Coláiste na hOllscoile Corcaigh, Éire
University College Cork, Ireland

Atmospheric Degradation of Naphthalene: Mechanism and SOA Formation

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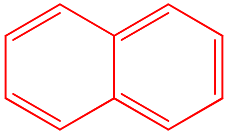
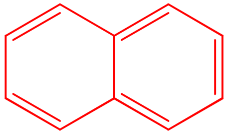


Naphthalene



- Simplest polycyclic aromatic hydrocarbon (PAH)
- Trace constituent in automobile fuels; by-product of combustion
- Most abundant PAH in the atmosphere: 0.1-1 µg m^{-3} (0.02 – 0.2 ppbV)
- Relatively high vapour pressure: 99% in the gas-phase at 298 K
- Tropospheric lifetime: 12 hr for OH: 50 hr for NO_3
- Degradation products include oxygenated PAH, quinones and nitroaromatics - all of which are toxic to humans

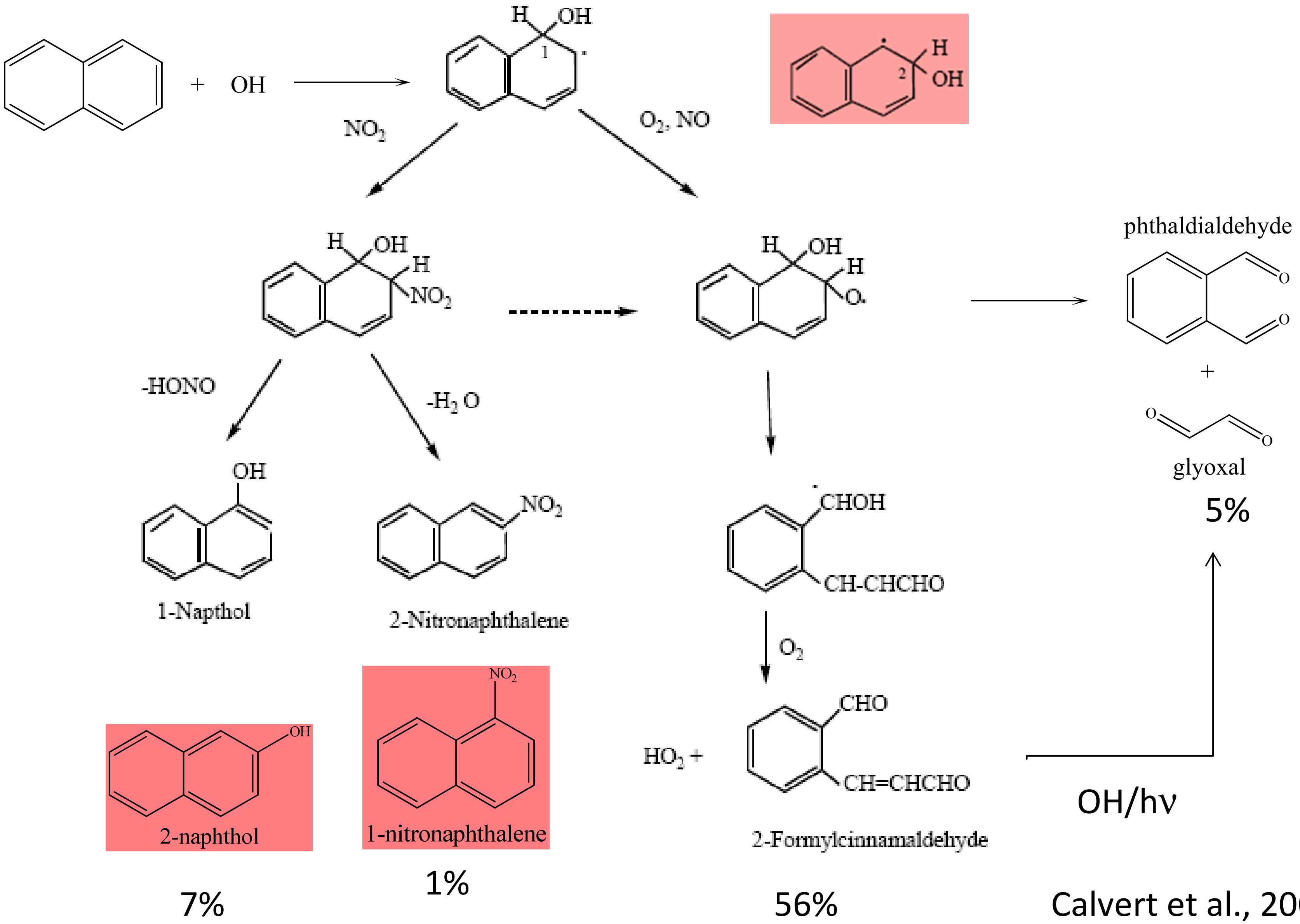
Oxidation Products

Product	Yield	Reference
2-Formylcinnamaldehyde	0.35; 0.10; 0.05	Sasaki et al. (1997)[a]
	0.16	Bunce et al. (1997)
2-Formylbenzaldehyde	*ca.* 0.027[b]	Sasaki et al. (1997)
1-Naphthol	0.071 ± 0.043	Atkinson et al. (1987a)
	0.029 ± 0.015	Sasaki et al. (1997)
2-Naphthol	0.042 ± 0.025	Atkinson et al. (1987a)
	0.038 ± 0.011	Sasaki et al. (1997)
1-Nitronaphthalene	0.0032	Atkinson et al. (1987a)
	0.012 ± 0.009	Sasaki et al. (1997)
	0.07	Bunce et al. (1997)
2-Nitronaphthalene	0.0027	Atkinson et al. (1987a)
	0.013 ± 0.011	Sasaki et al. (1997)
1-Hydroxy-2-nitronaphthalene	0.011 ± 0.011	Sasaki et al. (1997)
2-Hydroxy-1-nitronaphthalene	observed	Sasaki et al. (1997)
1,4-Naphthoquinone	0.010 ± 0.003	Sasaki et al. (1997)
	0.06	Bunce et al. (1997)
Phthalic anhydride	*ca.* 0.03[b]	Sasaki et al. (1997)
Compounds with molecular weight 174 and 176	*ca.* 0.018	Bunce et al. (1997)

[a]Data of Sasaki et al. (1997) were corrected for secondary reactions of observed products.
[b]Possibly second-generation products formed from 2-formylcinnamaldehyde.

Calvert et al., 2002

Oxidation Mechanism



Calvert et al., 2002

Secondary Chemistry

- Photolysis of 1- and 2-nitronaphthalene, 1,4-naphthoquinone and reaction with OH, NO_3, O_3 (Atkinson et al., Atmos Environ, 1989)

- Photolysis of phthaldialdehyde (black lamps) and reaction with OH (Wang et al., Environ. Sci. Technol., 2006)

- No studies on 2-formylcinnamaldehyde, but photolysis is expected to be the dominant loss process

SOA Formation

- Composition of naphthalene SOA by FTIR spectroscopy (Dekermenjian et al., Aerosol Sci. Technol., 1999)

- Gas-particle partitioning of photooxidation products (Mihele and Lane, Polycyclic Aromatic Hydrocarbons, 2002)

- No studies on SOA yield from photooxidation of naphthalene

Objectives of our study

- Improve knowledge of secondary chemistry:
  Photolysis of 2-formylcinnamaldehyde, 1-nitronaphthalene, phthaldialdehyde using natural sunlight

- Use available data to construct naphthalene degradation mechanism for MCM

- Determine SOA yields from photooxidation of naphthalene:
  Effect of reaction parameters on yield

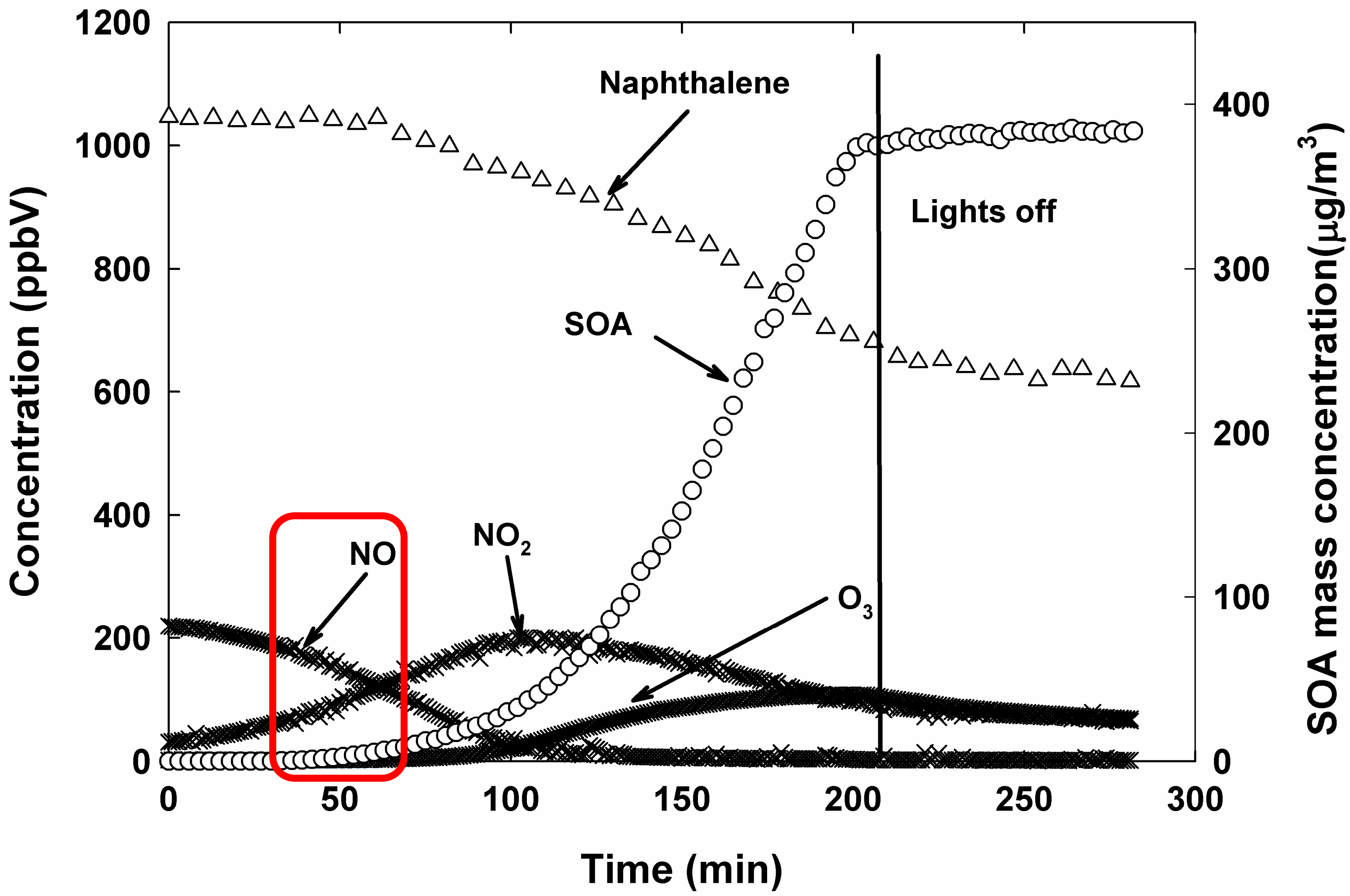
- Investigate chemical composition of SOA using off-line and on-line analytical methods

Atmospheric Simulation Chamber at UCC

- on-line GC
- NOx and O_3 analysers
- denuder – filter, GC-MS
- Particle Sizer and counter

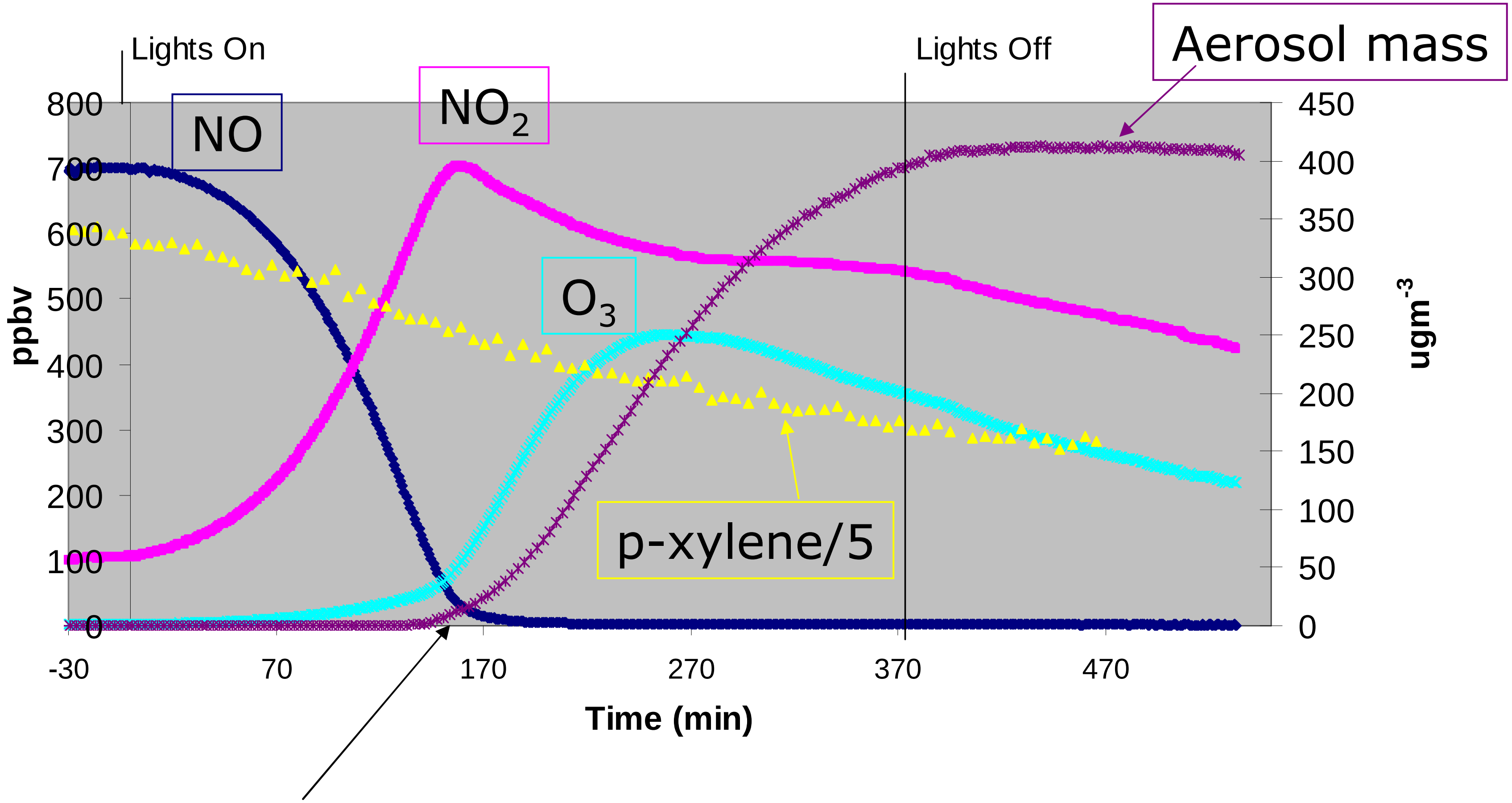
- FEP foil (6500 litres)
- Dry purified air
- Atmospheric P and T
- Humidity control

Time-concentration profile

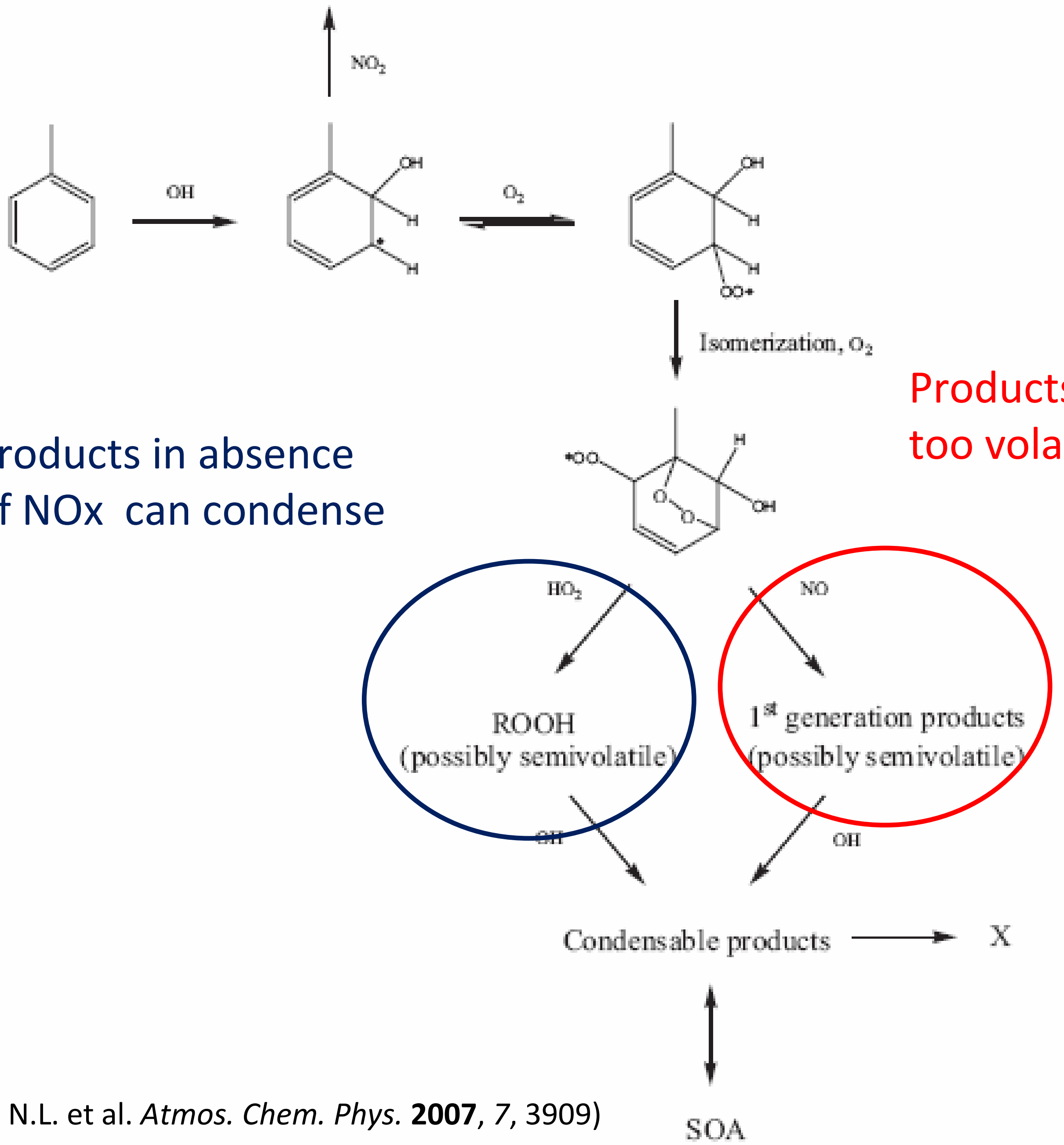


- SOA formation even when NOx = 150 ppbV

p-xylene photo-oxidation



- Aerosol formation only when NOx approaches 0



Products in presence of NOx are too volatile to condense

Products in absence of NOx can condense

Naphthalene products have a higher propensity to form SOA

(Ng, N.L. et al. *Atmos. Chem. Phys.* **2007**, *7*, 3909)

Expt.	RH (%)	HC_0 (ppbV)	NO_x (ppbV)	HC_0/NO_x (ppbV/ ppbV)	ΔHC (μg/m³)	M_0 (μg/m³)	SOA yield (%)
RH0_1	0.2	1070	520	1.95	2198	285.5	13.0
RH0_2	0.6	1040	240	4.35	1807	330.1	18.3
RH0_3	0.8	1084	250	4.34	2118	379.6	17.9
RH0_4	0.7	1081	510	2.13	2135	237.3	11.1
RH0_5	0.8	830	690	1.20	1310	136	10.3
RH0_6	0.8	602	145	4.15	1470	248.5	16.9
RH0_7	1.9	508	500	1.02	954	63.4	6.64
RH0_8	1.3	611	202	3.02	1444	230.8	16.0

- SOA yields up to 3 times higher than other aromatics toluene, p-xylene, 1,3,5-trimethylbenzene

Expt.	RH (%)	HC_0 (ppbV)	NO_x (ppbV)	HC_0/NO_x (ppbV/ ppbV)	ΔHC (μg/m³)	M_0 (μg/m³)	SOA yield (%)
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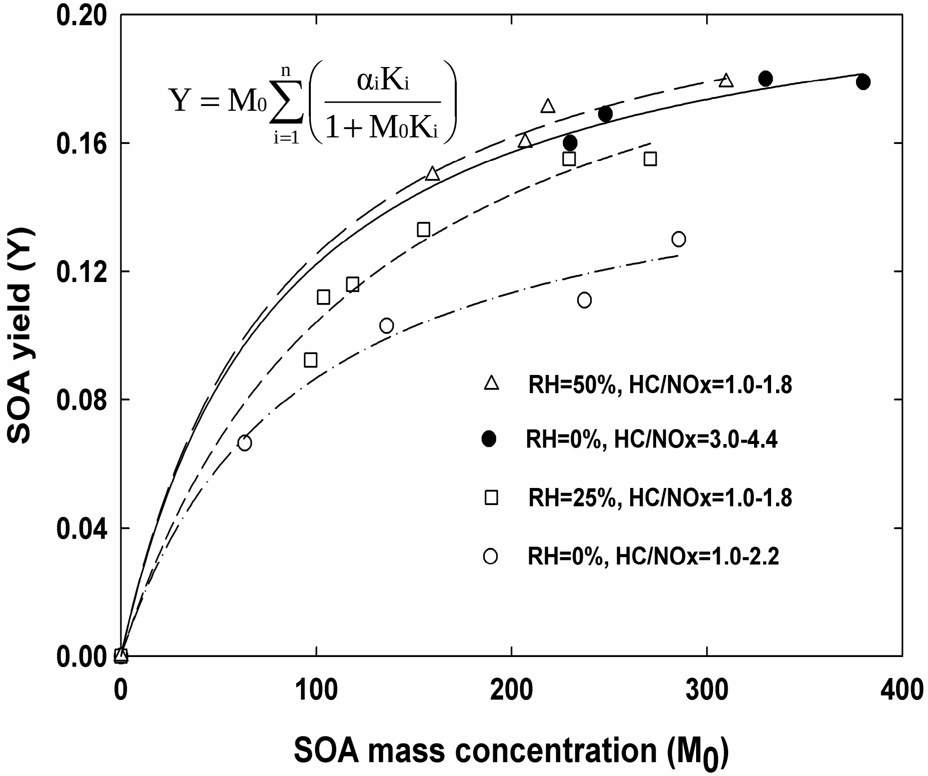
- Higher SOA yields when HC_0 is higher (expts 4 and 7)
- Higher SOA yields when NOx is lower (expts 3 and 4)

Expt.	RH (%)	HC_0 (ppbV)	NO_x (ppbV)	HC_0/NO_x	ΔHC [c] (µg/m³)	M_0 (µg/m³)	SOA yield (%)
RH0_7	1.9	508	500	1.02	954	63.4	6.64
RH25_3	25.1	532	520	1.02	1055	97.2	9.23
RH50_2	49.2	514	496	1.04	1061	159.4	15.0

- SOA yield increases with relative humidity
- Enhanced partitioning / reactive uptake of oxidation products e.g. glyoxal, other dicarbonyls in presence of water?
- Further experimental work in progress

SOA yield curves and parameters



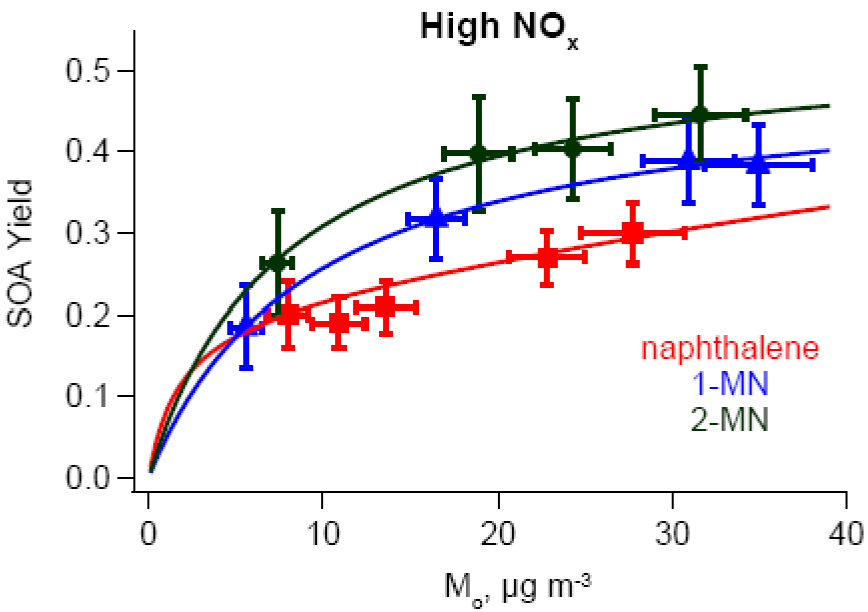
Group Exp.	α_1	K_1 (m^3 ug^{-1})
RH<2%, HC_0/NO_x=1.0-2.2	0.1645	0.0111
RH<2%, HC_0/NO_x=3.0-4.4	0.2246	0.0116
RH=25%, HC_0/NO_x=1.0-1.8	0.2324	0.0081
RH=50%, HC_0/NO_x=1.0-1.8	0.2595	0.0084

Atmos. Chem. Phys., 9, 3049–3060, 2009
www.atmos-chem-phys.net/9/3049/2009/

Atmospheric Chemistry and Physics

Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs)

A. W. H. Chan[1], K. E. Kautzman[1], P. S. Chhabra[1], J. D. Surratt[1], M. N. Chan[2], J. D. Crounse[1], A. Kürten[2,*], P. O. Wennberg[2,3], R. C. Flagan[1,2], and J. H. Seinfeld[1,2]

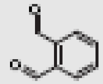
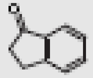
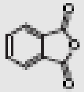
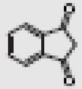
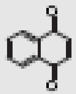
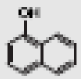
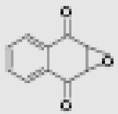


- SOA yields up to 3 times higher than monoaromatics
- PAHs may account for up to 54% of SOA from diesel exhaust and 80% from wood burning
- PAHs and other IVOCs (e.g. alkanes) are likely to be part of the “missing” SOA in models

SOA Composition by GCxGC-TOF-MS

J.Y. Lee, D.A. Lane / Atmospheric Environment 43 (2009) 4886–4893 4889

Table 1
Identified products observed by GC × GC-TOFMS from the gas-phase reaction of Naphthalene with the OH radical.

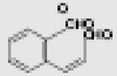
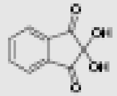
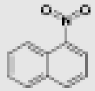
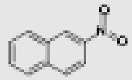
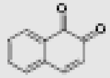
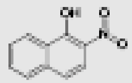
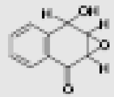
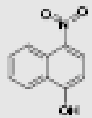
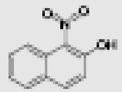
# in Fig. 1	Products	Structure	M.W.	1st R.T.[a]	2nd R.T[b]	Peak response		Identification method	Note
						Gas phase	Particle phase		
1	1,4-dihydro-1,4-epoxy-Naphthalene		144	855	0.92	m[c]	ND[d]	L(S[e]: 785, R[f]: 836)	New
2	Phthaldialdehyde		134	1000	0.85	l[b]	l	A	
3	Inden-1-one		132	1050	0.86	s[c]	s	L(S: 908, R: 908)	New
4	1,2-benzopyrone		146	1140	0.895	s	s	L(S: 671, R: 875)	New
5	Phthalic anhydride		148	1140	0.865	l	l	A	
6	Phthalide		134	1220	0.815	m	m	L(S: 936, R: 936)	Ref.[a,b]
7	1,3-indane-dione		146	1225	0.83	m	m	L(S: 871, R: 871)	New
8	1,4-naphthoquinone		158	1295	0.865	l	l	A	
9	$C_{10}H_8O_2$	–	160	1295	0.865	m	m	M[i]	See Fig. 2(c)
10	1-naphthalenol		144	1305	0.87	m	m	A	
11	2-naphthalenol		144	1410	0.9	m	m	A	
12	$C_{10}H_8O_2$	–	160	1415	0.86	m	m	M	See Fig. 2(c)
13	2,3-epoxy-naphthoquinone		174	1450	0.855	l	l	L(S: 850, R: 886)	

(continued on next page)

Lee and Lane
Atmos. Environ., 2009

SOA Composition by GCxGC-TOF-MS

Table 1 (continued)

# in Fig. 1	Products	Structure	M.W.	1st R.T.*	2nd R.T.*	Peak response		Identification method	Note
						Gas phase	Particle phase		
14	(E)-2-formylcinnamaldehyde		160	1485	0.89	l	l	M	Ref.[a,b]
15	2,2-dihydroxy-indene-1,3-dione		178	1510	0.805	m	m	L(S: 765, R: 948)	New
16	1-nitronaphthalene		173	1560	0.9	m	m	A	
17	(Z)-2-formylcinnamaldehyde		160	1570	0.87	l	l	M	Ref.[a,b]
18	2-nitronaphthalene		173	1605	0.92	m	m	A	
19	1,2-naphthoquinone		158	1645	0.82	m	m	A	
20	2-nitro-1-naphthol		189	1650	0.965	l	l	L(S: 881, R: 883)	
21	2,3-epoxy-1-hydroxy-naphthalen-4-one		176	1685	0.84	l	l	M	Ref.[a]
22	4-nitro-1-naphthol		189	2060	0.89	N.D	m	M	Tentative
23	1-nitro-2-naphthol		189	2195	0.865	s	m	L(S: 806, R: 814)	

*The information of the 1st and 2nd retention times and the values of the Library matches (Similarity and reverse) were determined from the gas phase (denuder) sample shown in Fig. 1(a). The difference of between 2nd retention times for the gas and particle phase samples was within 0.005 s.
[a] Medium.
[b] Large.
[c] Small.
[d] Not detected.
[e] Similarity.

Lee and Lane
Atmos. Environ., 2009

Aerosol Time-of-flight Mass Spectrometer (ATOFMS)

The TSI 3800 ATOFMS can measure the size and chemical composition of **individual** particles in the range 100-3000 nm

Allows the simultaneous determination of:

- Particle size
- Primary (e.g. metals and carbon) and secondary (nitrate and sulfate) particle composition
- Internal mixing state

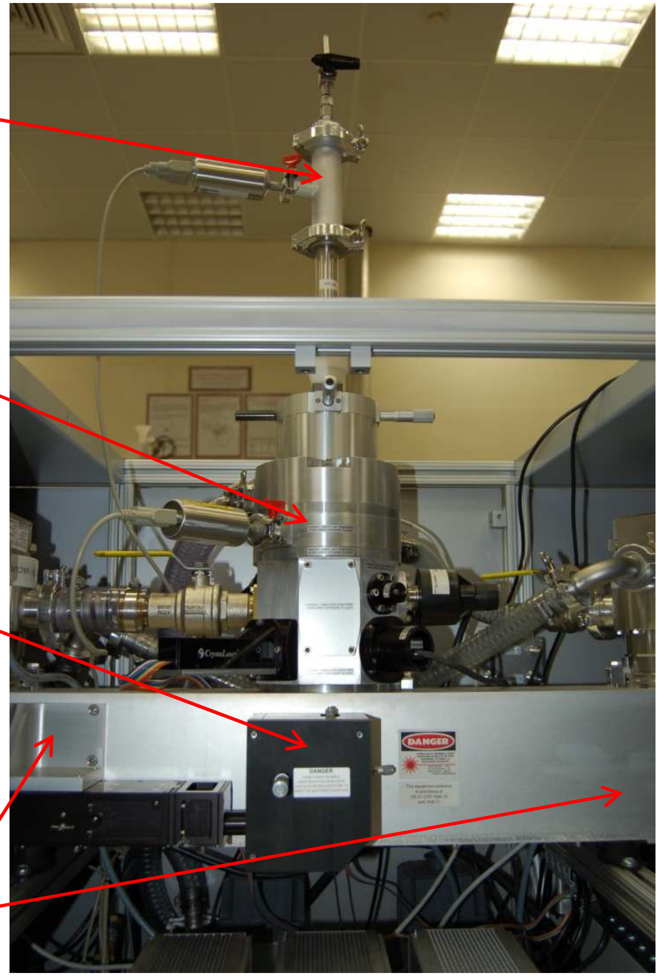
Aerosol Time-of-flight Mass Spectrometer (ATOFMS)

Aerodynamic lens

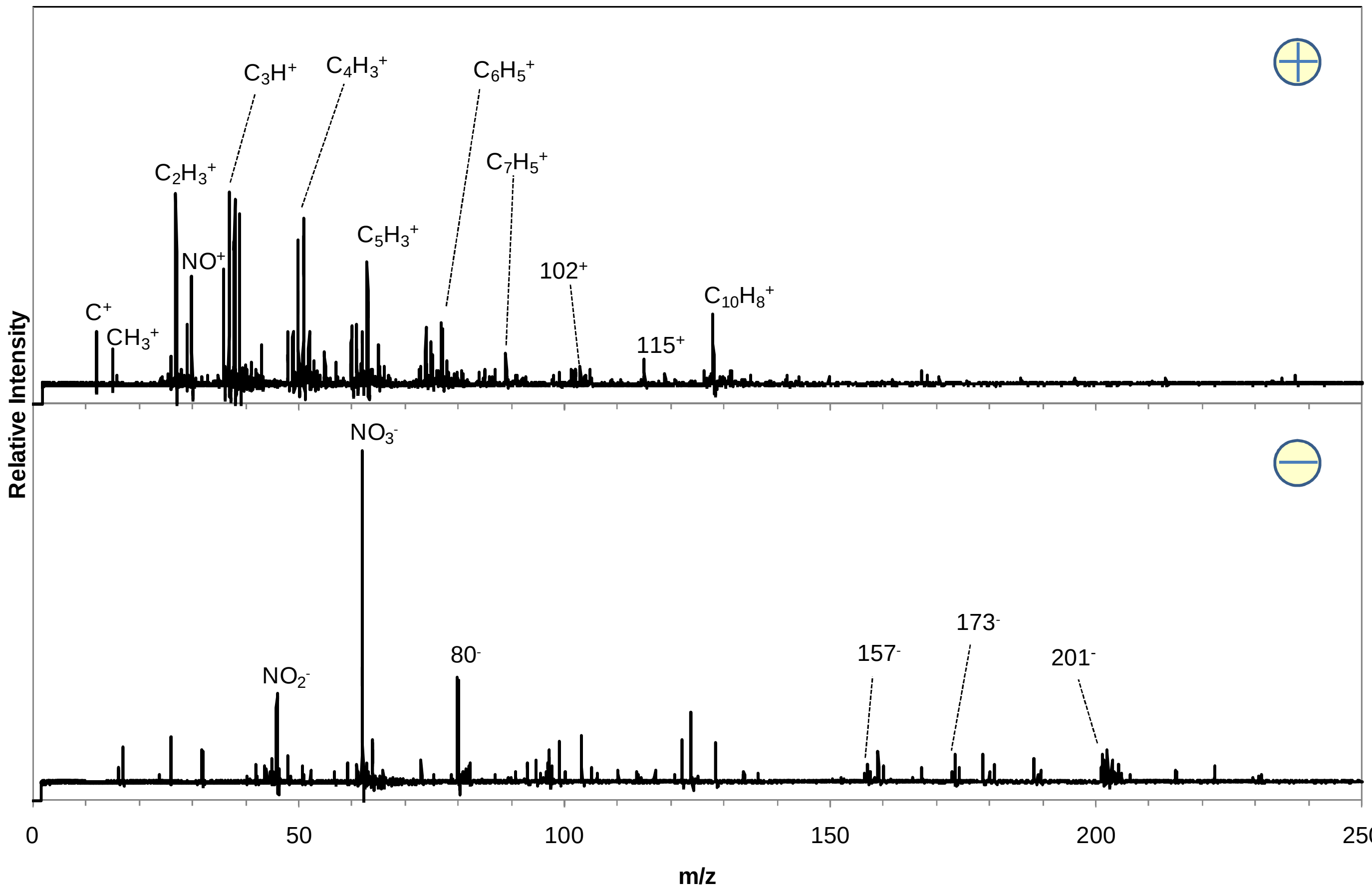
Sizing Region
(2 sizing lasers 532 nm)

Ionization laser
(266 nm)

Positive and negative
time-of-flight
mass spectrometers



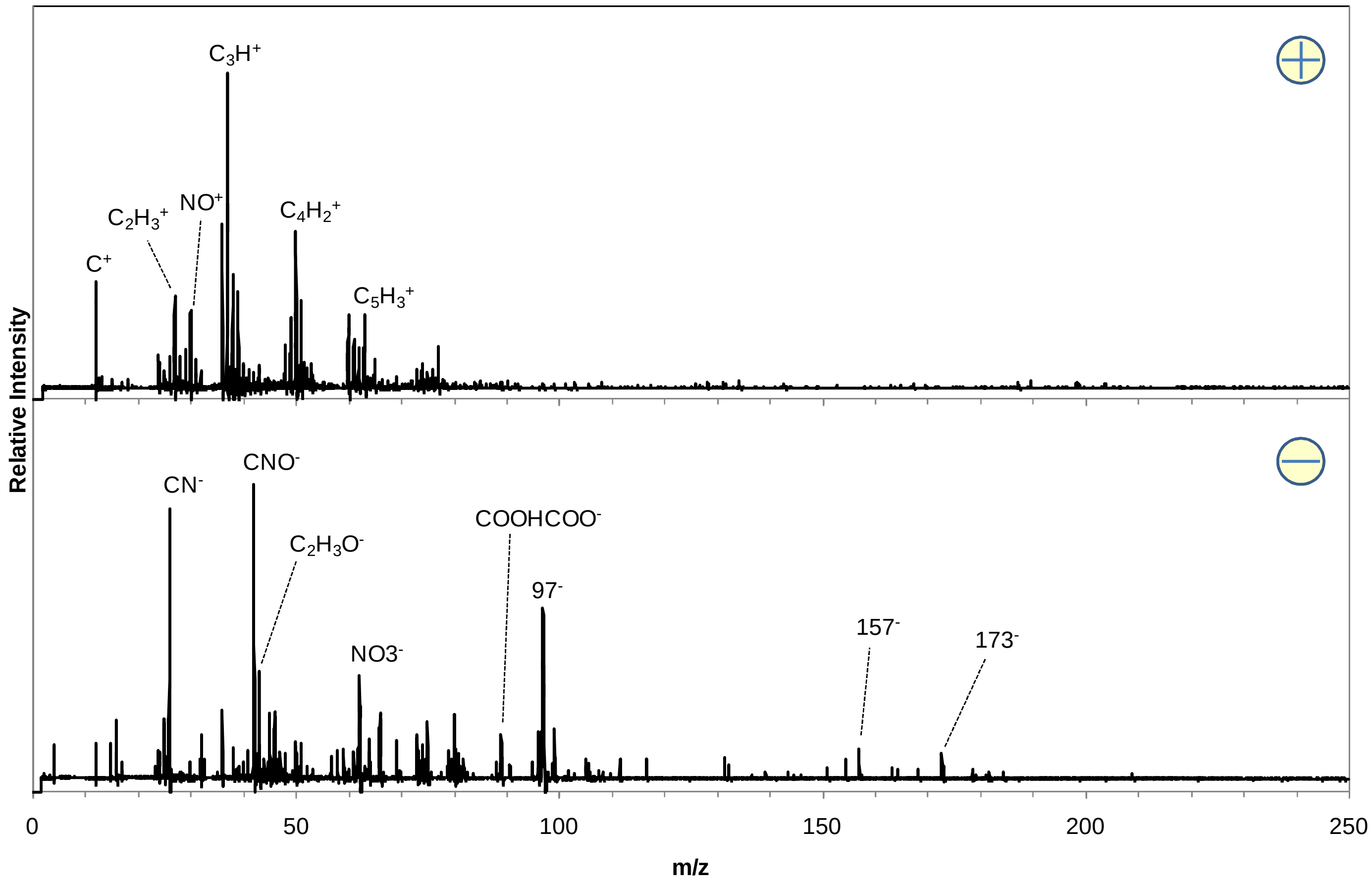
“Early” Mass spectra



- Positive ion mass spectrum shows hydrocarbon fragments typical of aromatic species likely due to ring-retaining oxidation products such as naphthol, nitronaphthalene, 2-formyl-cinnamaldehyde and phthaldialdehyde

- Peaks at 157 and 173 in the negative ion mass spectrum are tentatively attributed to nitronaphthalene

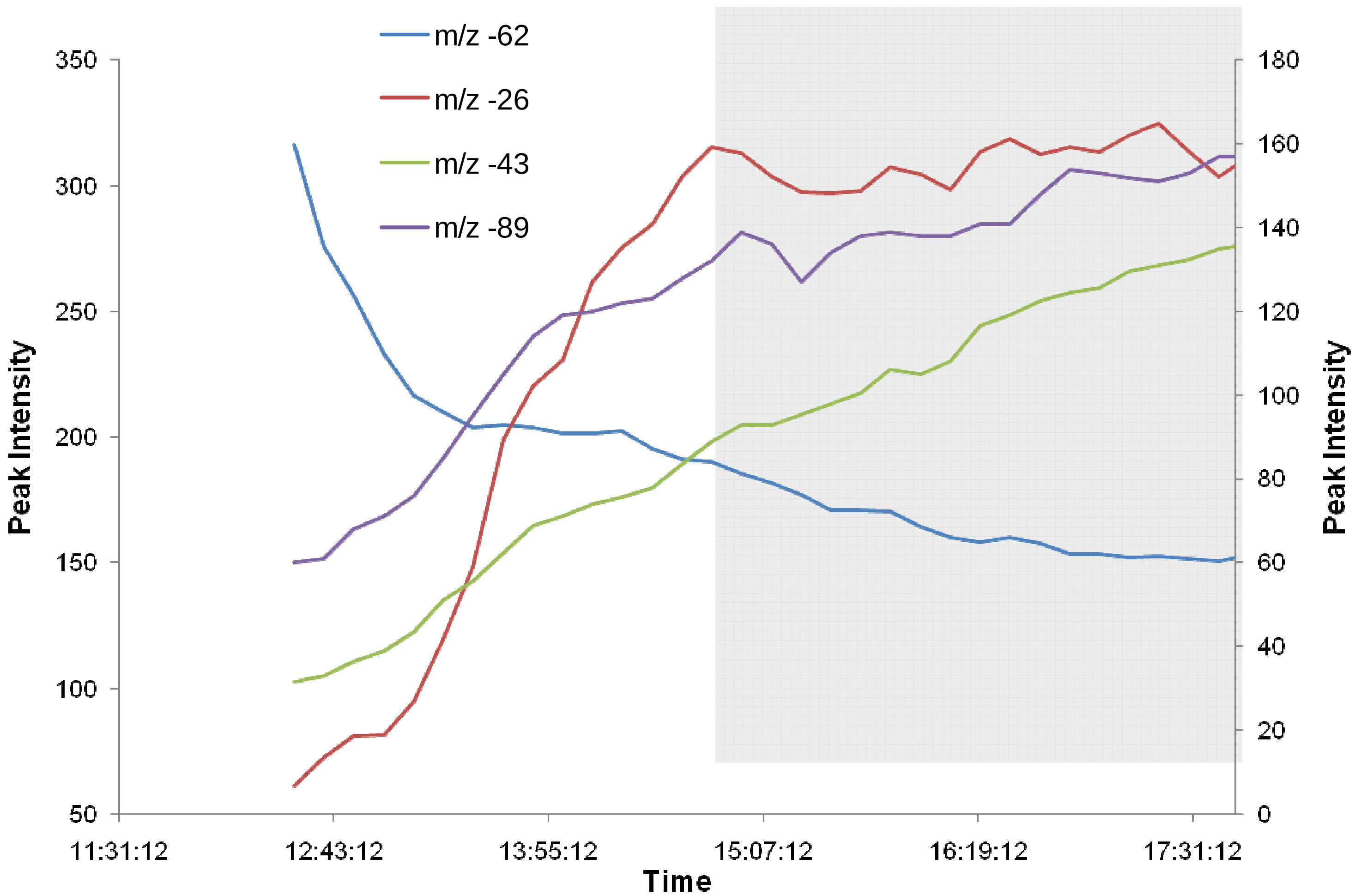
Mass spectra after 4 hours



• The larger hydrocarbon fragments are greatly reduced in intensity suggesting that the ring-retaining products may have reacted further

• An increased signal observed for CN^-, CNO^-, $C_2H_3O^-$ and $COOHCOO^-$, indicating that organic nitrates and oxidized organics were formed in the particle phase.

Evolution of Species

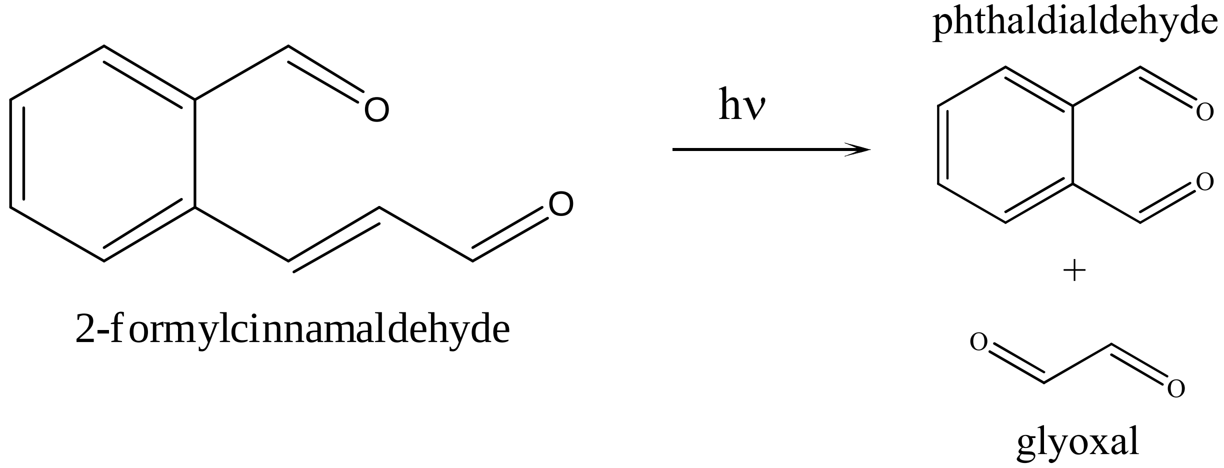


- Nitrate (-62) decreases and there is a corresponding increase in CN^- (-26)
- Increase in $C_2H_3O^-$ (-43), which is a marker ion for oxidised aerosol
- Increase in $COOHCOO^-$ (-89) indicating that oxalate is formed (glyoxal uptake?)
- **Chemical processing continues in the dark**

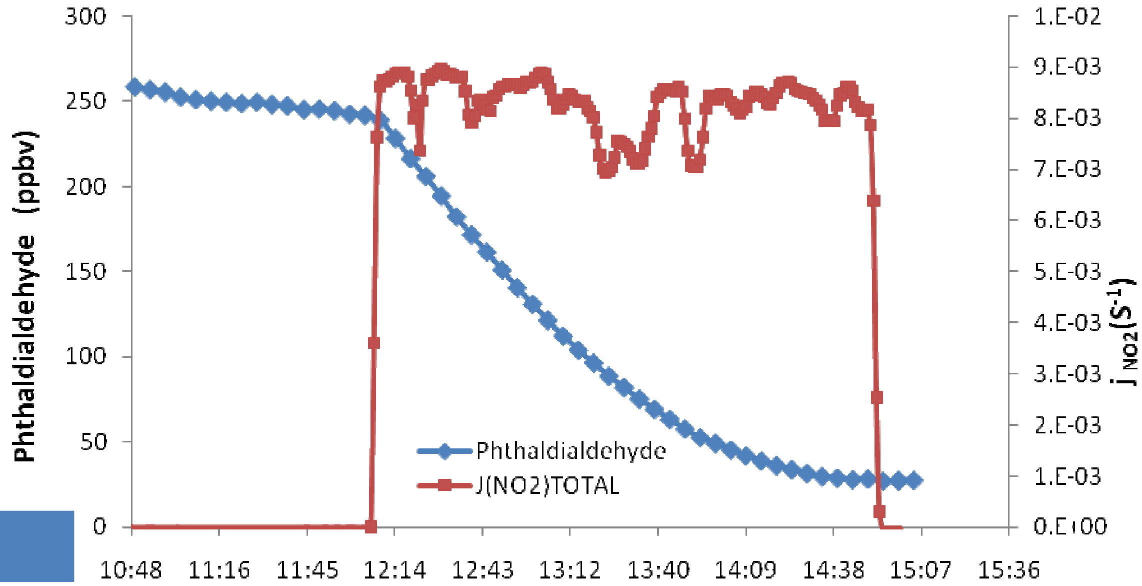
Photolysis of Oxidation Products at EUPHORE

- 0.1-1 ppmv of reactant, NOx free
- Radical scavenger or tracer added if required
- Monitor reactant by FTIR spectroscopy and GC
- Measure Flux between 290 and 520 nm

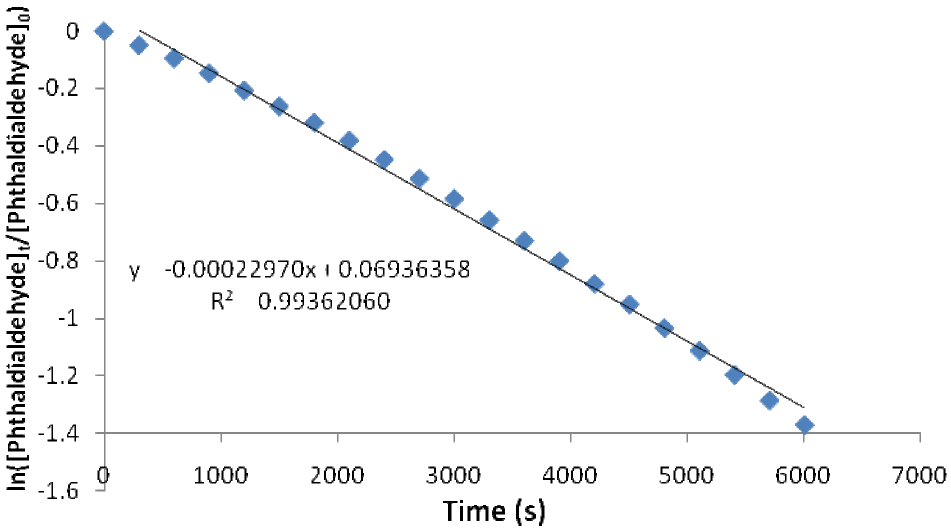
Sunlight photolysis of 2-formylcinnamaldehyde



Sunlight photolysis of Phthaldialdehyde



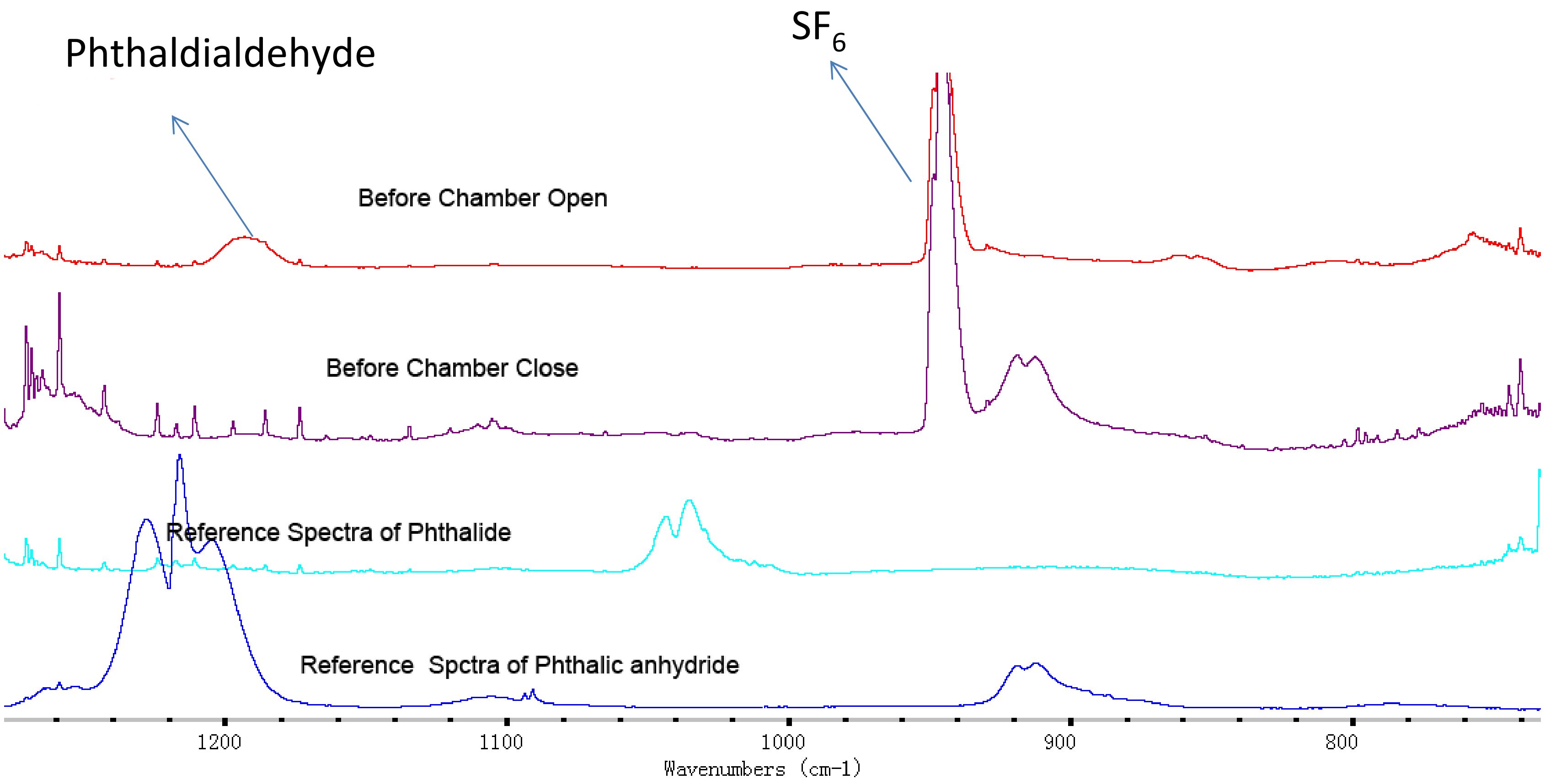
Date	1st July 2009
[phth](ppbv)	255
Irradiation time	2 hr 41 min
k_{SF6} (s^{-1})	$(5.51\pm0.29)\times10^{-6}$
k_{wall} (s^{-1})	$(1.55\pm0.23)\times10^{-5}$
j(phth) (s^{-1})	$(2.30\pm0.05)\times10^{-4}$
$j_{(NO2)\ average}$(s^{-1})	$(8.26\pm0.83)\times10^{-3}$
j(phth) /$j_{(NO2)}$	$(2.80\pm0.15)\times10^{-2}$

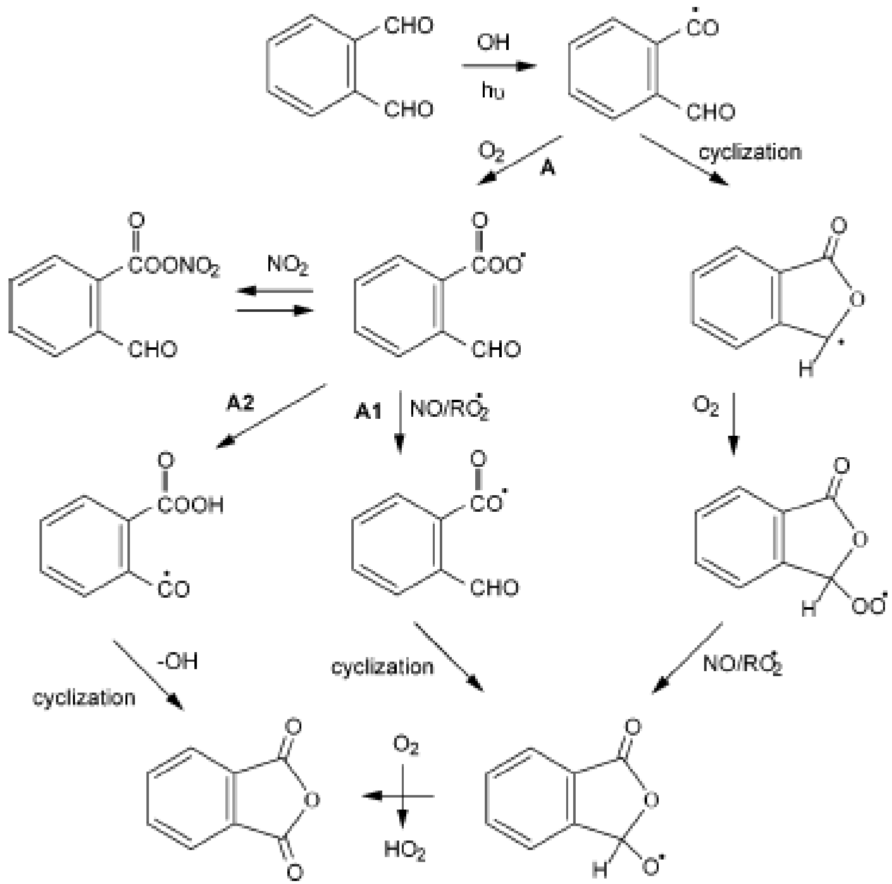


Wang et al. j(phth) /$j_{(NO2)}$ = 3×10^{-2}

Photolysis lifetime = 1-2 hr

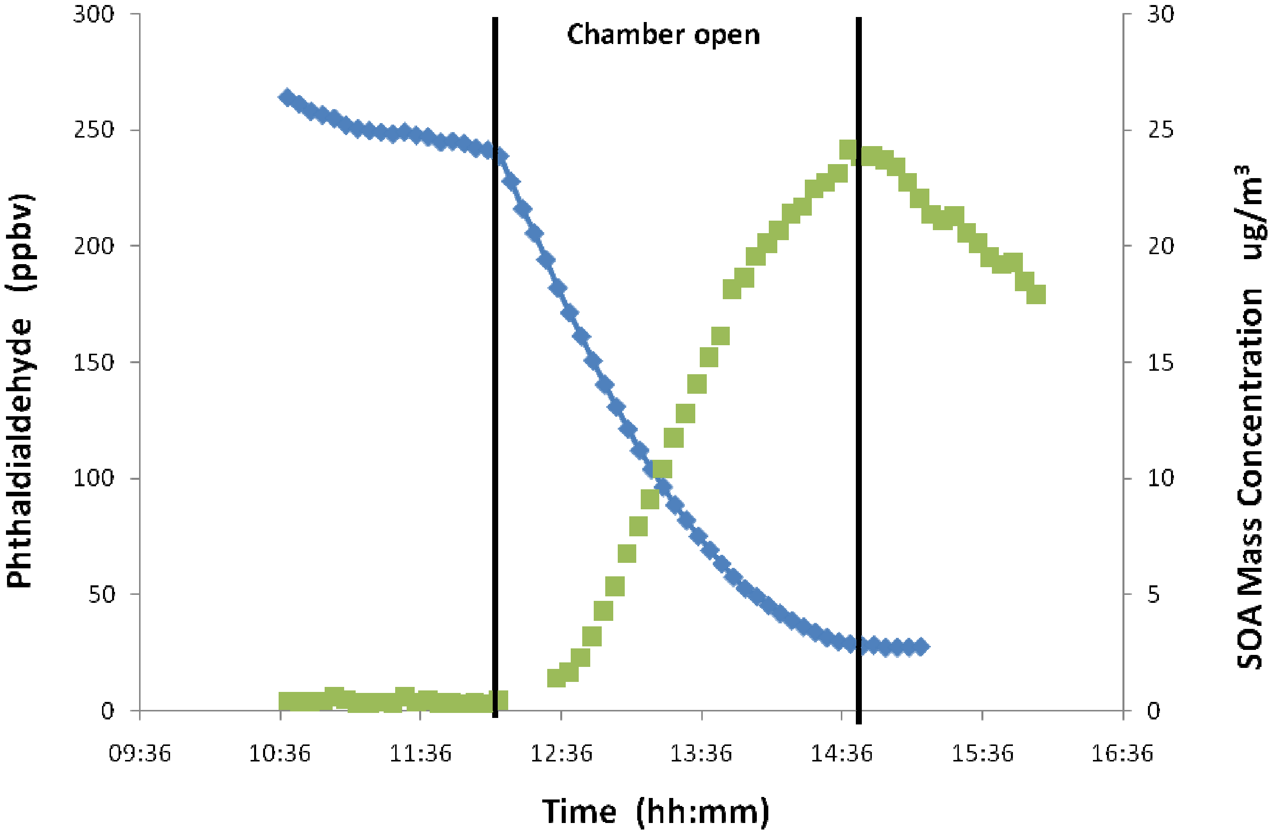
Sunlight photolysis of Phthaldialdehyde





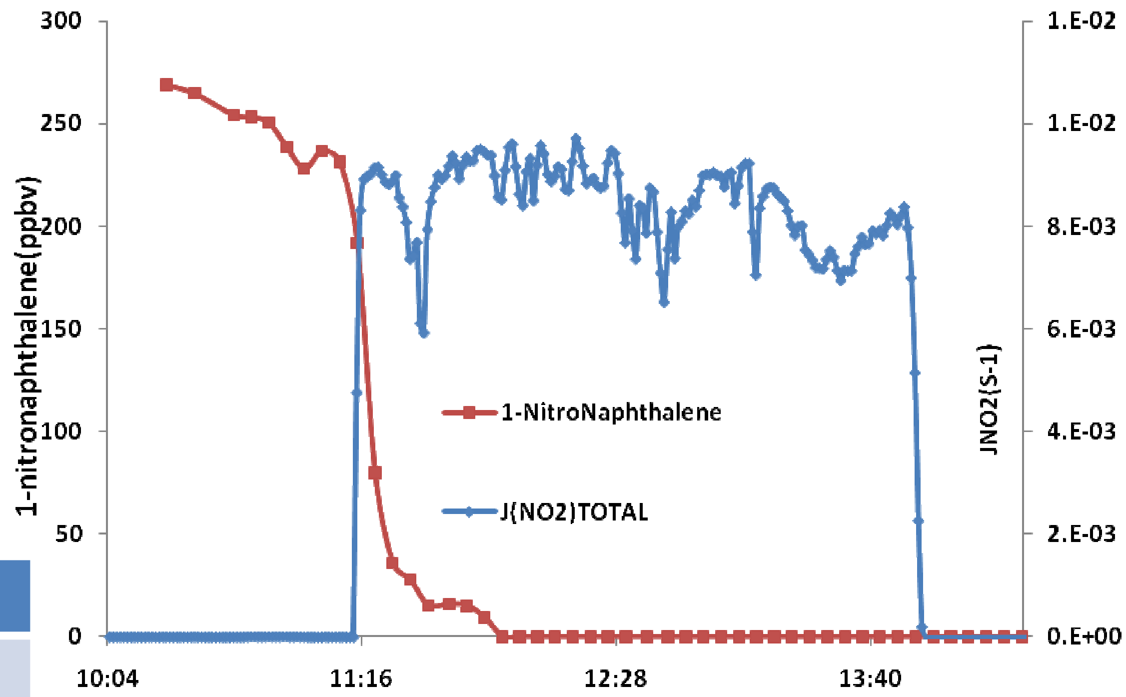
Wang et al, ES&T, 2006

Sunlight photolysis of Phthaldialdehyde



SOA yield ~ 2.0%

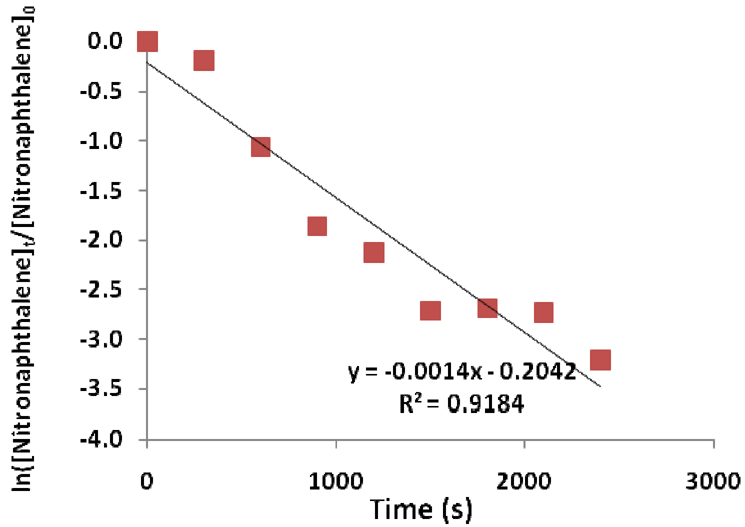
Sunlight photolysis of 1-nitronaphthalene



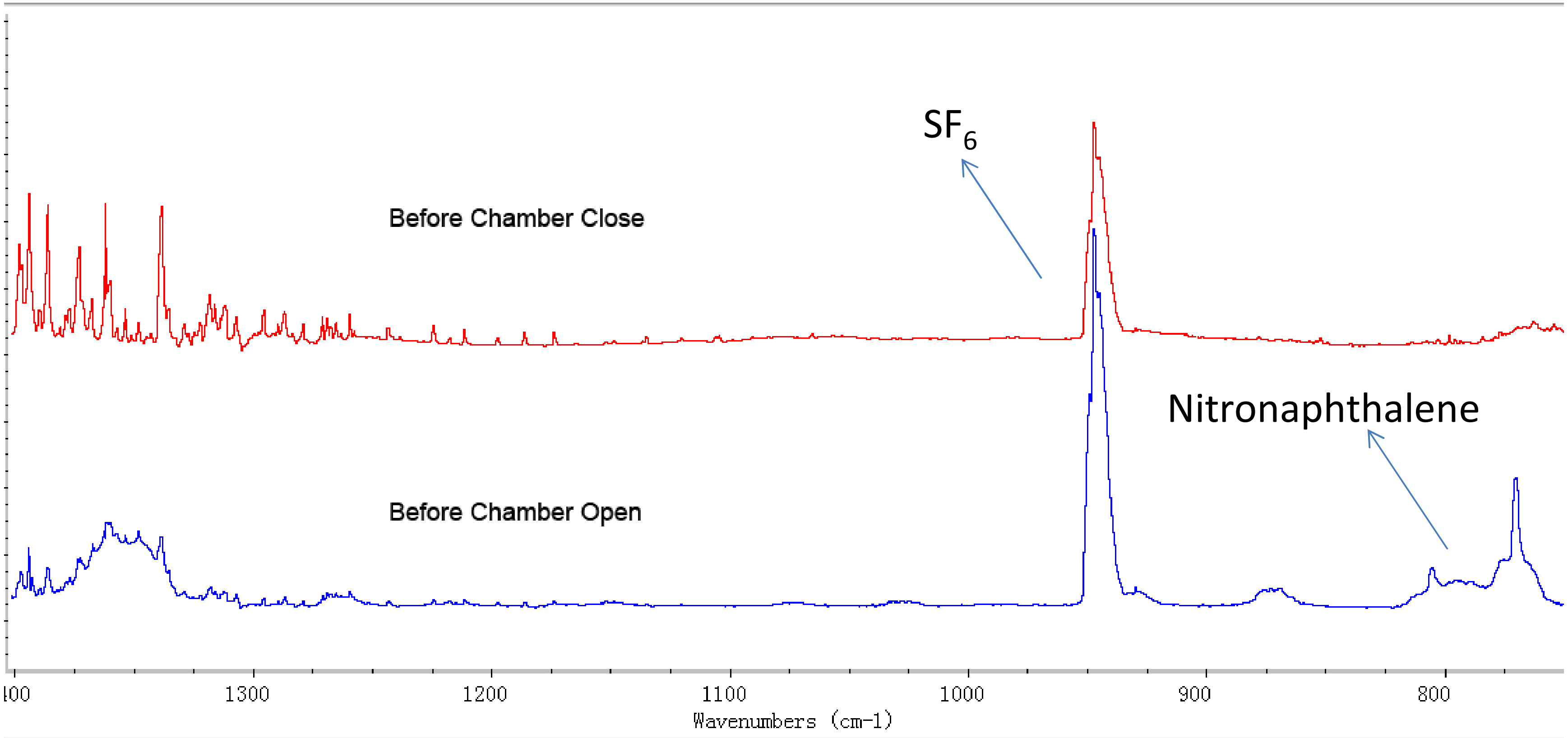
Date	6^{th} July 2009
[1-nn](ppbv)	269
Irradiation time	2 hr 38 min
k_{SF6} (s^{-1})	$(7.20\pm0.67)\times10^{-6}$
k_{wall} (s^{-1})	$(7.29\pm0.99)\times10^{-5}$
j(1-nn) (s^{-1})	$(1.37\pm0.30)\times10^{-3}$
$j_{(NO2)average}$ (s^{-1})	$(8.42\pm0.84)\times10^{-3}$
j(1-nn) /$j_{(NO2)}$	$(1.63\pm0.16)\times10^{-1}$

Atkinson et al. j(1-nn) = 1.6×10^{-3} s^{-1}

Photolysis lifetime = 10-12 min

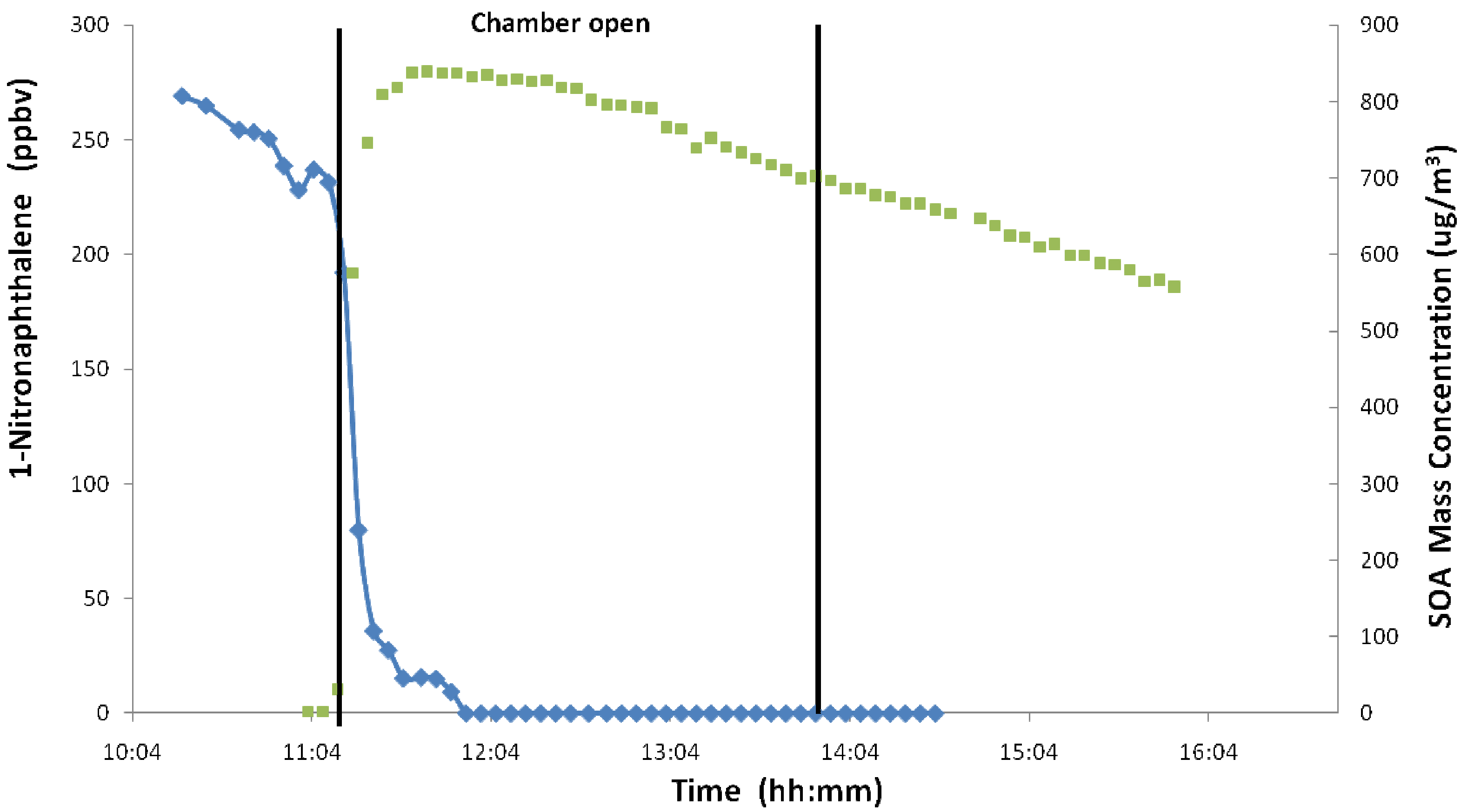


Sunlight photolysis of 1-nitronaphthalene



Formation of 1,4-naphthoquinone ???(Atkinson et al. Atmos. Environ., 1989)

Sunlight photolysis of 1-nitronaphthalene



SOA yield ~46%

Summary

- Naphthalene produces SOA in higher yields than monoaromatics

- Naphthalene and other PAHs are probably part of the “missing” SOA in urban atmospheres

- Large number of O- and N-containing aromatics in SOA

- On-line analysis indicates that chemical processing of naphthalene SOA continues even in the dark

- Direct photolysis of 1-nitronaphthalene, phthaldialdehyde and 2-formylcinnamaldehyde (?) is a potential source of SOA

Future Work

- Off-line analysis of SOA for carbonyls, phenols and carboxylic acids

- Detailed on-line analysis of SOA using ATOFMS – effect of RH, light, additional oxidants etc.

- Synthesis and photolysis of 2-formylcinnamaldehyde

- Chemical analysis of SOA from photolysis of 1-nitronaphthalene, phthaldialdehyde and 2-formylcinnamaldehyde

- Construction and testing of naphthalene degradation mechanism for MCM

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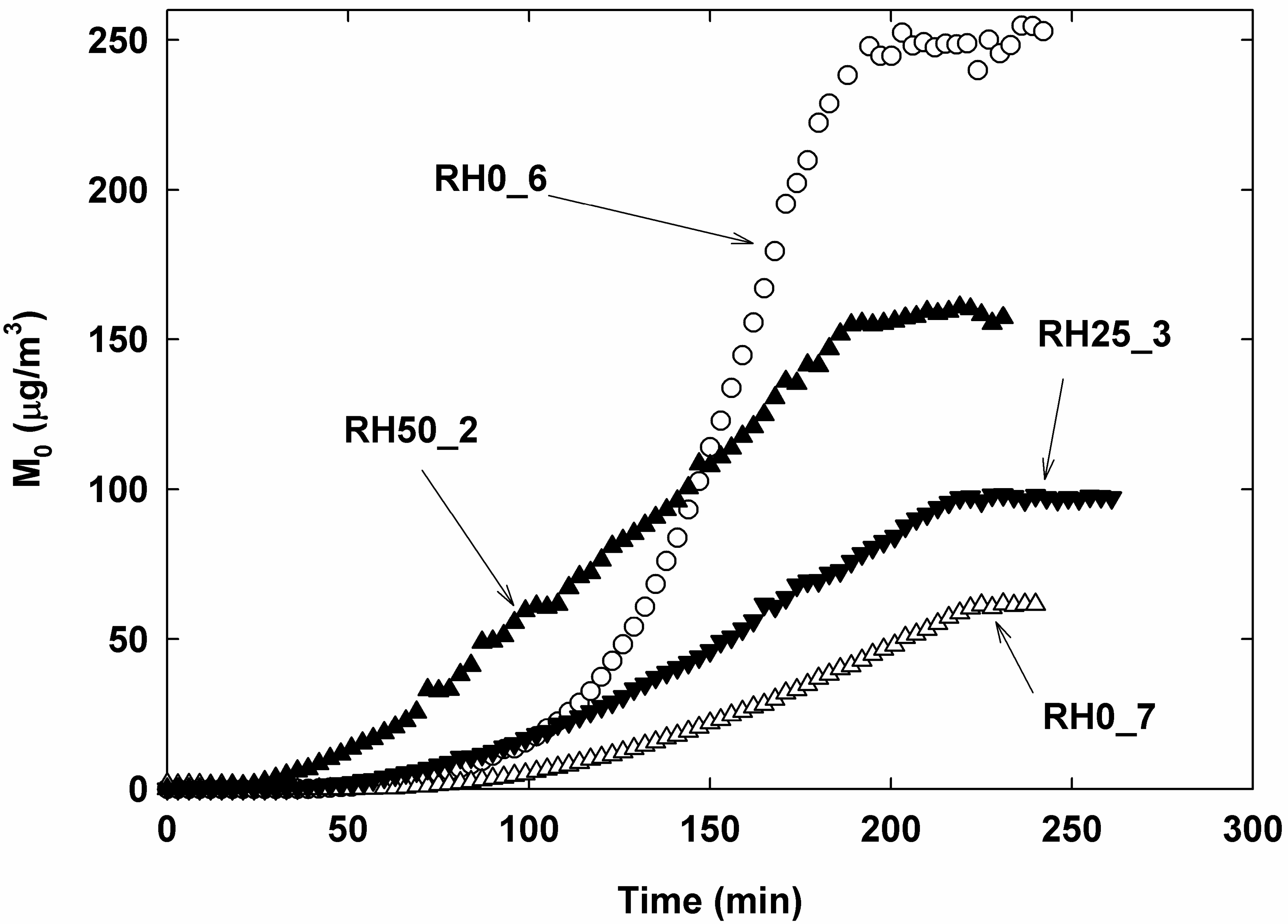
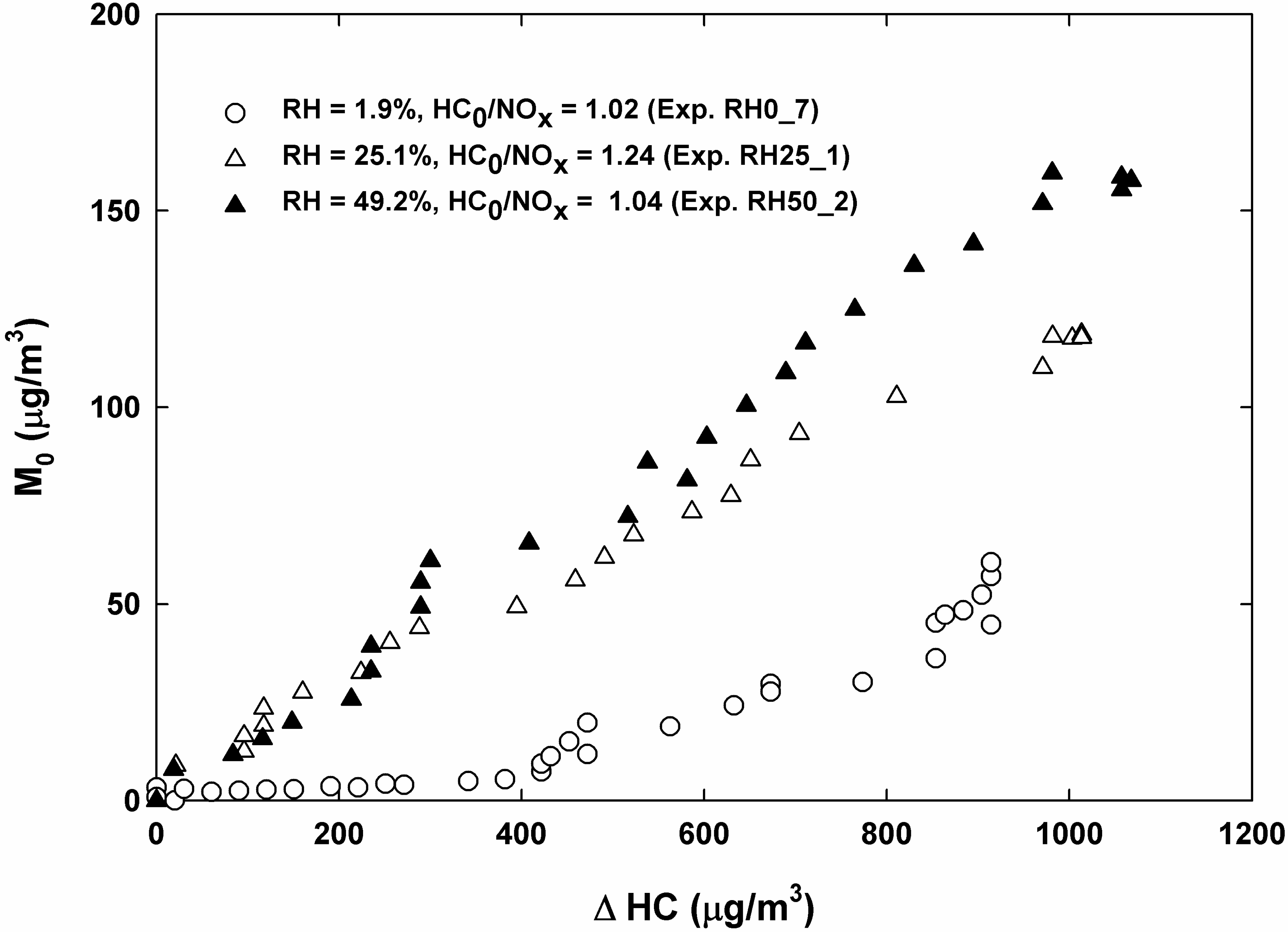
HEA

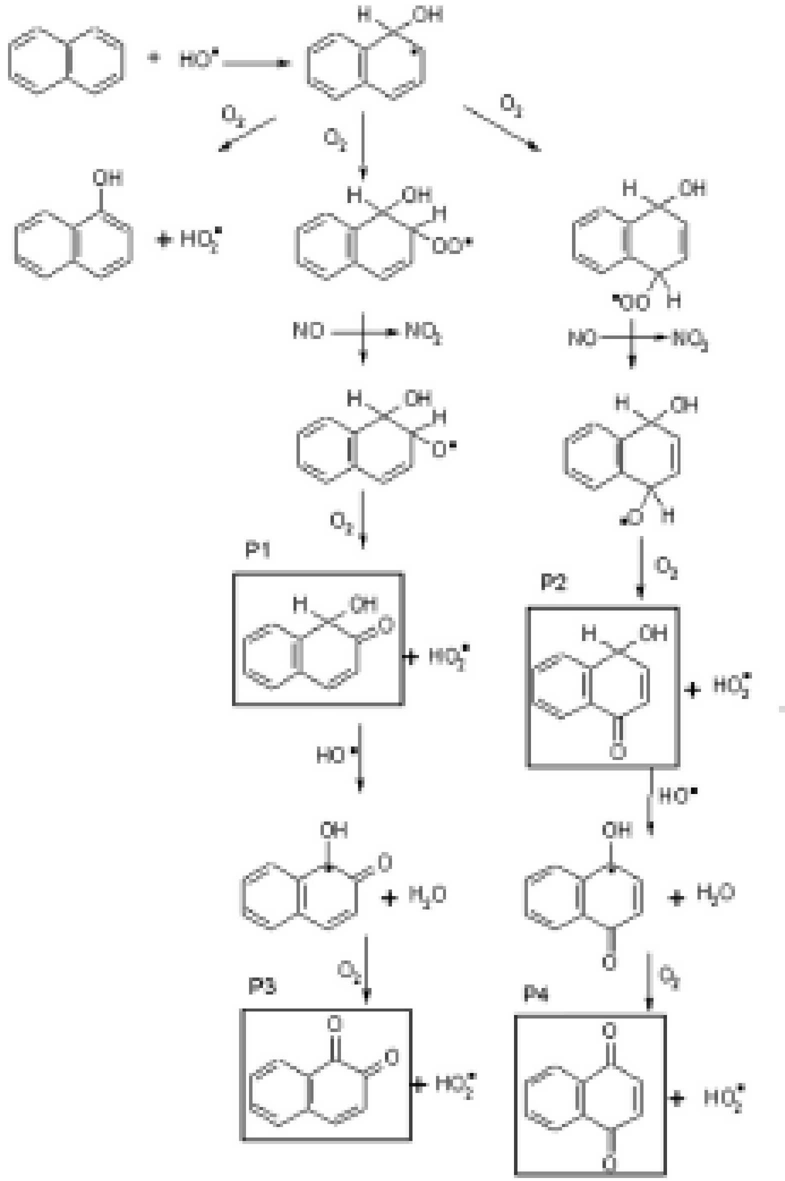
EUROCHAMP



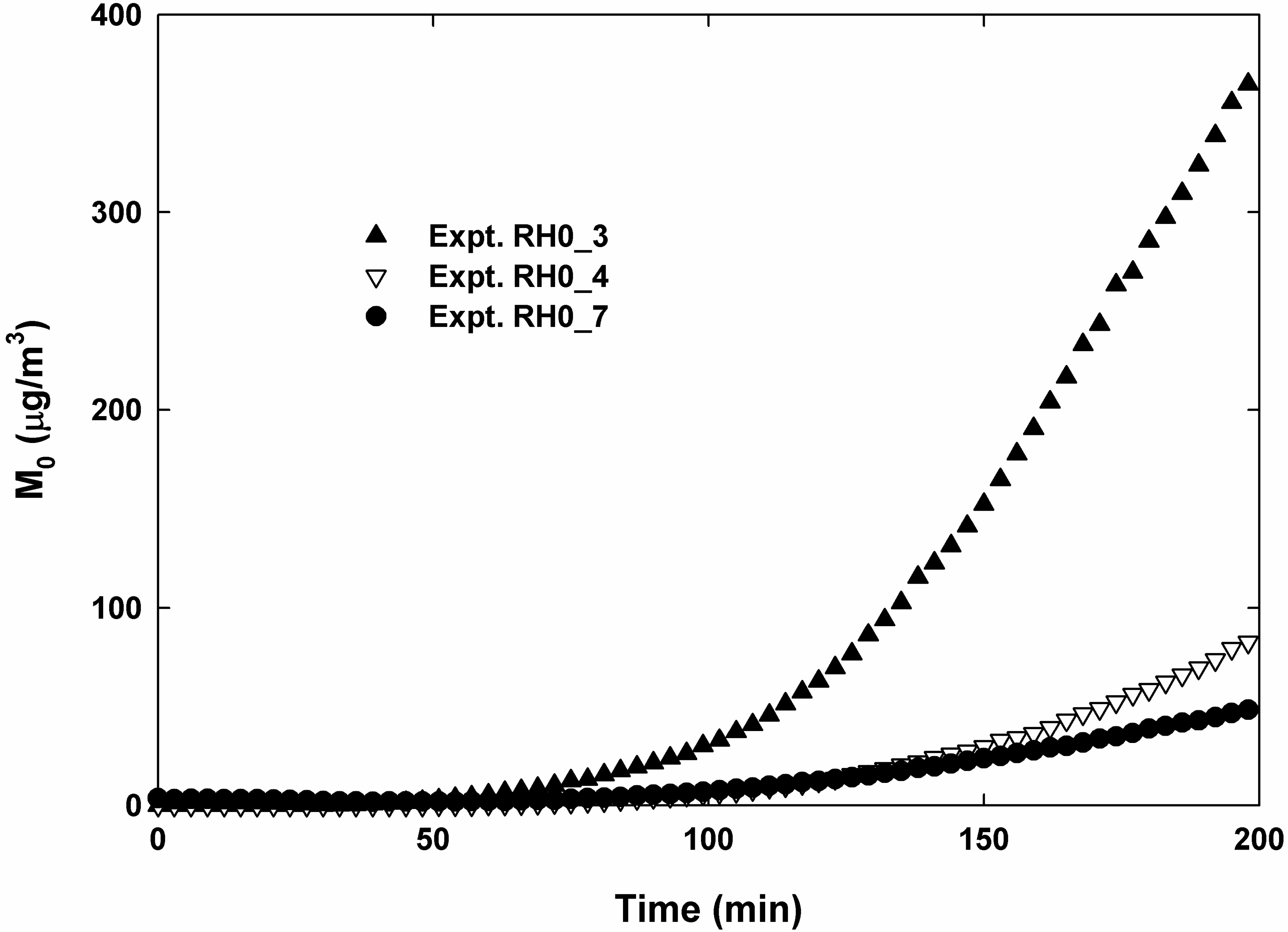
RH0_6
RH50_2
RH25_3
RH0_7
M0 (µg/m3)
Time (min)
0
50
100
150
200
250
300


RH = 1.9%, HC0/NOx = 1.02 (Exp. RH0_7)
RH = 25.1%, HC0/NOx = 1.24 (Exp. RH25_1)
RH = 49.2%, HC0/NOx = 1.04 (Exp. RH50_2)
M0 (μg/m3)
Δ HC (μg/m3)
0
50
100
150
200
0
200
400
600
800
1000
1200

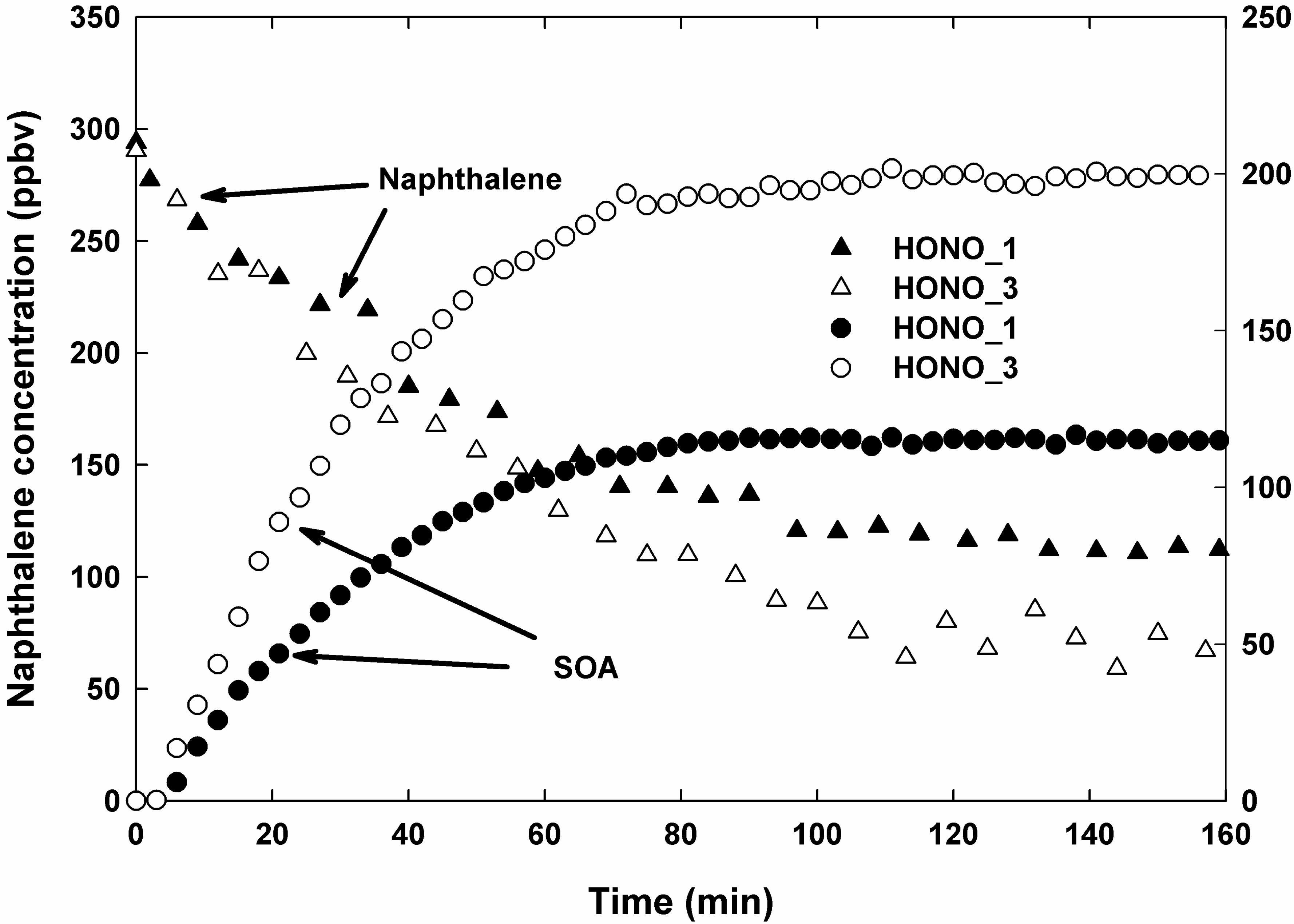
Oxidation Mechanism



Lee and Lane
Atmos. Environ., 2009



Expt. RH0_3
Expt. RH0_4
Expt. RH0_7
M_0 (μg/m^3)
Time (min)
0
100
200
300
400
0
50
100
150
200



Naphthalene
SOA
HONO_1
HONO_3
HONO_1
HONO_3
Naphthalene concentration (ppbv)
M_0 ($\mu g/m^3$)
Time (min)