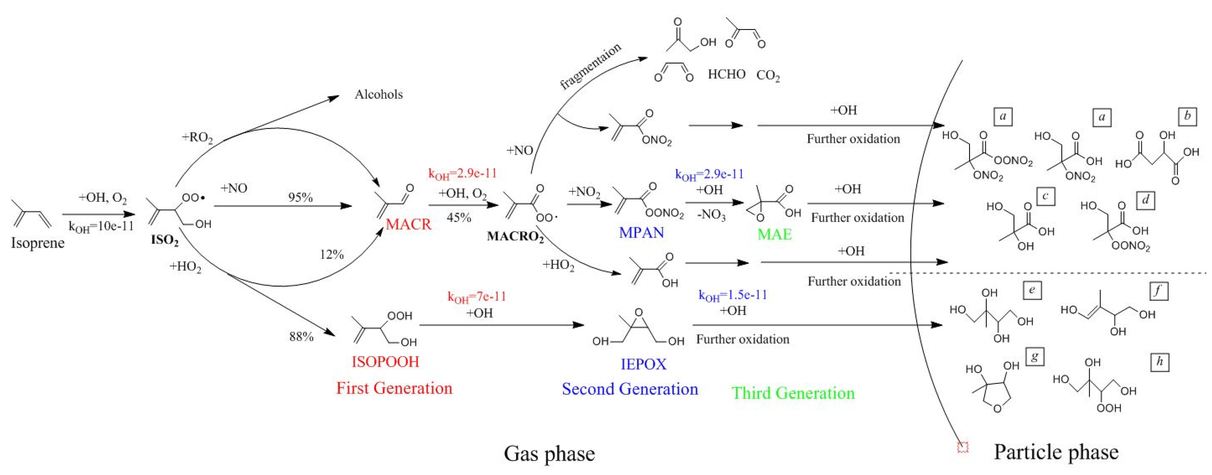


Both VFR and oxidation continuously increase.

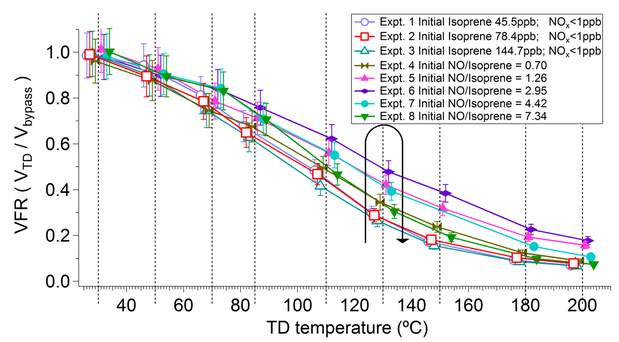


Both VFR and oxidation remain relatively constant. Note: the temporal evolution of the VFR varies with initial NO/isoprene ratios

Simplified Isoprene Oxidation Mechanism

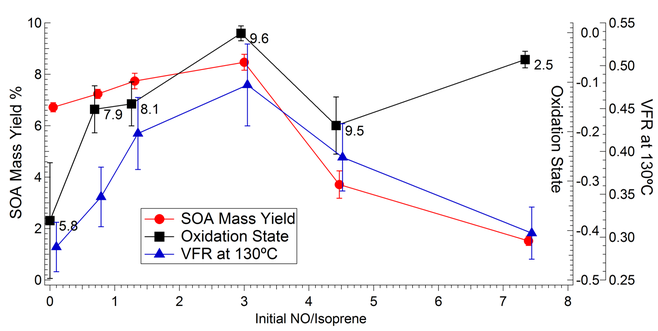


Effect of NO_x on volatility



VFR increases with an initial NO/isoprene ratio up to 3. Beyond this ratio, increasing initial NO/isoprene ratio leads to a decrease in VFR.

Non-linear NO_x effect



The volatility and yield of Isoprene SOA vary with NO_x level in a non-linear manner:

- Dynamic effect of NO_x:
  - ISO_2+NO vs ISO_2+HO_2
  - $MACRO_2$ + HO_2/NO_2 → 2-MG (key intermediate)
  - $MACRO_2$ + NO → fragment
- Oligomerization: more extensive in mixed experiments
  - 1) oligomer length: three/four monomer units vs dimer
  - 2) most frequent monomer: 2-MG ($C_4H_8O_4$) vs acetaldehyde ($C_2H_6O_2$)

Summary

- In this study, we highlight the different roles of NO and NO_2 in SOA formation, dynamic changes between NO and NO_2, and competitive chemistry of RO_2 among various pathways and their effects on aerosol composition and volatility.
- SOA volatility is sensitive to NO_x and varies with NO_x level in a non-linear manner, need to take into account to in future experiments
- SOA aging in laboratory chamber studies is highly dependent on NO_x levels.

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