Fundamental Studies of
Secondary Organic Aerosol (SOA) Formation

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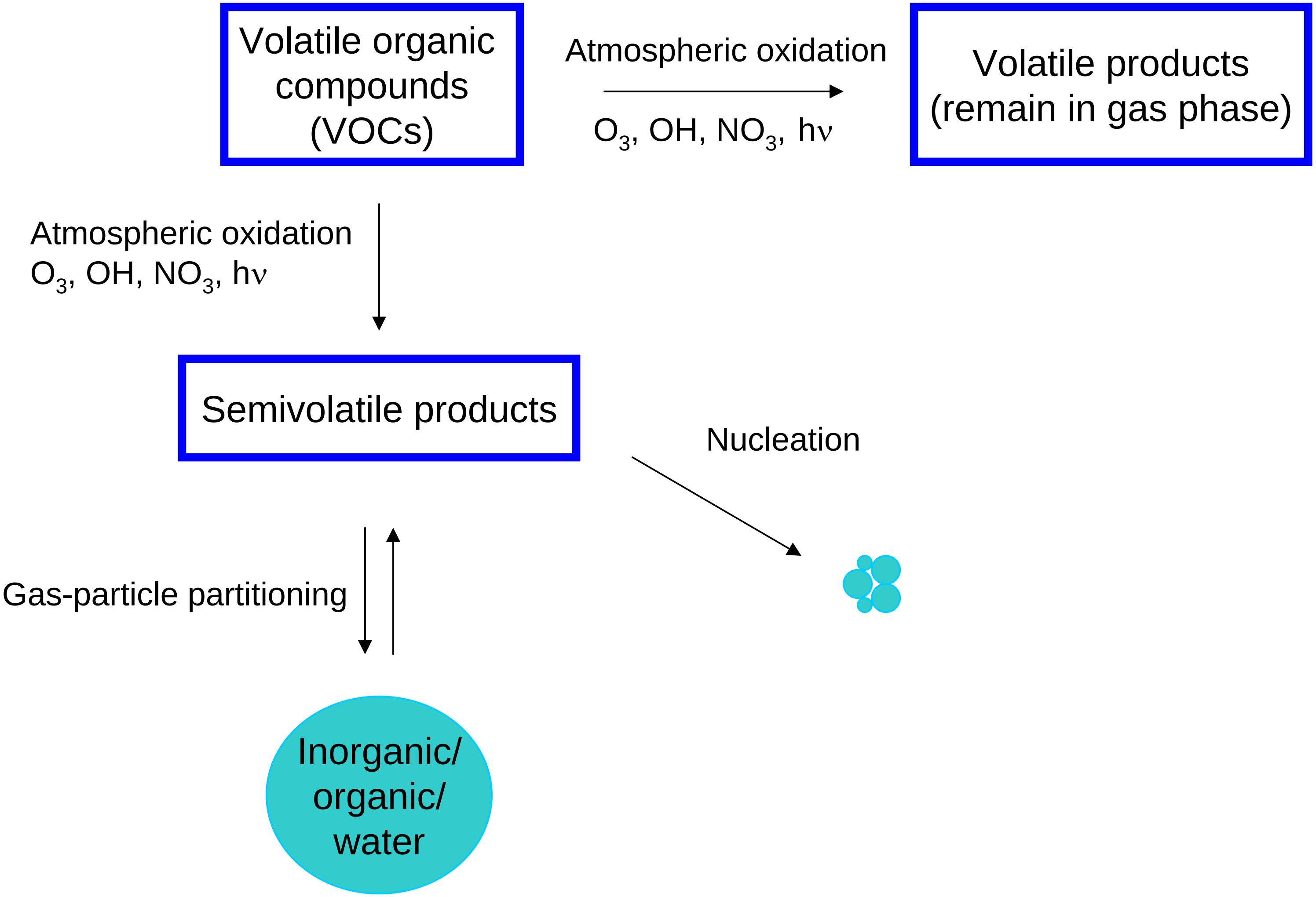
EPA Atmospheric Science Progress Review Meeting
June 22, 2007

Formation of secondary organic aerosol (SOA)



Volatile organic compounds (VOCs)

Atmospheric oxidation

O_3, OH, NO_3, $h\nu$

Volatile products (remain in gas phase)

Atmospheric oxidation
O_3, OH, NO_3, $h\nu$

Semivolatile products

Nucleation

Gas-particle partitioning

Inorganic/ organic/ water

Secondary organic aerosol (SOA)

- Globally: ~10-40% of organic aerosol is secondary [*Kanakidou et al.,* 2005]
- Urban areas: ~50-80% [*Kanakidou et al.*, 2005]
- SOA precursors
  - Biogenic emissions (isoprene, monoterpenes, sesquiterpenes)
  - Anthropogenic emissions (aromatic hydrocarbons)

Hydrocarbon	Emission [Tg / y]	SOA Production [Tg / y]
aromatics	19	3.7
terpenes	153	12
alcohols	41	1.9
sesquiterpenes	15	2.3
isoprene	461	?
Total	689	19.9

Henze et al., 2007

Caltech environmental chambers

- 2 Teflon chambers, 28 m^3 each
- Differential Mobility Analyzer (DMA): particle size distribution, volume
- Time-of-flight Aerodyne Aerosol Mass Spectrometer (AMS): particle mass, composition
- GC-FID: hydrocarbon
- Proton Transfer Reaction Mass Spectrometer (PTR-MS): hydrocarbon, reaction products
- Filter samples: off-line chemical analysis
- O_3, NO_x, RH, T

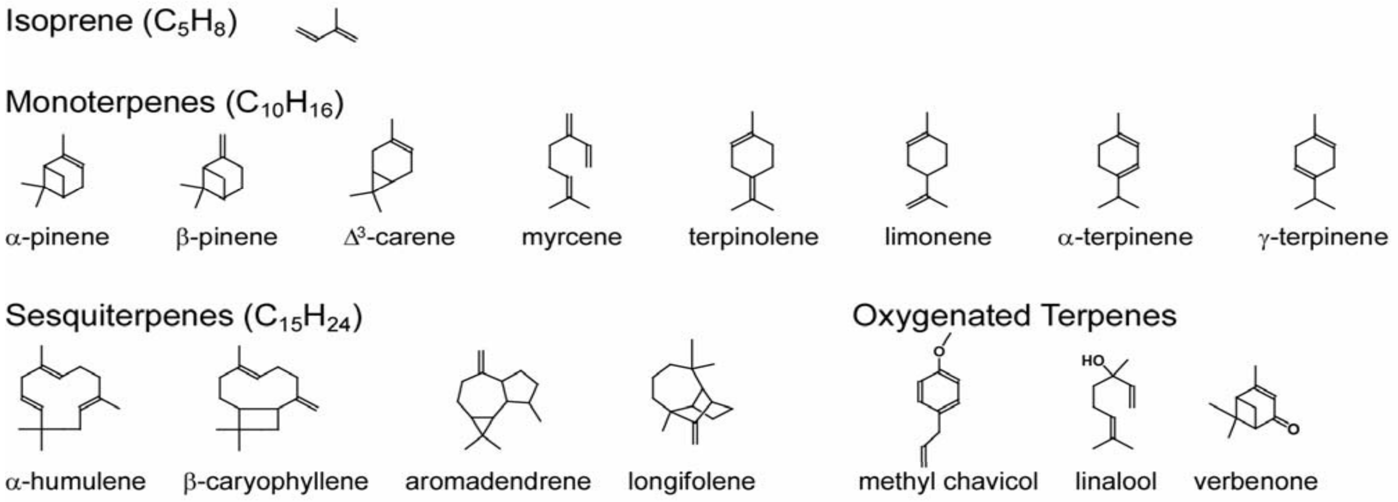
Oxidation of biogenic hydrocarbons

Ozonolysis:

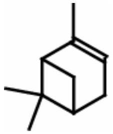
- T=20ºC, RH<10%
- OH Scavenger: cyclohexane
- $(NH_4)_2SO_4$ seed
- Reaction initiated upon addition of O_3

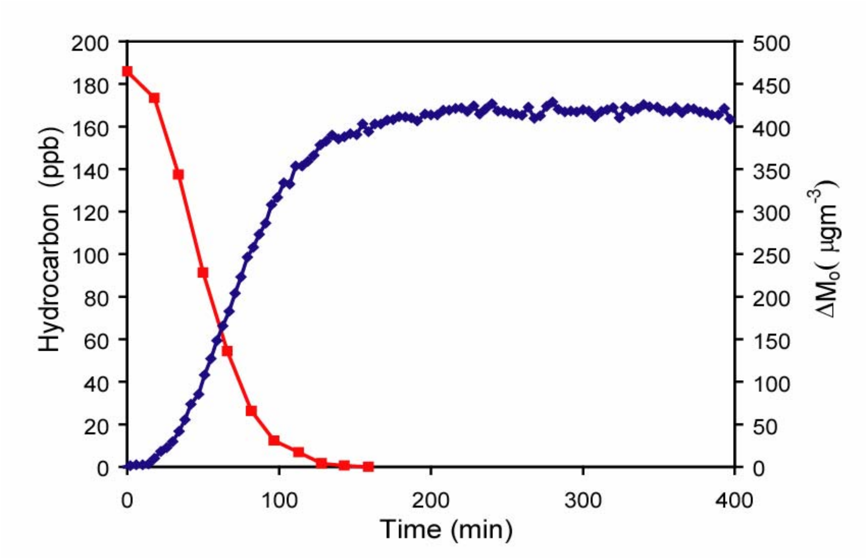
Photooxidation:

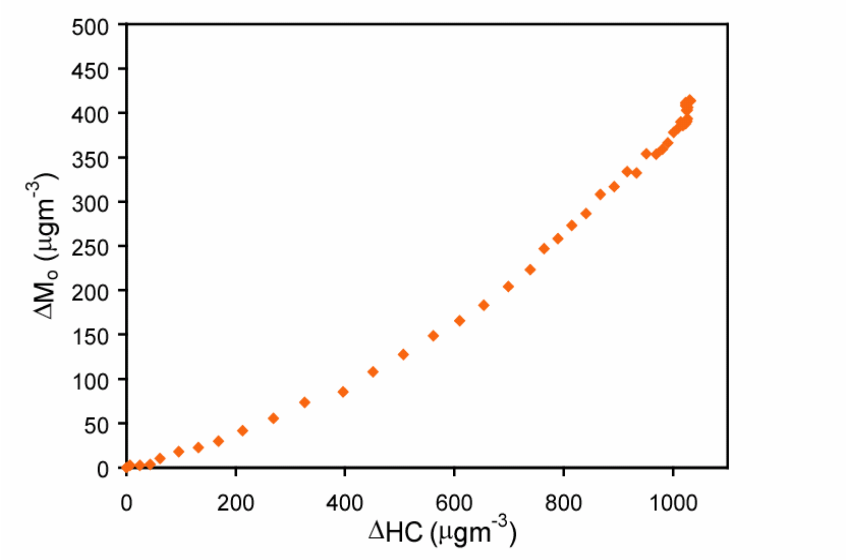
- T=20-22ºC, RH~50%
- HONO as OH precursor: dropwise addition of 1% $NaNO_2$ into 10% H_2SO_4
- $(NH_4)_2SO_4$ seed
- Reaction initiated by irradiation with UV lights



α-pinene ozonolysis





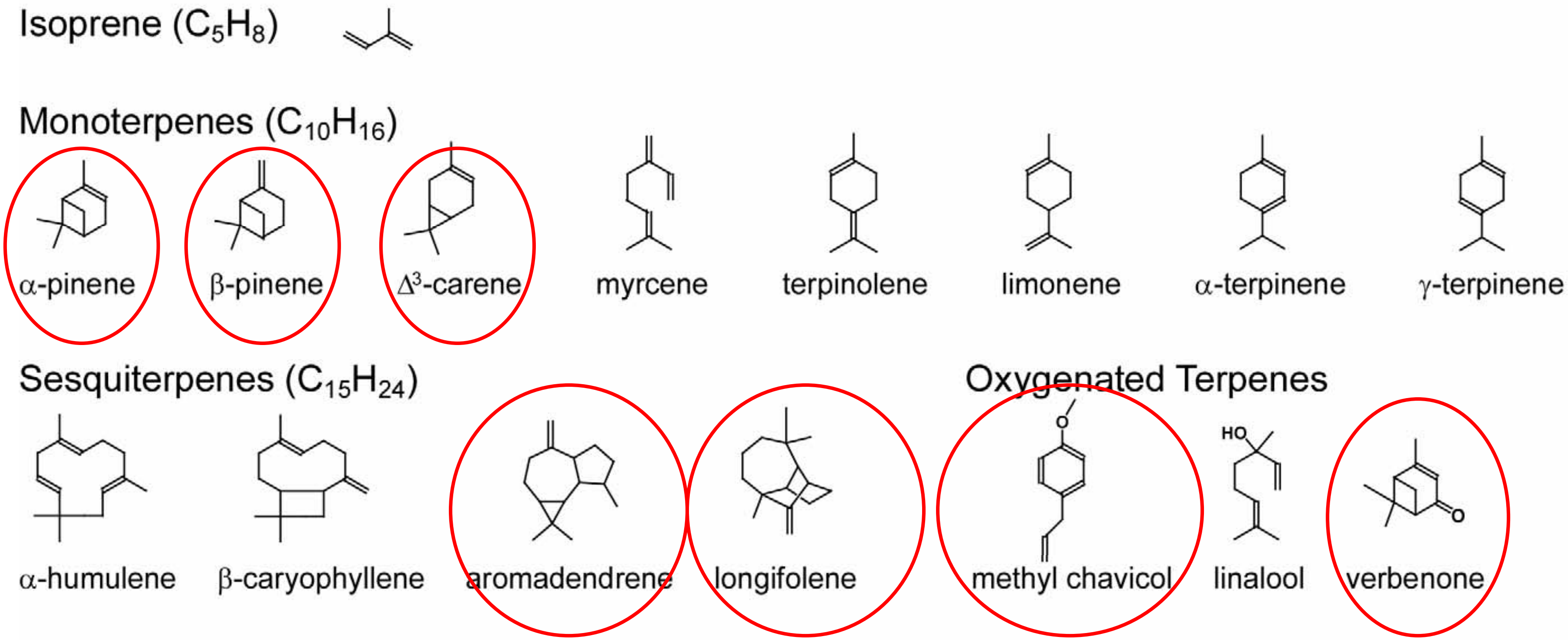


- SOA is formed from the condensation of first-generation products and the first oxidation step is the rate-limiting step

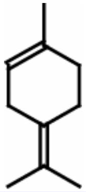
- Organic acids have been identified as major particle-phase products: monocarboxylic acids (pinonic acid and norpinonic acid), dicarboxylic acids (pinic acid and norpinic acid), and hydroxy pinonic acid [e.g. *Yu et al.,* 1999]

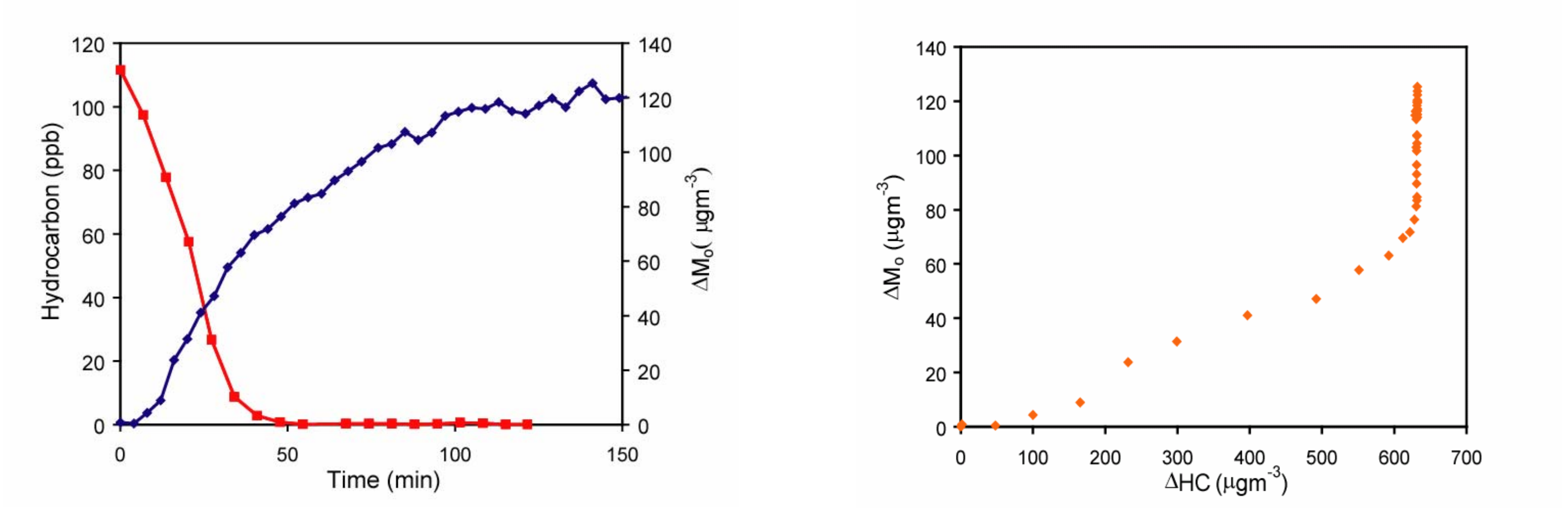
- *Jenkin et al.* [2000] proposed pinic and hydroxy pinonic acid are first-generation products, which is consistent with our study

Compounds with one double bond



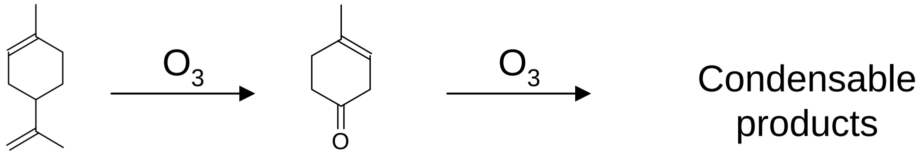
Terpinolene ozonolysis



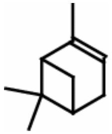


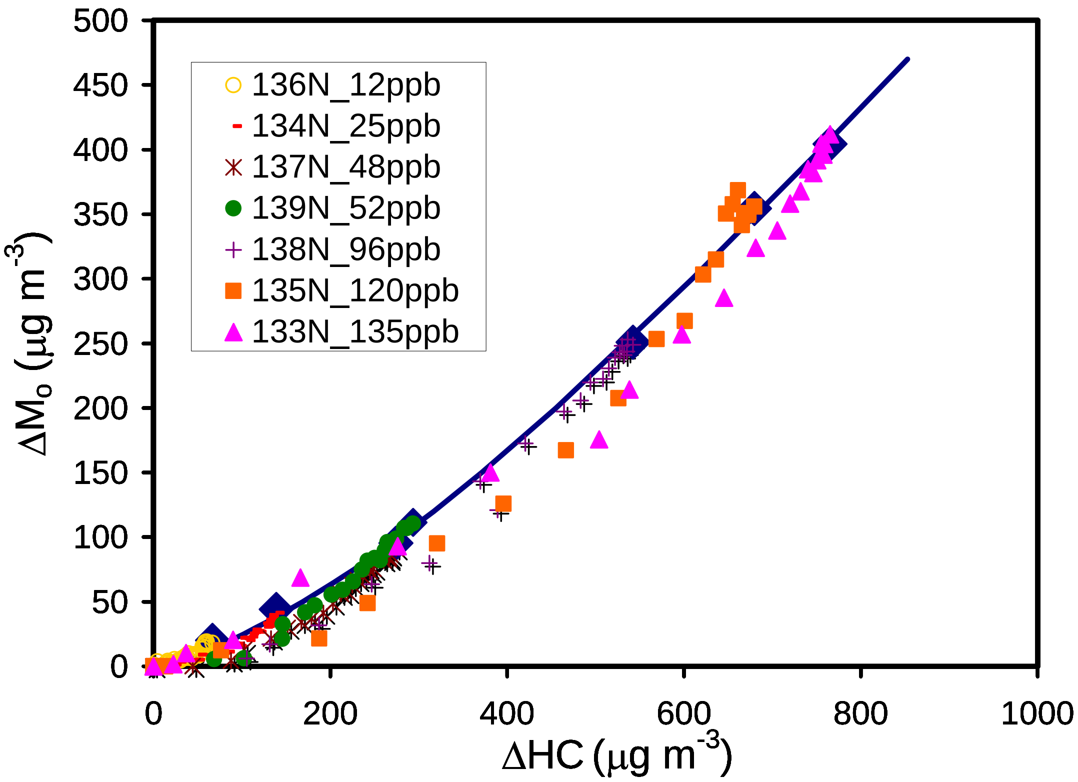
- Terpinolene has multiple double bonds, so its first-generation products formed are still unsaturated, and they will further react with the ozone in the chamber to produce additional condensable products

- Further oxidation of first-generation products contributes significantly to SOA and this oxidation step may also be rate-limiting



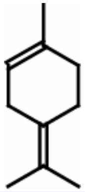
Time dependent growth vs. Final SOA growth
α-pinene ozonolysis

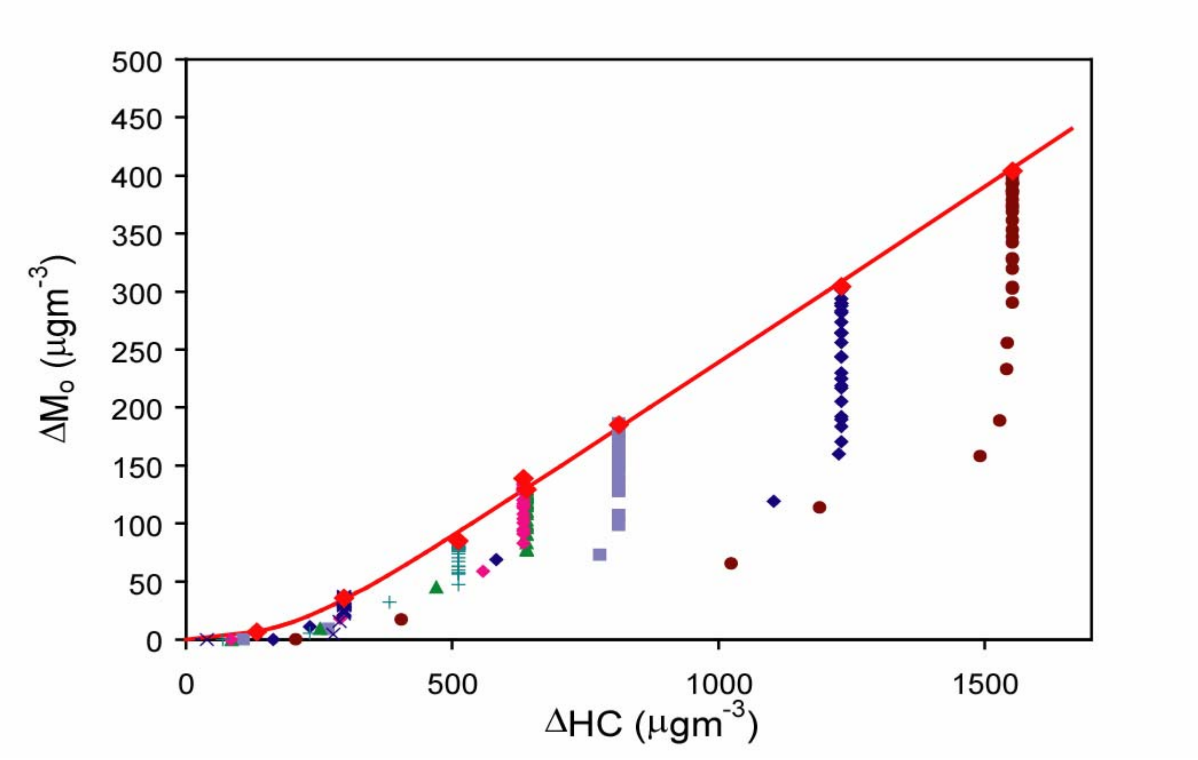




- Time-dependent data overlap remarkably well with the final SOA growth curve
  - – Odum equation (as well as the growth curve equation) is valid for the final growth as well as the time-dependent data

Time dependent growth vs. Final SOA growth terpinolene ozonolysis

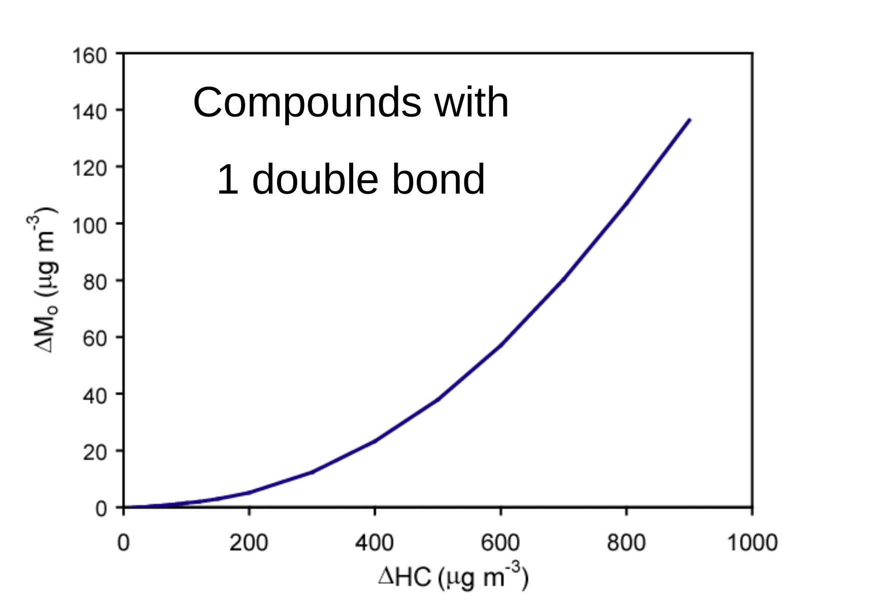




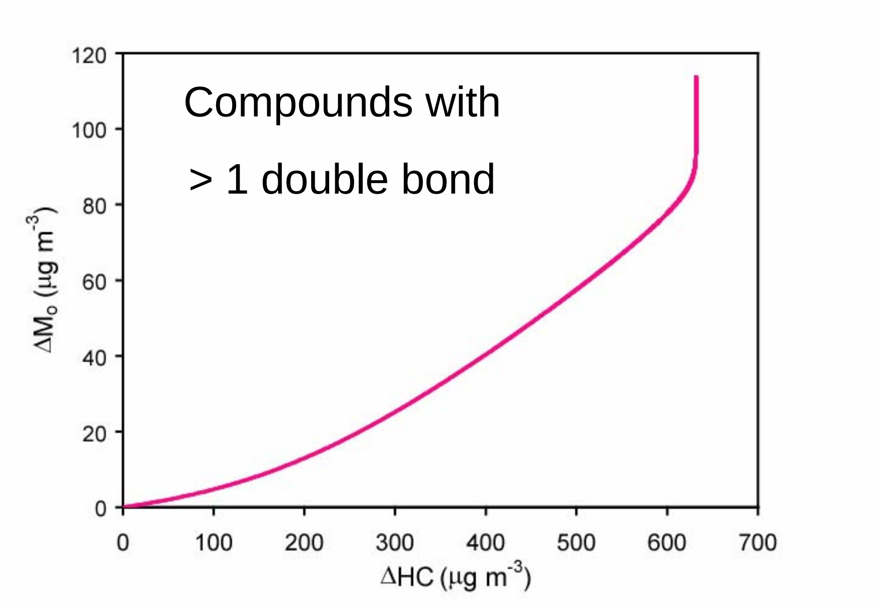
- Time-dependent growth curves and final growth curve do not overlap; time-dependent growth curves show clearly the contribution of the secondary reactions

- Cannot fit the time-dependent growth curves for terpinolene ozonolysis with Odum equation, confirming that this model is only valid when the data represent final SOA growth

Conclusions


Compounds with

1 double bond


Compounds with

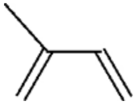
> 1 double bond

- Growth stops when all hydrocarbon is consumed
  - First step is rate-limiting
  - SOA formed from nonvolatile first-generation products

- Growth continues after all hydrocarbon is consumed
- Aerosol formed from further oxidation of first-generation products and this second oxidation step may also be rate-limiting

Effect of NO_x level on SOA Formation from Photooxidation of Biogenic Hydrocarbons

Isoprene



- Global emissions of ~500 Tg/year [*Henze et al.*, 2007]
- First-generation oxidation products: all are volatile, not expected to partition into the aerosol phase
- *Pandis et al.* [1991], *Edney et al.* [2005] observed no SOA formation from irradiation of isoprene/NO_x mixtures
- Possible contributions of isoprene to organic aerosol by heterogeneous chemistry [*Limbeck et al.,* 2003], [*Claeys et al.,* 2004], [*Edney et al.,* 2005]

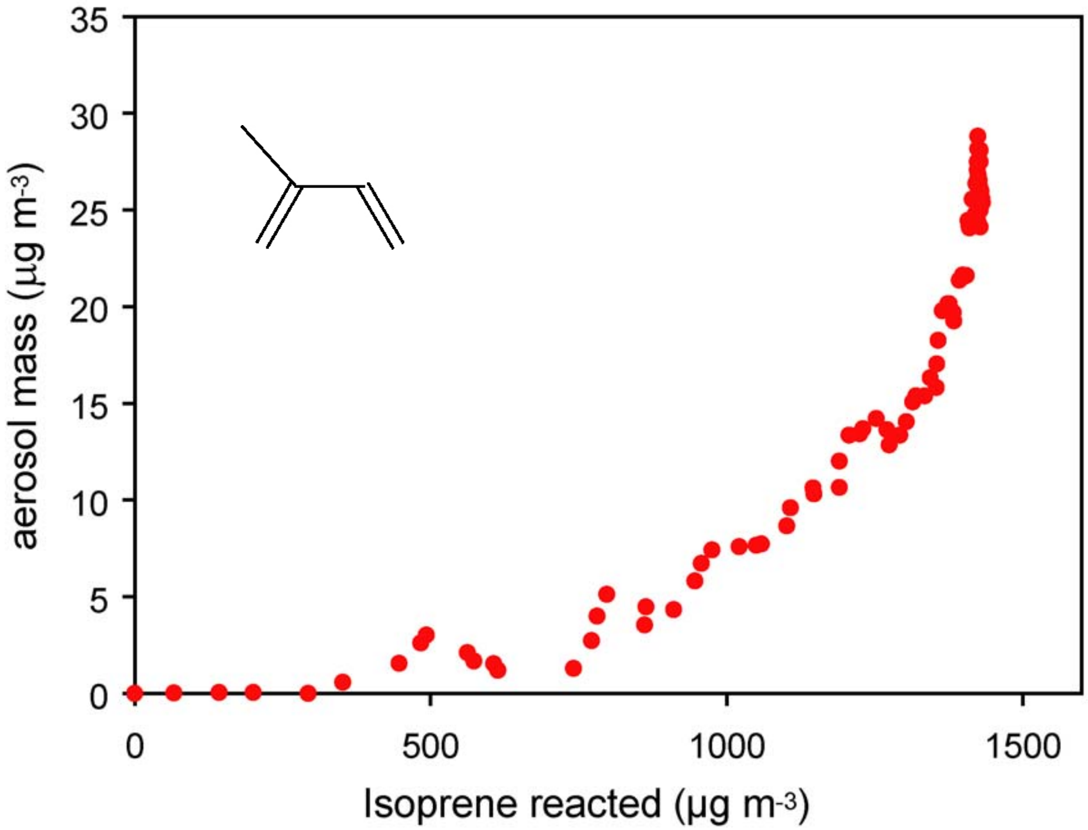
Experimental conditions

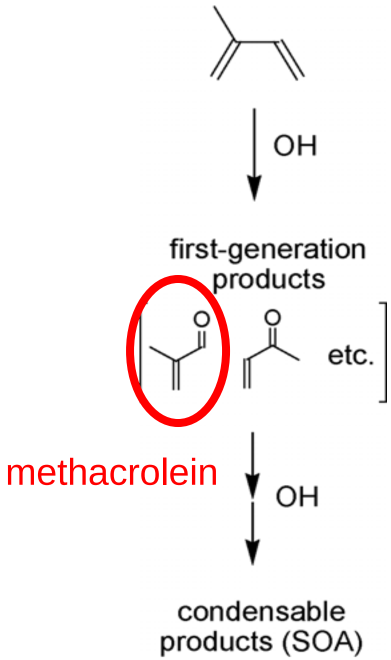
- Ammonium sulfate seed; T~25^{o}C, RH<10%

- Low-NO_x experiments
  - Radical source: $H_2O_2 + h\nu \rightarrow OH + OH$
  - Peroxy radicals react with HO_2

- High-NO_x experiments
  - Radical source: $HONO + h\nu \rightarrow OH + NO$
  - NO_x is produced as side product
  - Peroxy radicals react with NO

Isoprene and SOA formation




OH

first-generation products

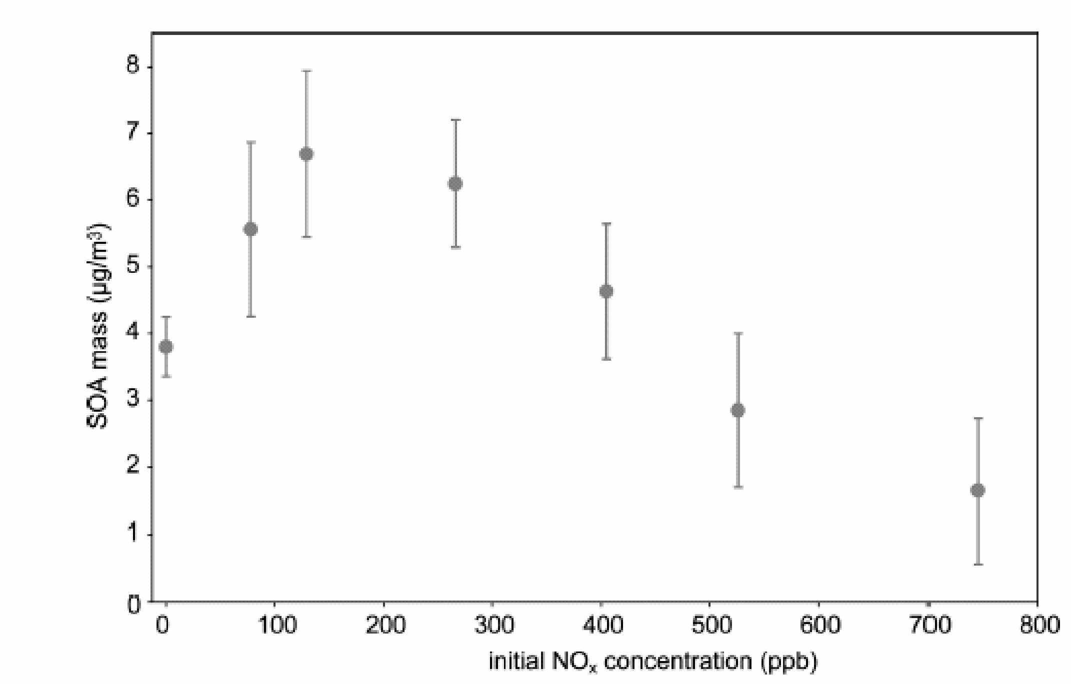
methacrolein

OH

condensable products (SOA)

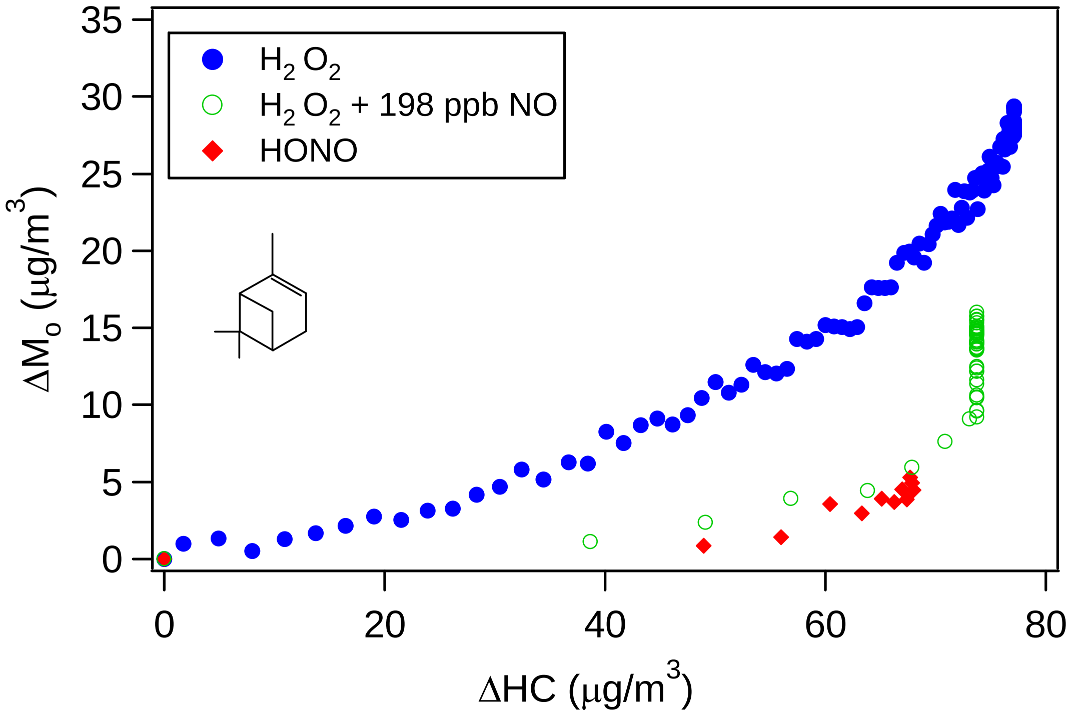
Isoprene: NO_x dependence

40-45 ppb isoprene



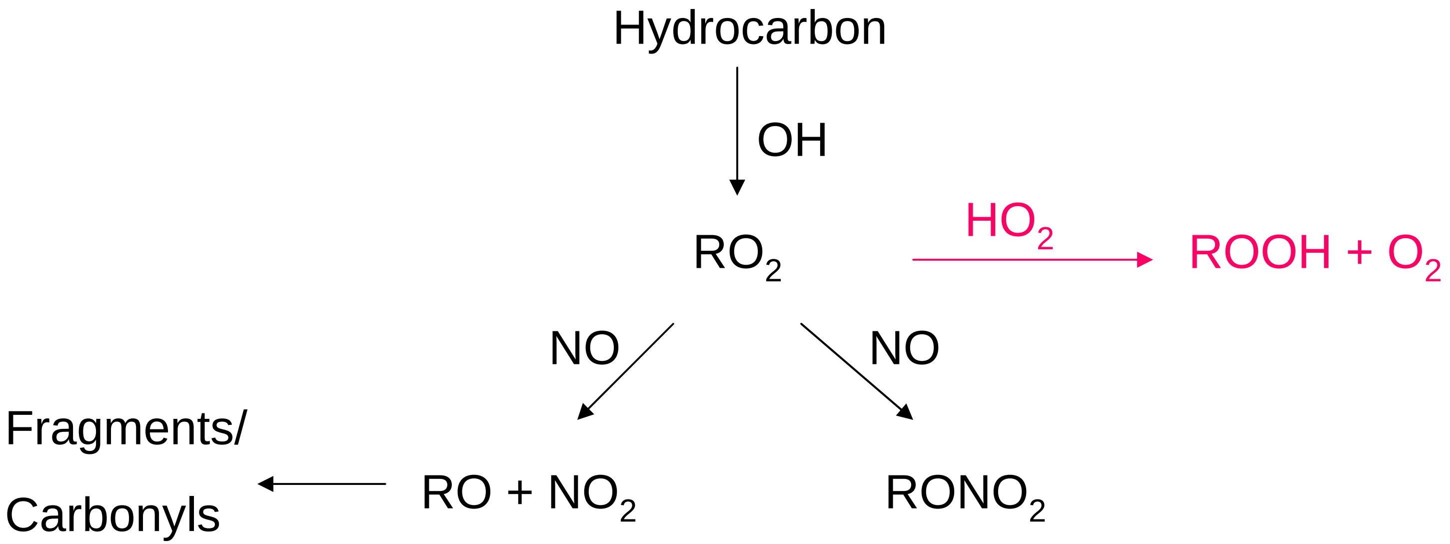
- Decrease in SOA yield at high NO_x [*Pandis et al.* 1991; *Zhang et al.*, 1992; *Hurley et al.*, 2001; *Johnson et al.*, 2004; *Song et al.*, 2005; *Presto et al.*, 2005]

Growth curve: α-pinene photooxidation



- Same NO_x dependence as isoprene: higher NO_x, lower SOA growth
- SOA formed from the condensation of first-generation products and the first oxidation step is rate-limiting
- H_2O_2+NO: Multiple SOA formation steps; α-pinene only has one double bond, further SOA growth by
    - Particle-phase reaction
    - Further gas-phase reaction of reactive oxidation products (aldehydes, furans etc)

Peroxy radical chemistry


Hydrocarbon

OH

RO_2

HO_2

$ROOH + O_2$

NO

NO

Fragments/

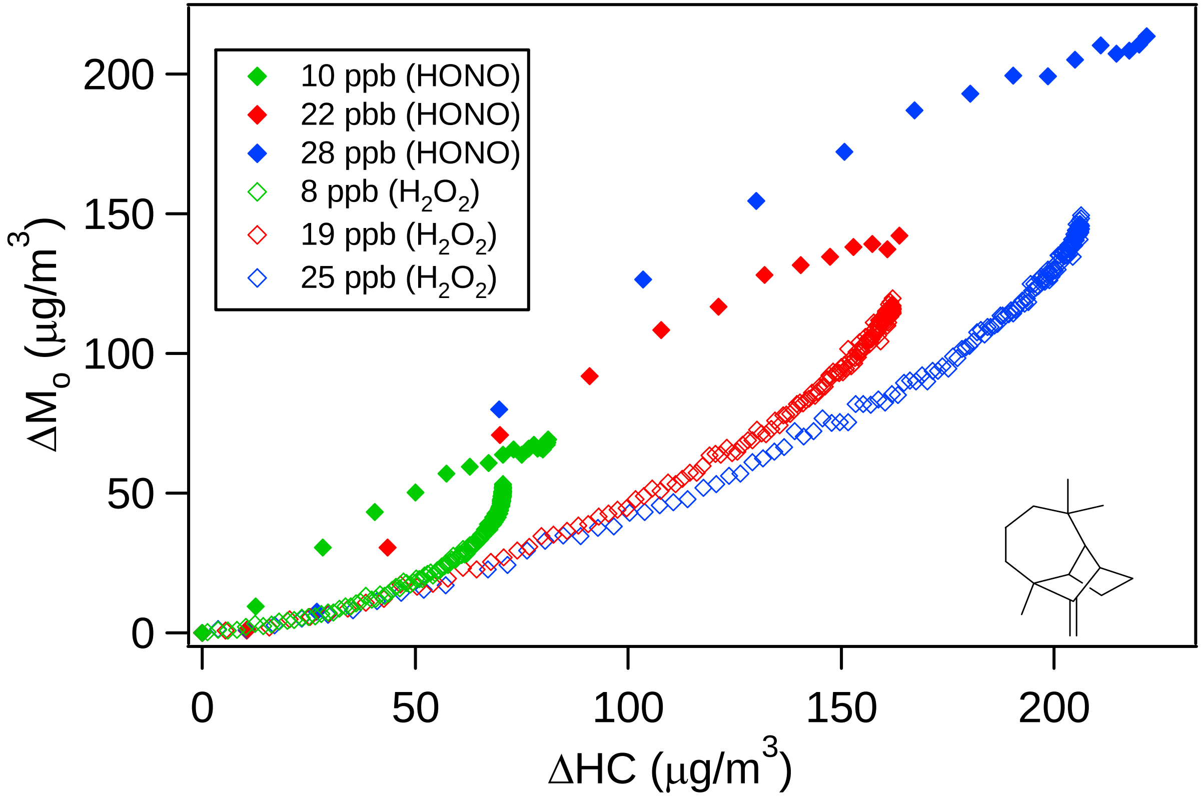
Carbonyls

$RO + NO_2$

$RONO_2$

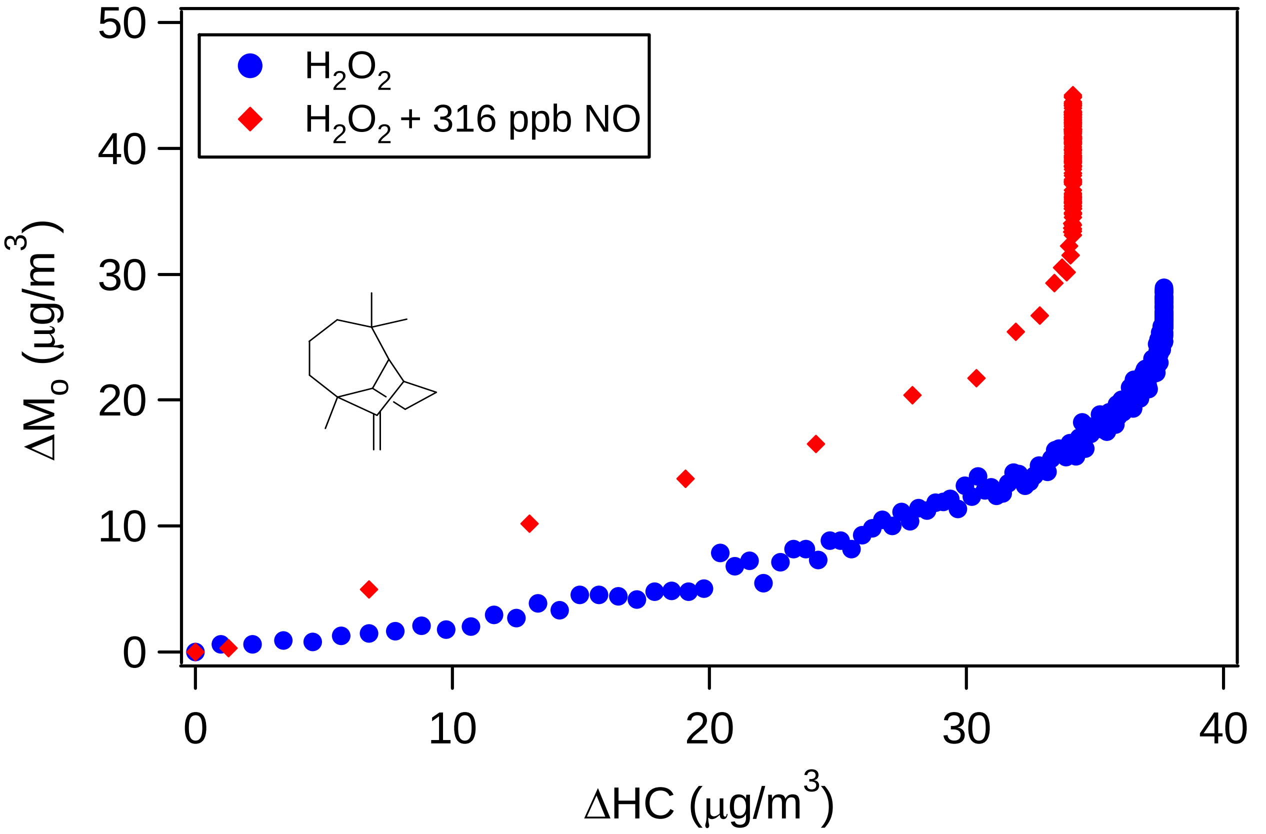
- Small alkoxy radical easily fragmented
- Organic nitrates relatively volatile [*Presto et al.*, 2005]
- Peroxides: important SOA components [*Bonn et al.*, 2004; *Docherty et al.*, 2005]

Growth curve: longifolene photooxidation



- Reversed NO_x dependence: higher NO_x, higher SOA growth
- High-NO_x: maximum yield = 100-120%
- Low-NO_x: constant yield = 75%

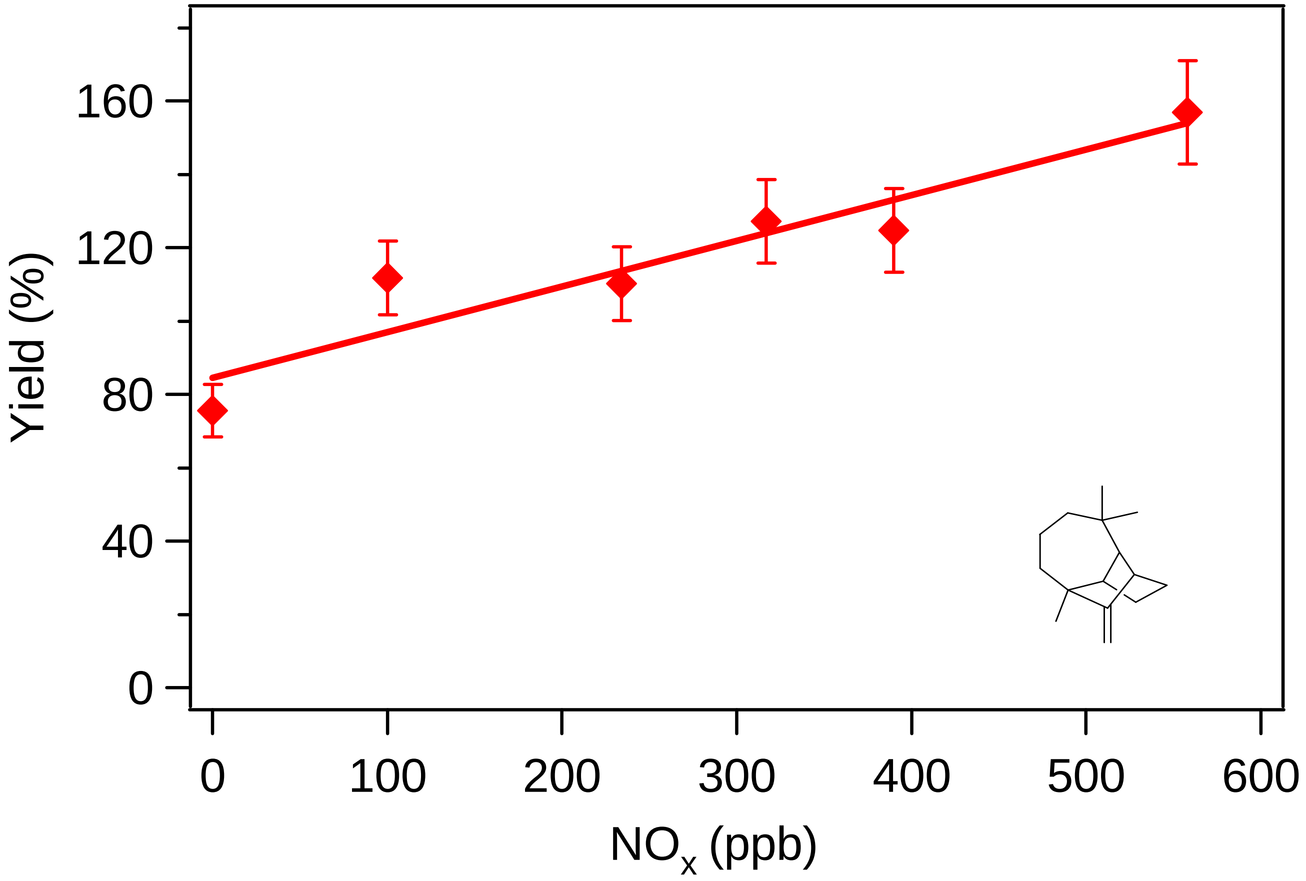
Longifolene: NO_x dependence



- Low NO_x: SOA Yield = 75%
- With ~300 ppb NO: SOA Yield = 127%;

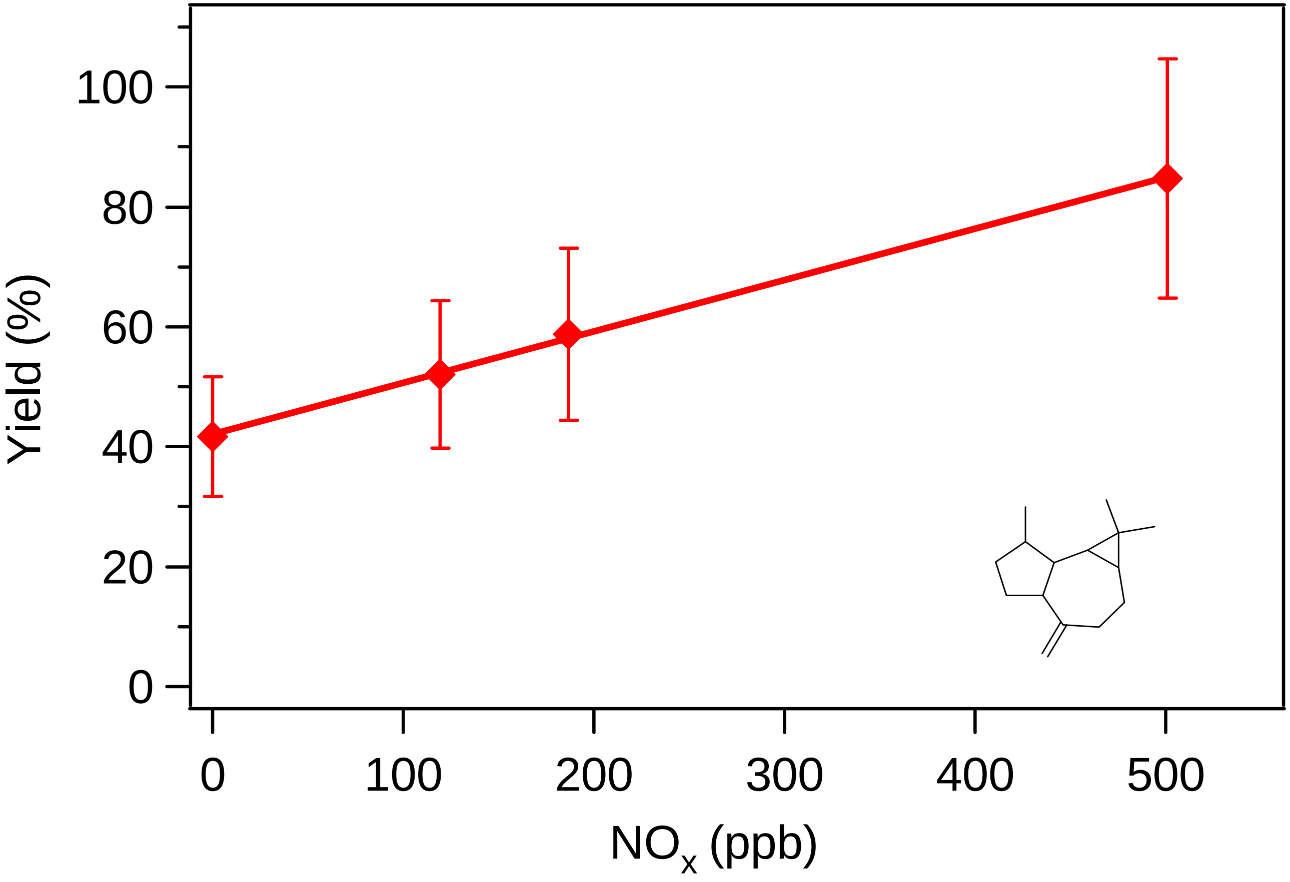
Longifolene: NO_x dependence

~5 ppb longifolene: increase in yield at high NO_x

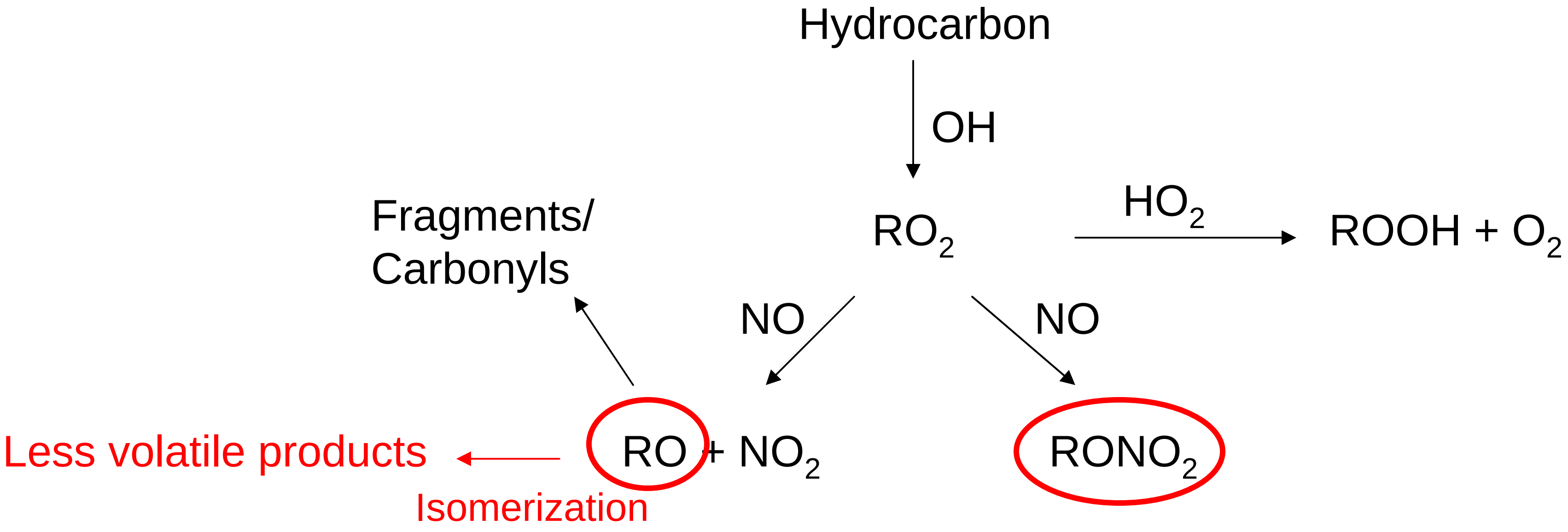


Aromadendrene: NO_x dependence

~5 ppb aromadendrene: increase in yield at high NO_x



Isomerization of alkoxy radicals



Hydrocarbon

OH

Fragments/
Carbonyls

RO_2

HO_2

$ROOH + O_2$

NO

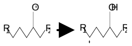
NO

Less volatile products

$RO + NO_2$

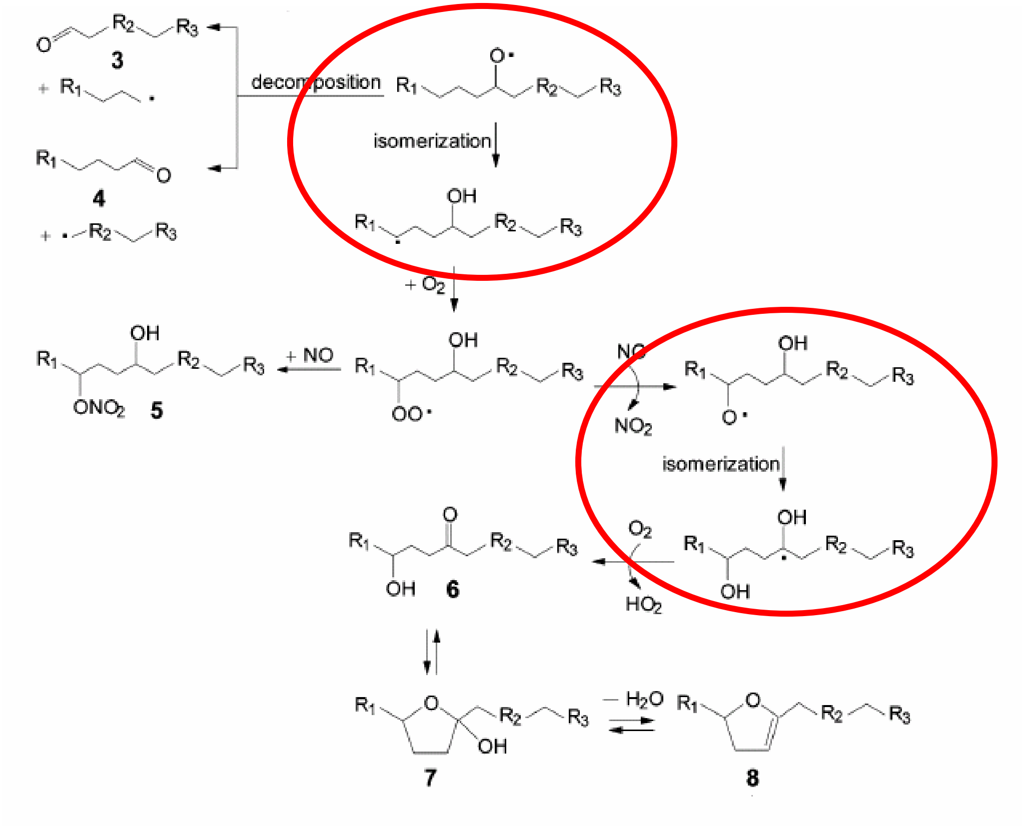
$RONO_2$

Isomerization



Isomerization of alkoxy radicals

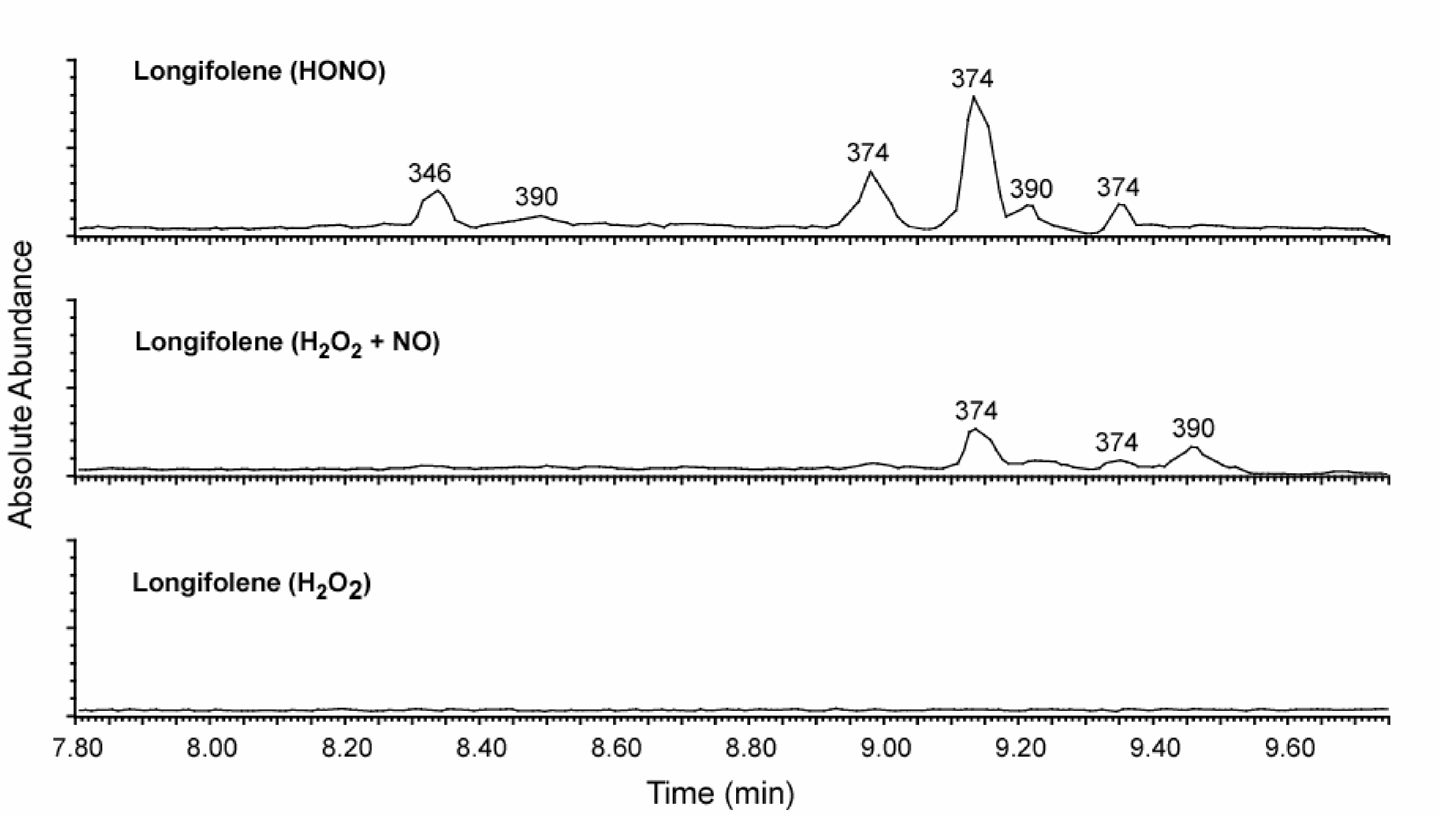
- SOA growth from large alkanes at ppm levels of NO [*Lim et al*., 2006]



Lim et al., 2006

Organic nitrates: UPLC/ESI-TOFMS

- Extracted ion chromatograms shows the presence of *acidic* nitrates in longifolene SOA



Conclusions

- Isoprene is an important SOA precursor (SOA: 14 Tg / year, *Henze et al.,* 2007)
  - Condensable products are second-generation

- Change in NO_x dependence going from isoprene to sesquiterpene
  - Isoprene (C_5H_8) and α-pinene ($C_{10}H_{16}$): SOA yield decreases at high NO_x
  - Longifolene and aromadendrene ($C_{15}H_{24}$): SOA yield increases at high NO_x

- Isomerization of alkoxy radicals and formation of nonvolatile organic nitrates could be an efficient channel of SOA formation (for large hydrocarbon precursors

SOA Formation from Photooxidation of Aromatic Hydrocarbons

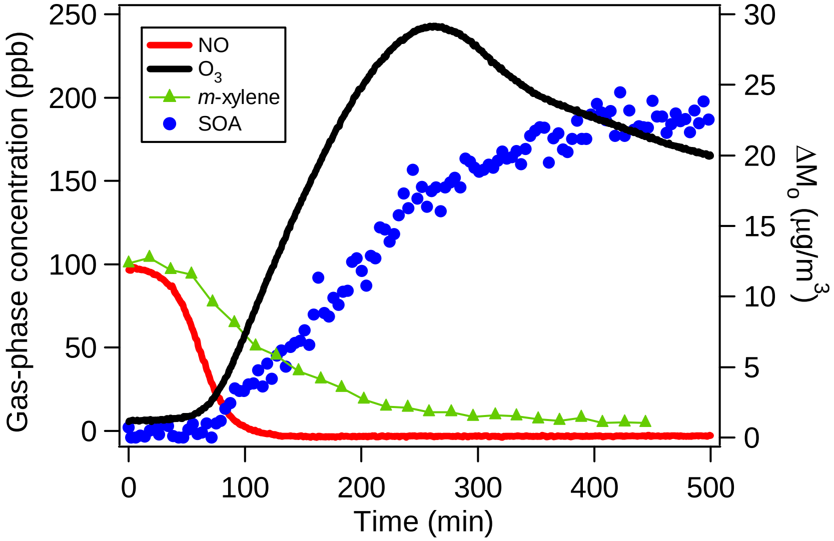
Background

- Field studies suggest higher SOA formation than models predict [*De Gouw et al.,* 2005; *Volkamer et al.,* 2006]
    - SOA formed from anthropogenic sources is higher than currently thought

- SOA formation from aromatic hydrocarbons
    - Mechanisms poorly understood
    - Poor carbon balance, typically < 50% [*Calvert et al.,* 2002]
    - SOA yields vary with different NO_x levels [*Hurley et al*., 2001; *Johnson et al*., 2005; *Martin-Reviejo et al*., 2005, *Song et al*., 2005]

Previous studies

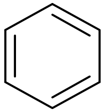
- Irradiation of aromatics/NO_x mixture [*Hurley et al*., 2001; *Johnson et al*., 2005; *Martin-Reviejo et al*., 2005, *Song et al*., 2005]
  - Changing oxidation conditions over the course of the experiments
  - Aerosol growth does not begin until NO approaches zero



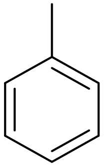
- Problems
  - Urban areas are high-NO_x, so this would suggest no aerosol formed from anthropogenic hydrocarbons
  - Experiments with higher levels of NO, and CH_3ONO, aerosols observed before NO approaches zero [*Stroud et al*., 2004]

Goals of experiments

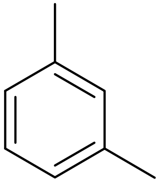
- Study systematically the effect of NO_x on SOA formation from selected aromatic hydrocarbons



Benzene



Toluene



m-xylene

- Obtain SOA yields at high- and low-NO_x conditions (the limiting cases), parameterize the NO_x dependence for modeling purposes

- Investigate the effect of particle phase acidity on aerosol growth

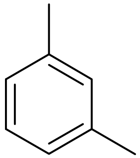
Experimental conditions

- Ammonium sulfate seed; T~25°C, RH<10%

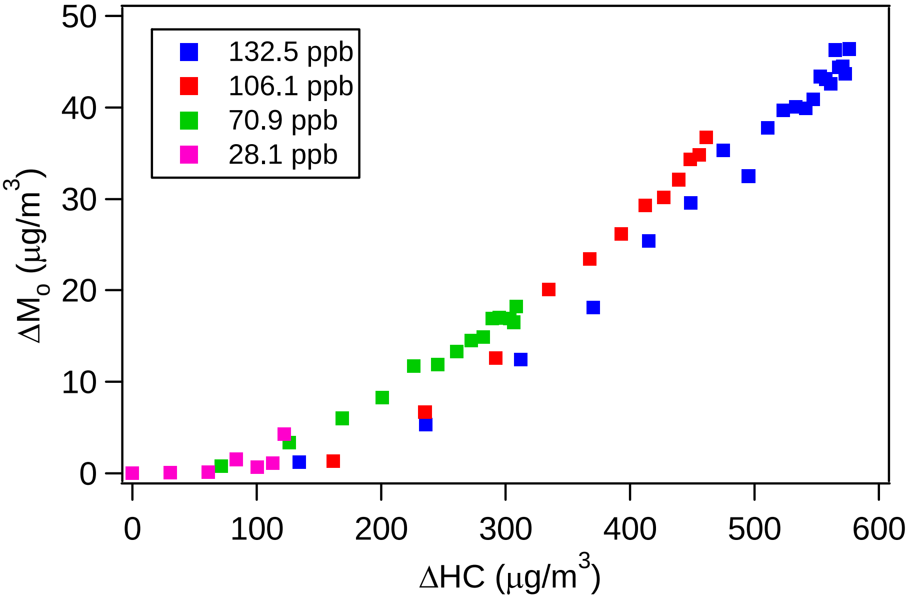
- Low-NO_x experiments
  - Radical source: $H_2O_2 + h\nu \rightarrow OH + OH$
  - Peroxy radicals react with HO_2

- High-NO_x experiments
  - Radical source: $HONO + h\nu \rightarrow OH + NO$
  - NO_x is produced as side product
  - Peroxy radicals react with NO

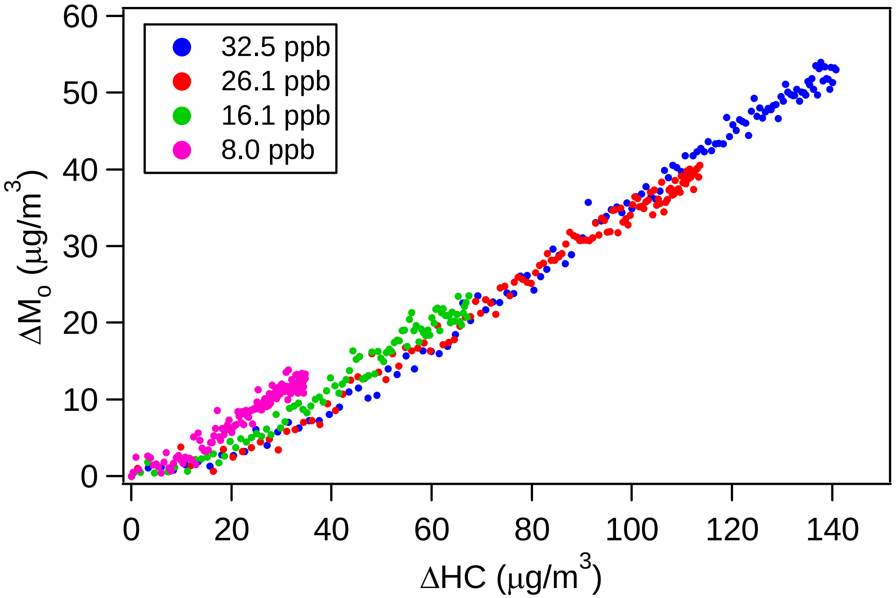
Growth curves: *m*-xylene



High-NO_x



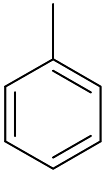
Low-NO_x



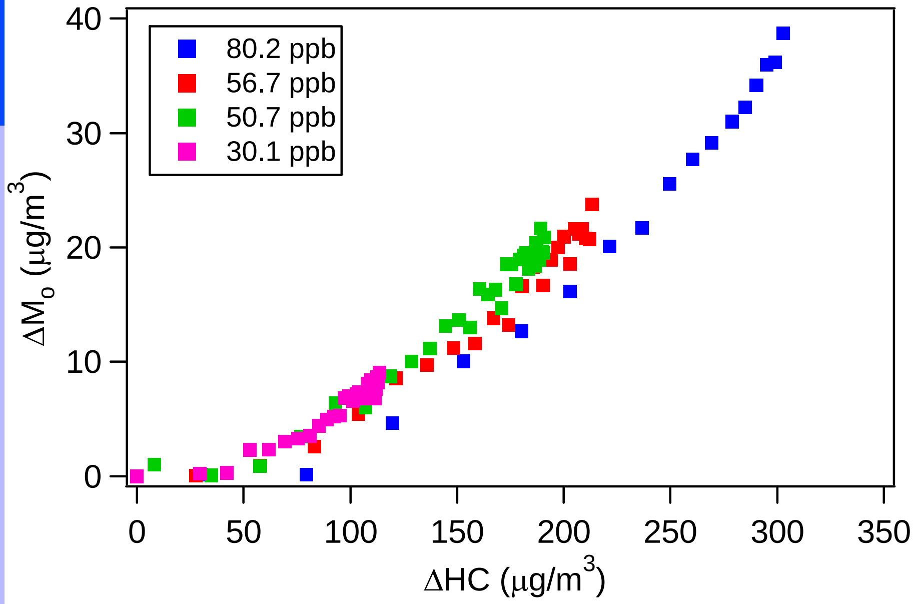
- High-NO_x: Growth curves do not overlap, multiple rate-limiting steps in SOA formation (first step is the slowest)
- Further-generation oxidation products

- SOA yields much higher than high-NO_x experiments
- Constant SOA yield implies essentially nonvolatile oxidation products (36% yield)

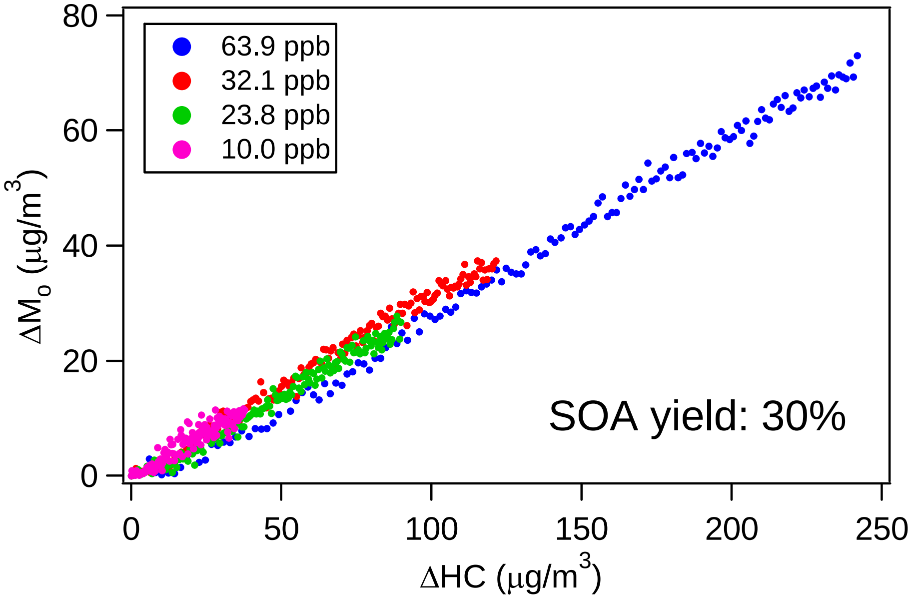
Growth curves: toluene



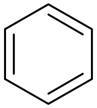
High-NO_x

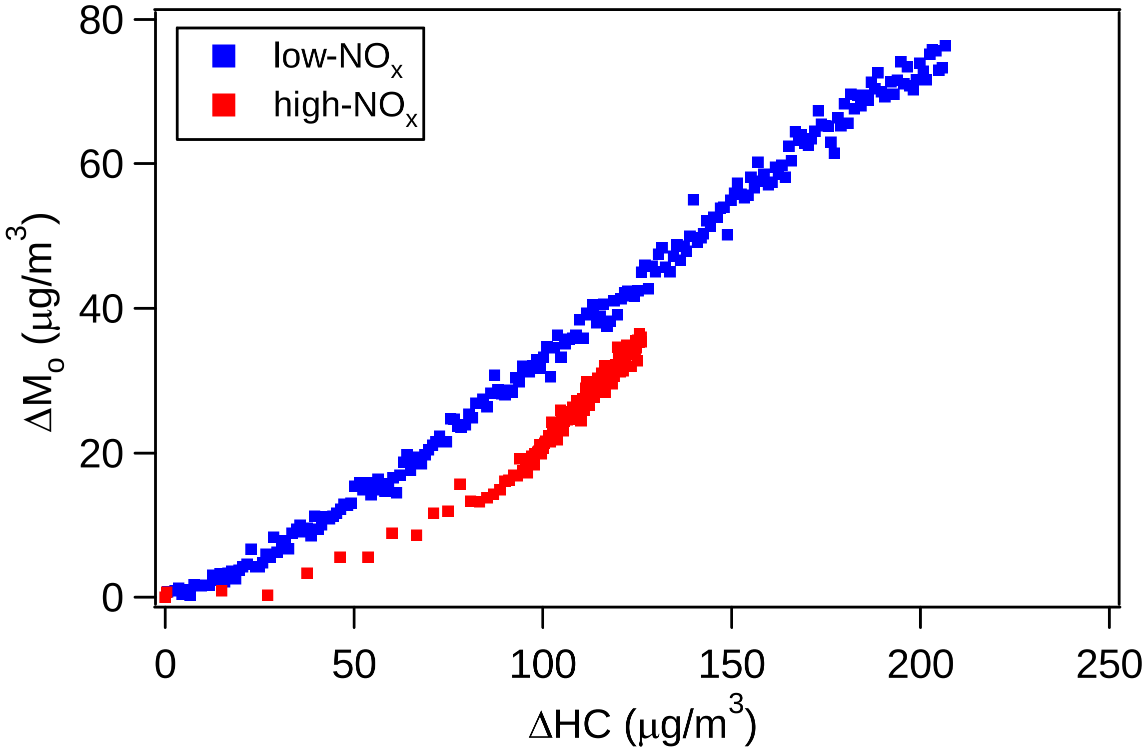


Low-NO_x



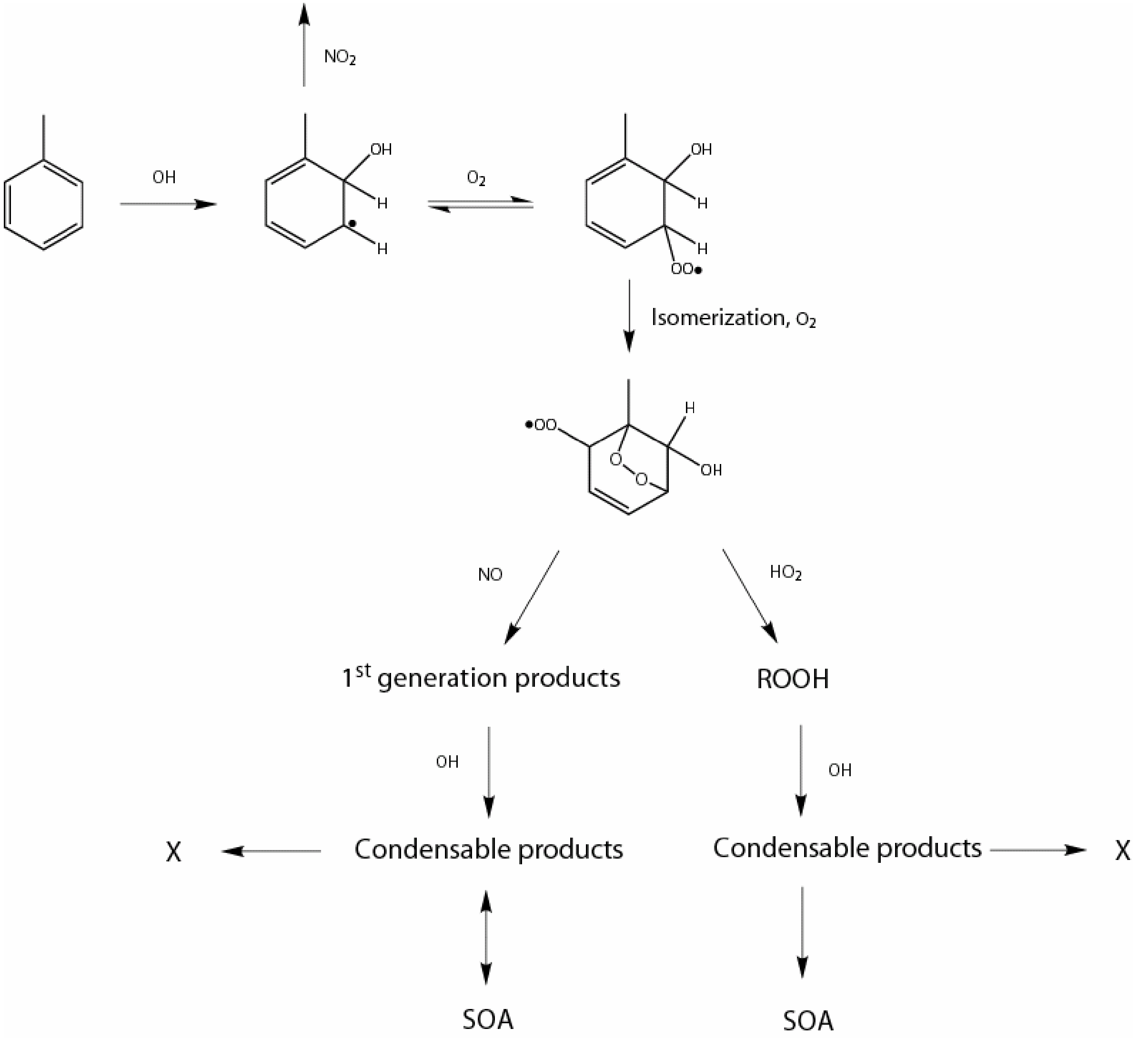
Growth curves: benzene





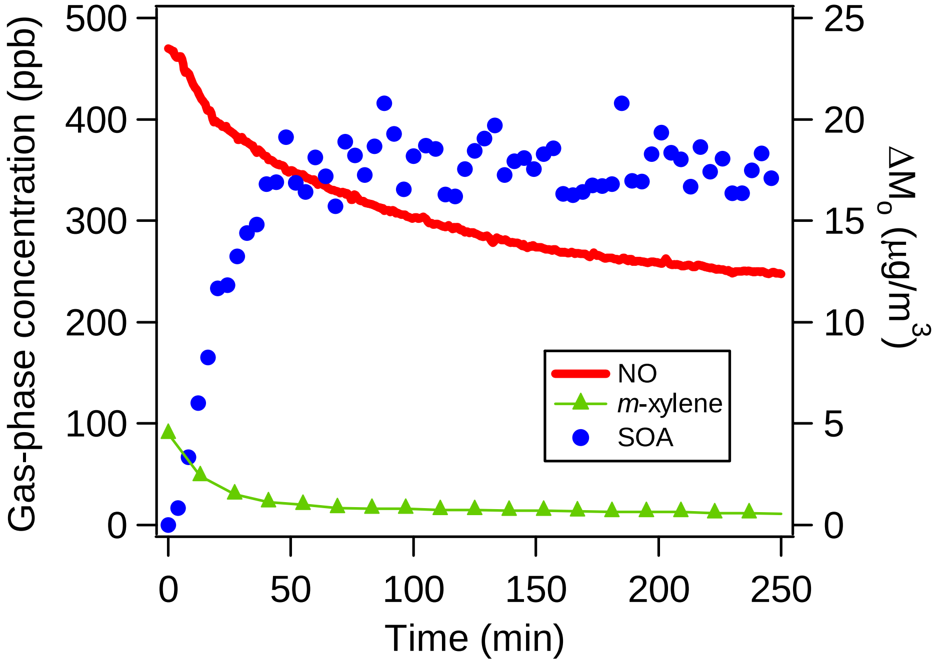
- ~400 ppb benzene (slow reaction rate, <20% reacted)
- Same NO_x dependence as *m*-xylene and toluene: high NO_x, lower yields
- Low NO_x: constant yield of 37%

Peroxy radical chemistry

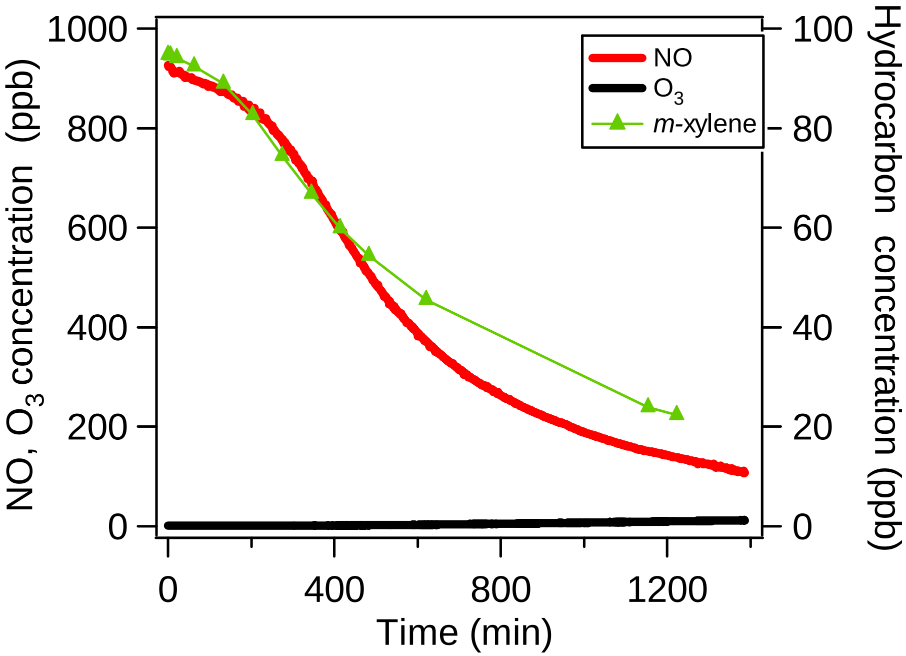


Effect of oxidation rate

HONO experiment

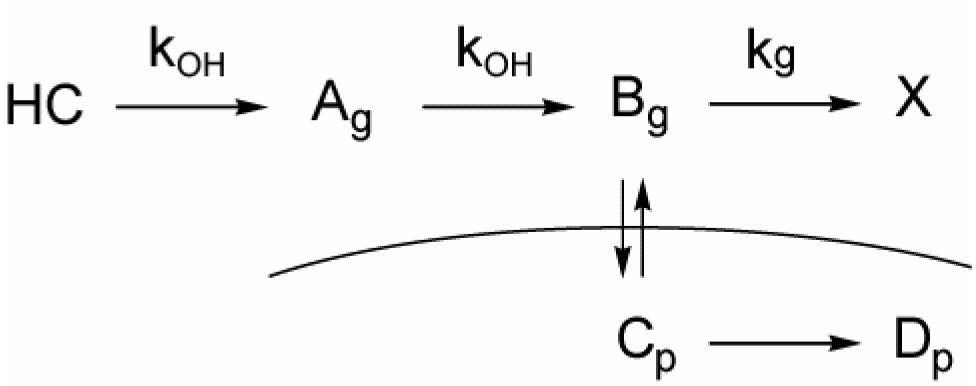


Classical experiment



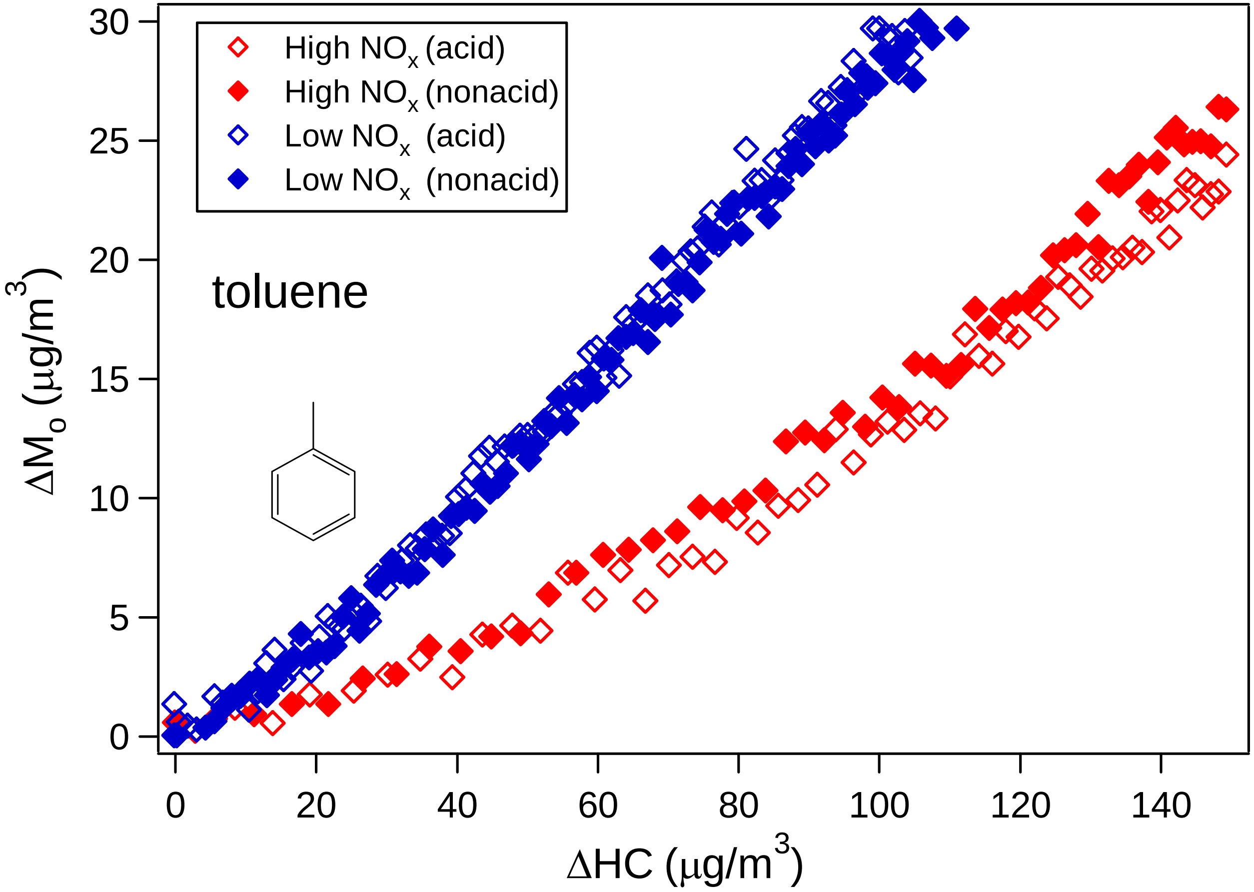
- Loss of semivolatiles ⟶ rate effect

Loss of semivolatiles



- Loss of semivolatiles (by photolysis, reactions in the gas phase to form volatile products, or deposition to chamber walls)
  - Lowers the concentration of the gas-phase semivolatile, thereby reducing the amount that partitions into the aerosol phase

Seed acidity: acid seed vs. non-acid seed



- No acid effect observed
- Same observations in *m*-xylene oxidation

Conclusions: Aromatic SOA

- SOA yields are highly dependent on NO_x levels (peroxy radical chemistry)
  - High NO_x: Usual Odum yield curve behavior (Yield ~ 5 -10%)
  - Low NO_x: Constant yield (Yield ~30%)
- Condensable compounds are second-generation products (further gas-phase and/or particle-phase reactions)
- No effect of particle phase acidity observed

What do all these studies tell us?

- Growth curve (ΔM_0 vs. ΔHC) as a powerful approach to infer the general mechanism of SOA growth
- Profound effect of NO_x level on SOA formation (isoprene, monoterpenes, aromatics, sesquiterpenes)
- Discrepancy between modeled vs. measured SOA:
  - Of compounds studied in the laboratory, biogenics are the largest contributor to ambient SOA, and isoprene is the most important single precursor
  - SOA formation from aromatics significantly higher than previously measured but not sufficiently large to rival that of biogenics on a continental scale
  - According to recent CMU study (Robinson et al., 2007), SVOCs from primary organic aerosol emissions may themselves constitute a major class of SOA precursors