

Aromatic Hydrocarbons Current Research

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*Organics in the Atmosphere with Focus on Low Volatile OC and Particles
– Sources, Chemistry and Impacts.
Vienna, October 6-8, 2008*

- major sources are automobile exhaust emissions, industrial scale combustion and the evaporation of fuels and solvents
- Benzene is carcinogenic and irradiation of hydrocarbon mixtures containing aromatic hydrocarbons produces species with mutagenic properties (Kleindienst *et al.* 1992)
- Of the 32 most prevalent non-methane hydrocarbons observed in urban air 7 are aromatic hydrocarbons
- Toluene is often the most abundant aromatic compound in urban air accounting for approximately 6% of the observed NMHC

- On a global scale total aromatic emissions are of the order of 15.8 Tg y^{-1}
- Typical ambient concentrations of alkylated benzenes in cities:
 - low 25 ppbC high 590 ppbC
- Aromatic hydrocarbons have high photochemical ozone creation potentials and contribute significantly to ozone pollution and secondary organic aerosol (SOA) formation in urban air

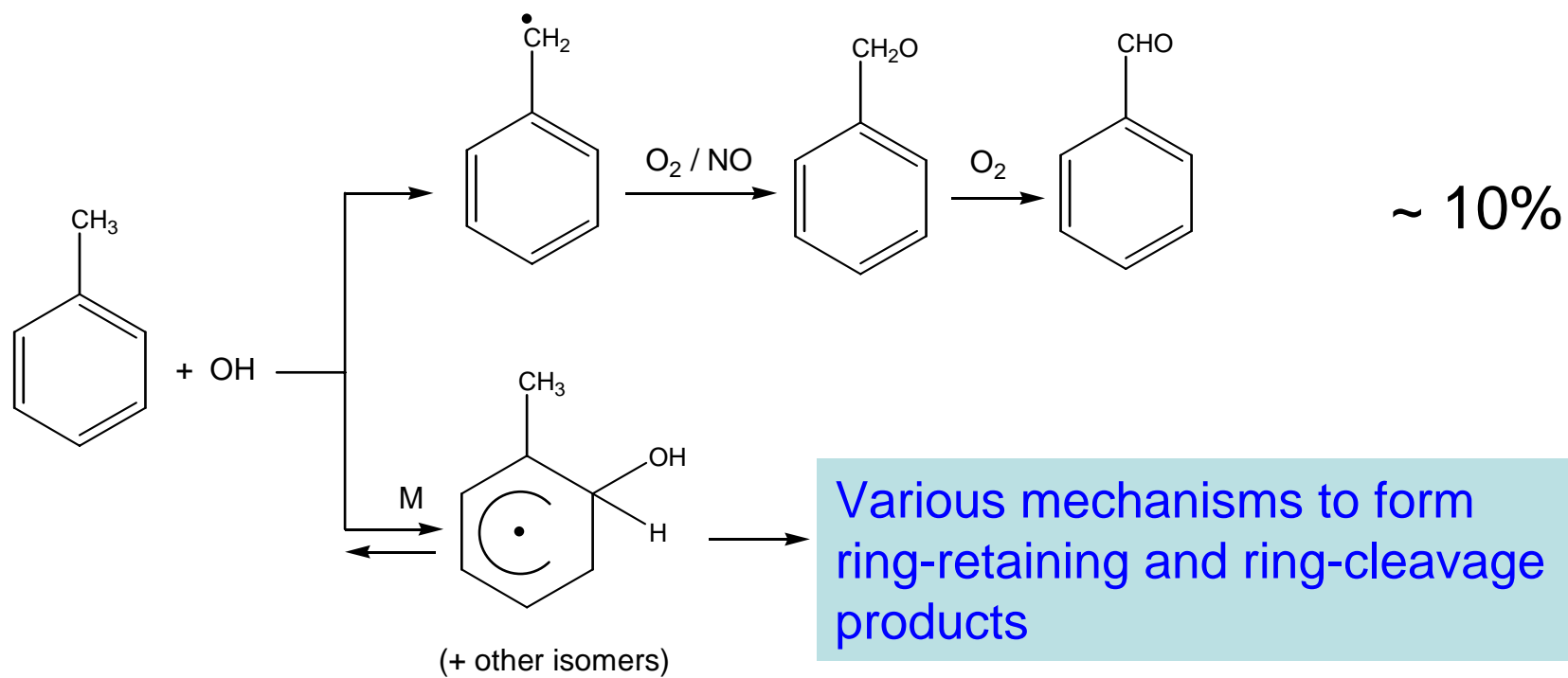
Derwent et al. *Atmos. Environ.* *41*, 2570-2579, 2007.

Derwent et al. *Environ. Sci. Policy* *10*, 445-453, 2007.

Derwent et al. *Atmos. Environ.* *37*, 1983-1991 2003.

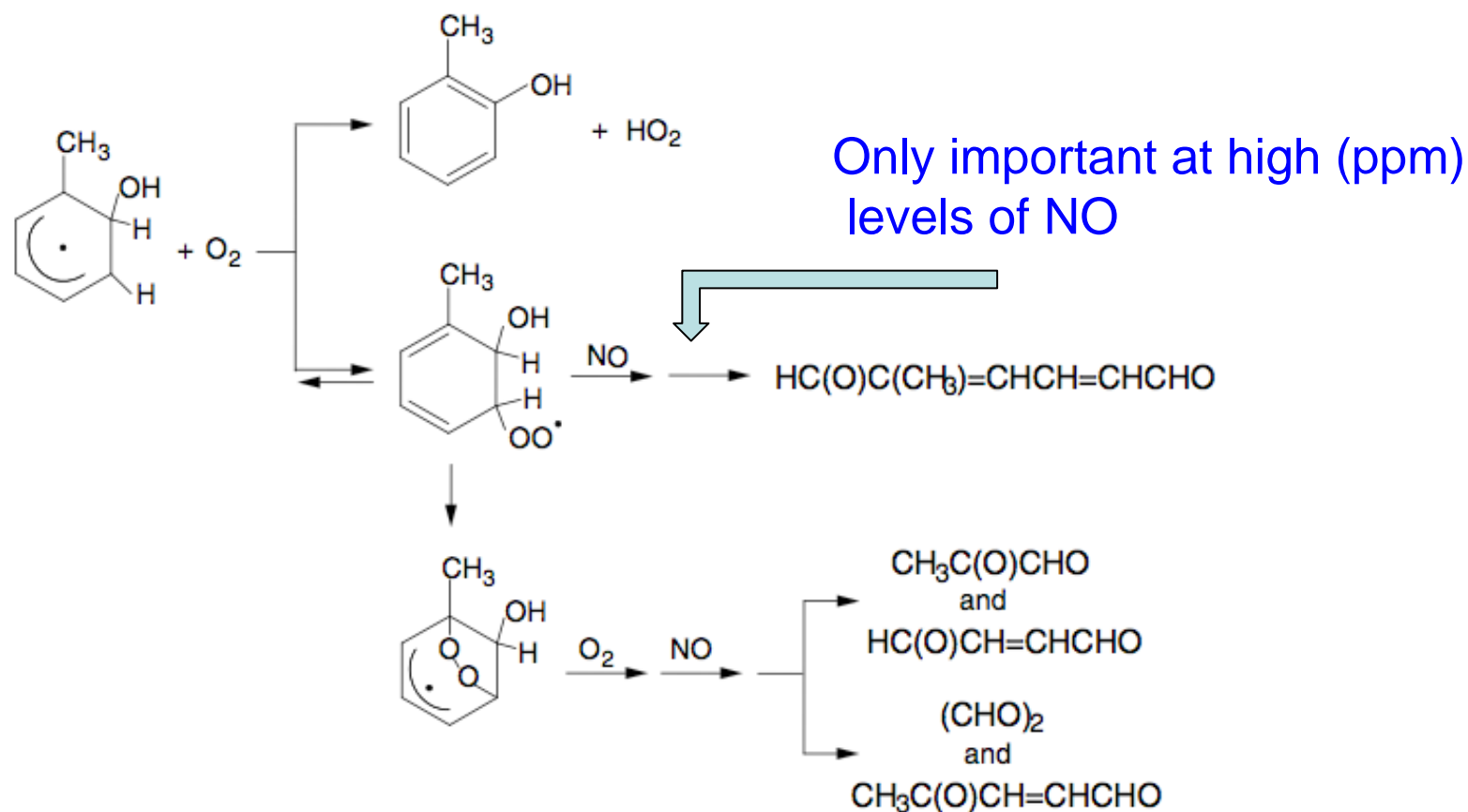
- New studies on aromatic hydrocarbon first generation products
- New studies on SOA formation from aromatic hydrocarbon oxidation

Aromatic hydrocarbons – OH radical reaction first steps

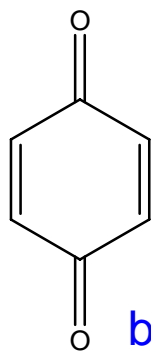
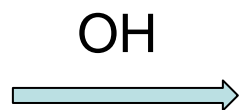
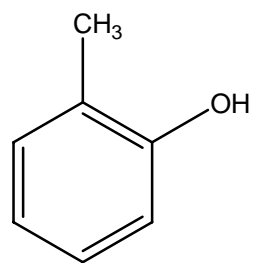


- OH-aromatic adducts react almost exclusively with O_2 in the troposphere
- OH-aromatic adducts can react with NO_2
- OH-aromatic adduct reactions with O_2 and NO_2 in air are of equal importance for NO_2 mixing ratios of around 1-2.5 ppmV
- Paper on kinetics of the reactions of aromatic adducts with NO , NO_2 and O_2
(Koch et al. Atmos. Chem. Phys. 2007, 7, 2057)

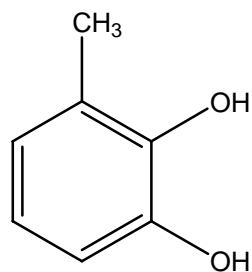
Possible reactions of OH-toluene adduct with O₂



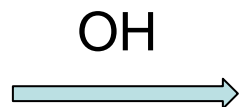
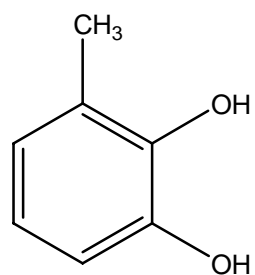
(Arey et al. ES&T 2008)



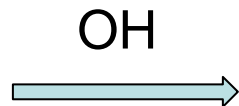
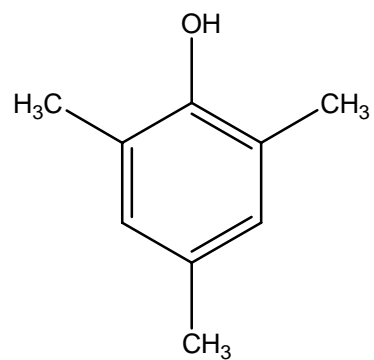
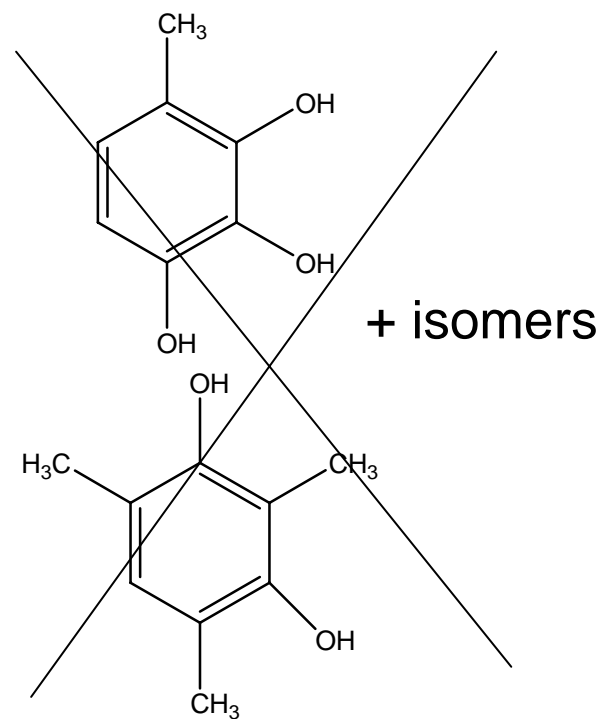
benzoquinone



high yields of catechols (diols)



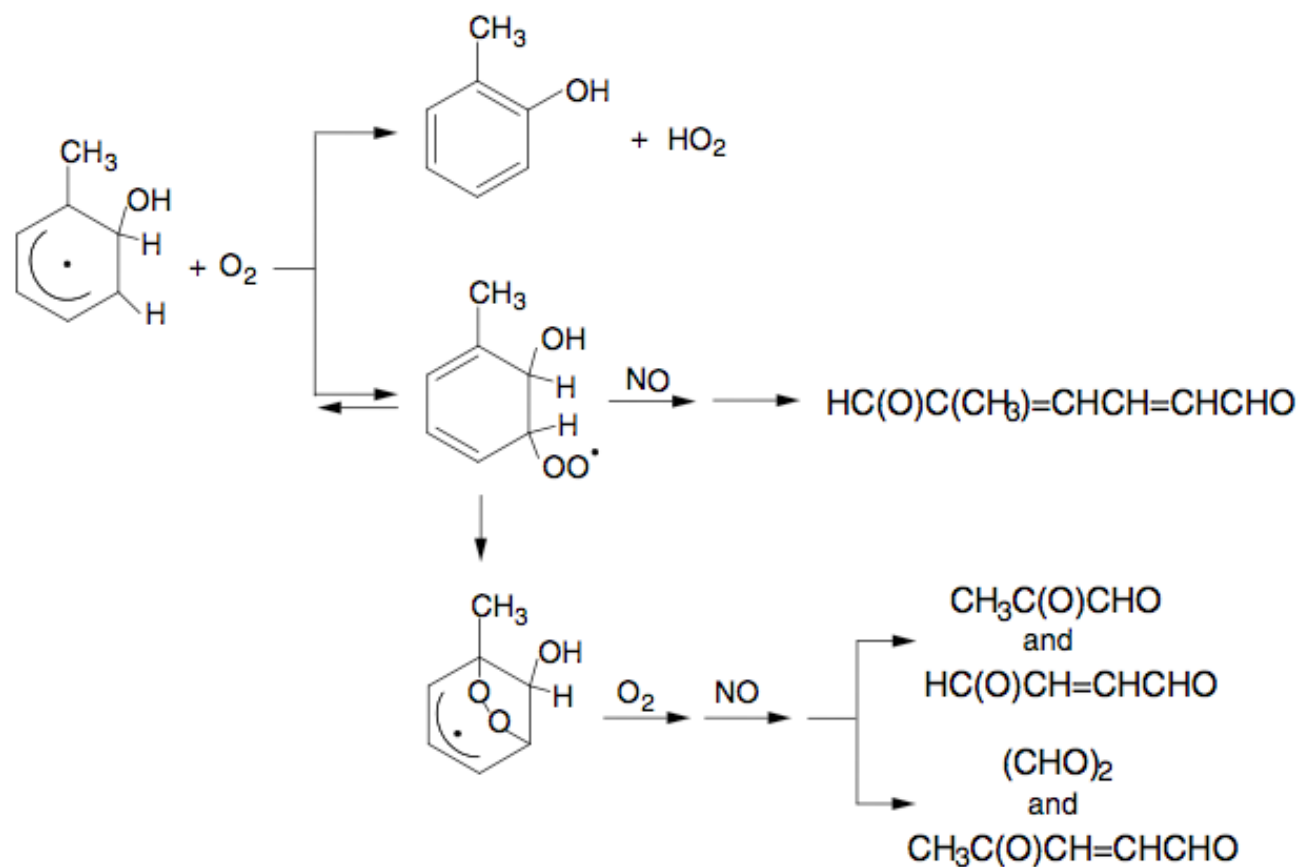
no indication for formation of triols



no indication for formation of diols

+ isomers

Possible reactions of OH-toluene adduct with O₂



Studies on dicarbonyls from monocyclic aromatics + OH

- Arey *et al.*, Environ. Sci. Technol. 2008

Method: Denuder derivatization technique with methane positive ionization
GC/MS

Compounds: toluene, xylenes and trimethylbenzenes

- Gomez Alvarez *et al.*, Environ. Sci. Technol. 2007, 41, 8362

Methods: solid phase microextraction (SPME) with derivatization followed
by GC-MS and PTR-MS

Compounds: benzene, toluene

- Berndt and Böge, Phys. Chem. Chem. Phys. 2006, 8, 1205

Method: flow system- GC/MS

Compound: benzene

Ring-opened Dicarboxyls

Ring-opened dicarboxyls	m.w.	benzene	toluene	xylene			trimethylbenzene		
				<i>o</i> -	<i>m</i> -	<i>p</i> -	1,2,3-	1,2,4-	1,3,5
HC(O)CHO	58	X	X	X	X	X	X	X	
CH ₃ C(O)CHO	72		X	X	X	X	X	X	X
CH ₃ C(O)C(O)CH ₃	86			X			X	X	
HC(O)CH=CHCHO	84	X	X	X					
CH ₃ C(O)CH=CHCHO	98		X	X	X		X		
HC(O)C(CH ₃)=CHO	98		X		X	X		X	
CH ₃ C(O)C(CH ₃)=CHCHO	112			X			X	X	
CH ₃ C(O)CH=C(CH ₃)CHO	112				X			X	X
CH ₃ C(O)CH=CHC(O)CH ₃	112					X		X	
HC(O)C(CH ₃)=C(CH ₃)CHO**	112			X				X	
CH ₃ C(O)C(CH ₃)=C(CH ₃)CHO	126						X		

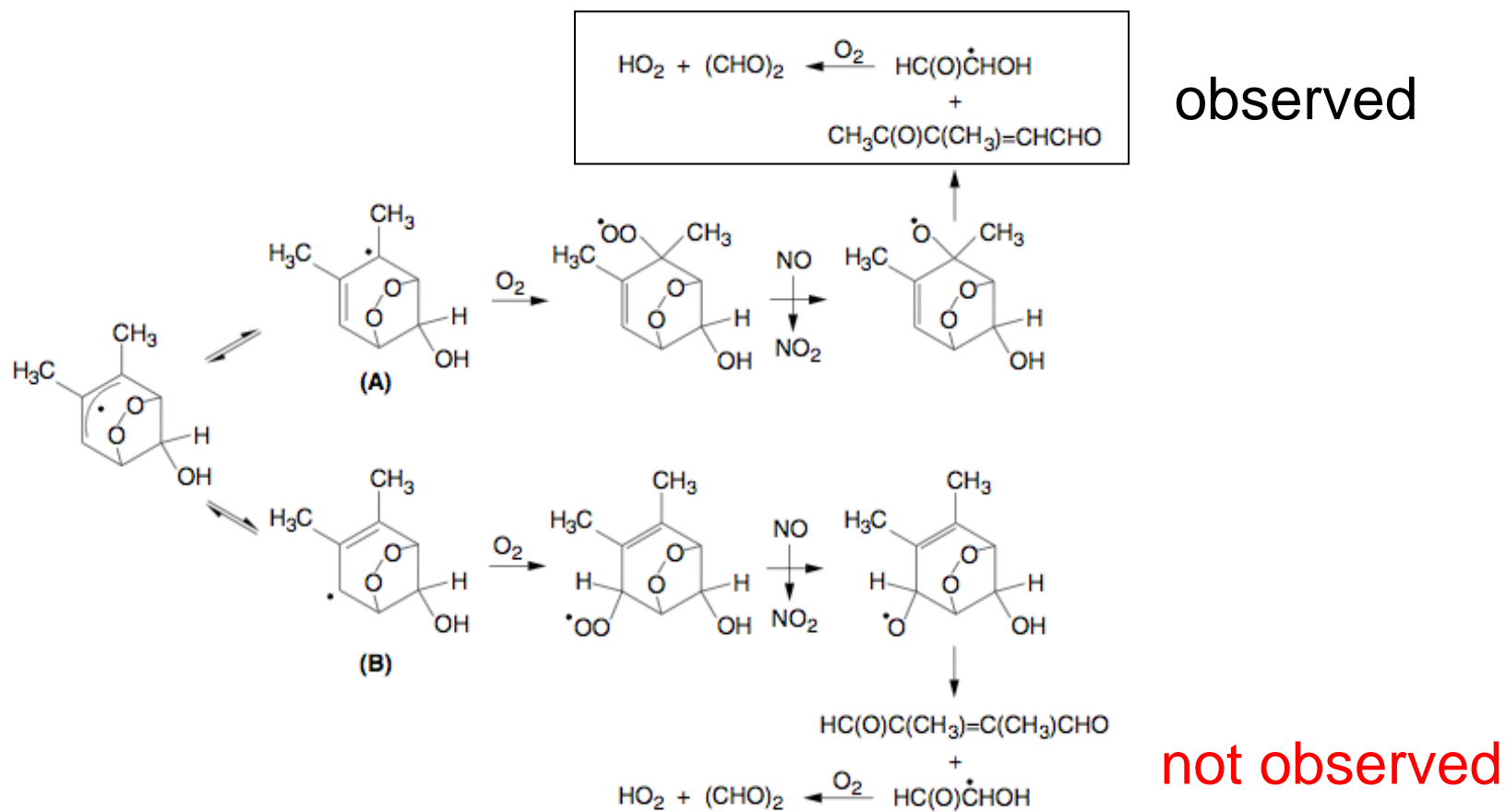
} 1,2-dicarbonyls
 } 1,4-unsaturated dicarbonyls

**Theoretically possible but not observed - preferred CH₃C(O)C(CH₃)=CHCHO

Aromatic hydrocarbons - observations of dicarbonyls

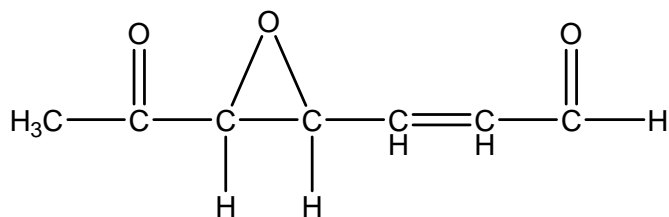
- Most of possible 1,2-dicarbonyl and 1,4-unsaturated dicarbonyl co-products now detected for benzene, toluene, xylenes and trimethylbenzenes
- Yields of unsaturated 1,4-diketones similar to those of possible 1,2-dicarbonyl co-products
- Yields of unsaturated 1,4-dialdehydes generally lower than those of possible 1,2-dicarbonyl co-products

Dicarbonyls from OH + o-xylene

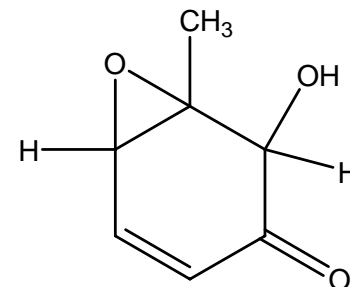


Epoxy reaction route?

- The most recent denuder GC/MS technique (Arey *et al.* 2008) found no evidence for the formation of epoxides such as unsaturated epoxy-1,6-dicarbonyl and epoxycyclohexenone from OH + toluene



3-(3-acetyloxiran-2-yl)acrylaldehyde

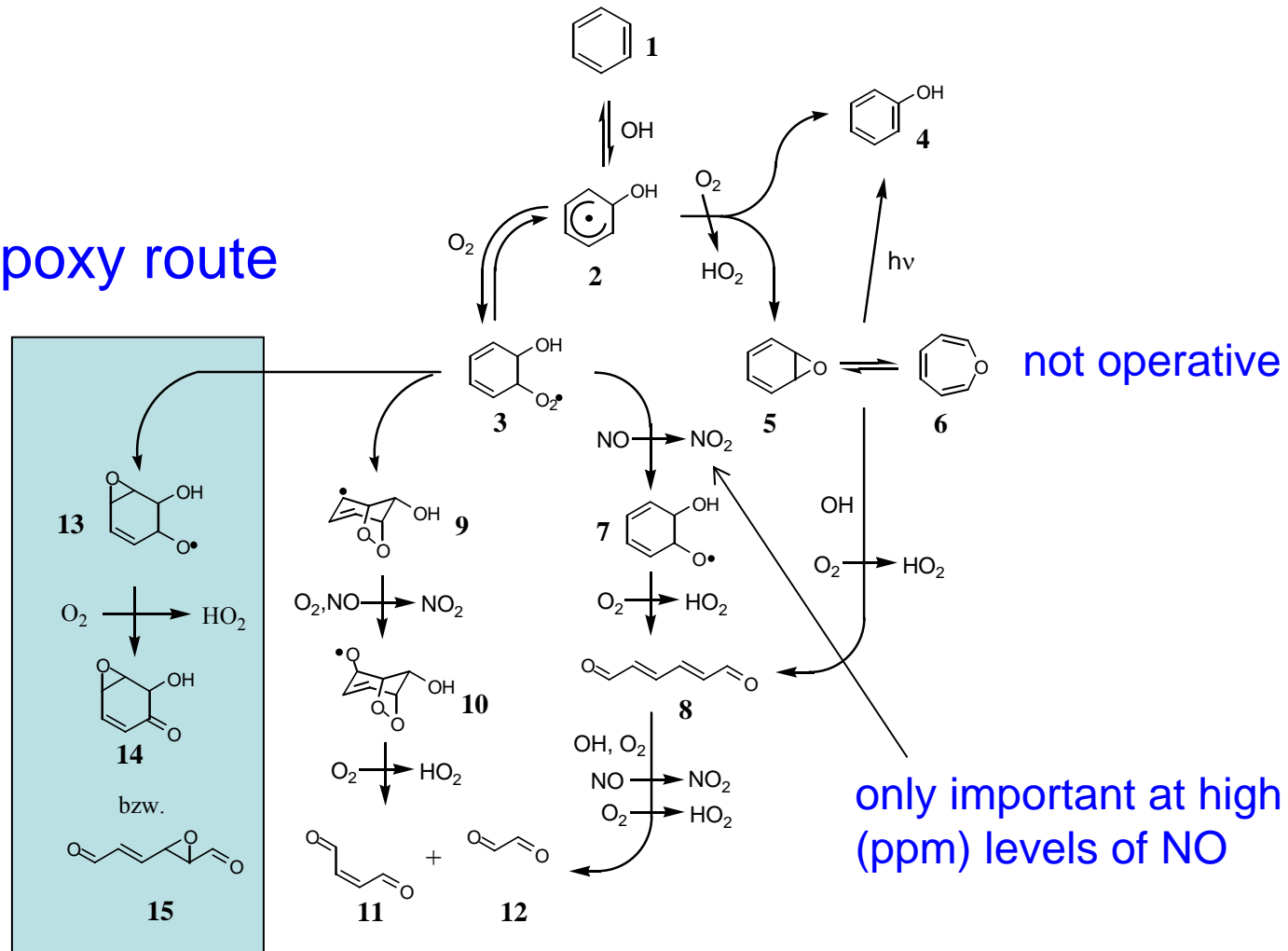


2-hydroxy-1-methyl-7-oxa-bicyclo[4.1.0]hept-4-en-3-one

- Also no evidence for the formation of di-unsaturated 1,6-dicarbonyls, e.g. $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CHCH}=\text{CHCHO}$

Route to epoxy formation for benzene

Epoxy route



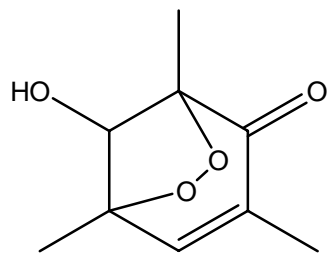
even assuming the unsaturated 1,4-dicarbonyls have yields similar to the 1,2-dicarbonyls

the sum of the quantified first-generation products:

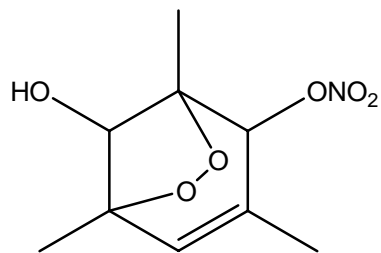
- aromatic aldehydes
- benzyl nitrates
- phenols
- 1,2-dicarbonyls and unsaturated 1,4-dicarbonyls

still only account for 60-70% of the products

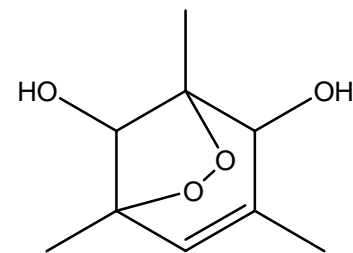
Primary bicyclic compounds from 1,3,5-trimethylbenzene



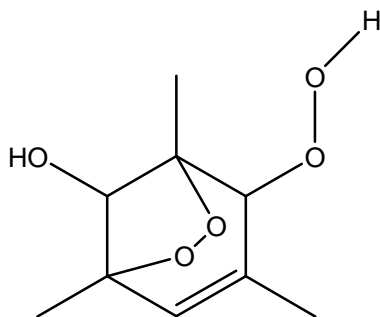
carbonyl



nitrate



diol



O₂-bridged peroxide

*no direct measurement
possibly important for SOA formation*

Photolysis studies on unsaturated dicarbonyls

- Absorption cross sections determined for:

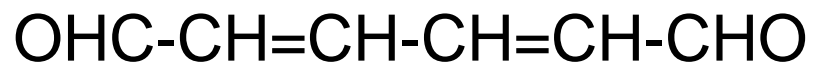
4-oxo-2-pentenal (190-460 nm)

Xiang *et al.* J. Phys. Chem. A **2007**, *111*, 9025



E,E-2,4-hexadienedial (248, 290-430 nm)

Xiang and Zhu, Chem. Phys. Letters **2007**, *450*, 31

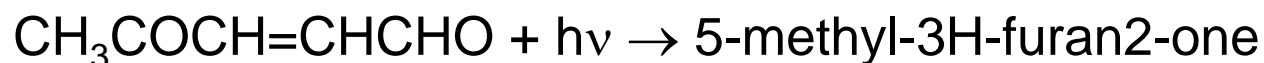
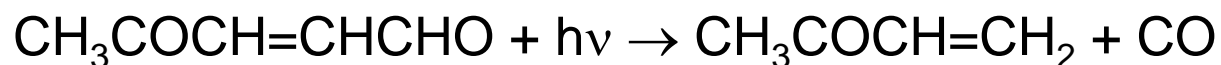
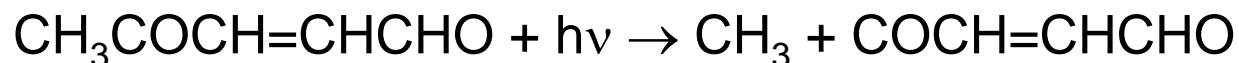


(O'Connor *et al.* Phys. Chem. Chem. Phys. **2006**, *8*, 5236; Klotz *et al.* Environ Sci. Technol. **1995**, *29*, 2322)

Photolysis products 4-oxo-2-pentenal

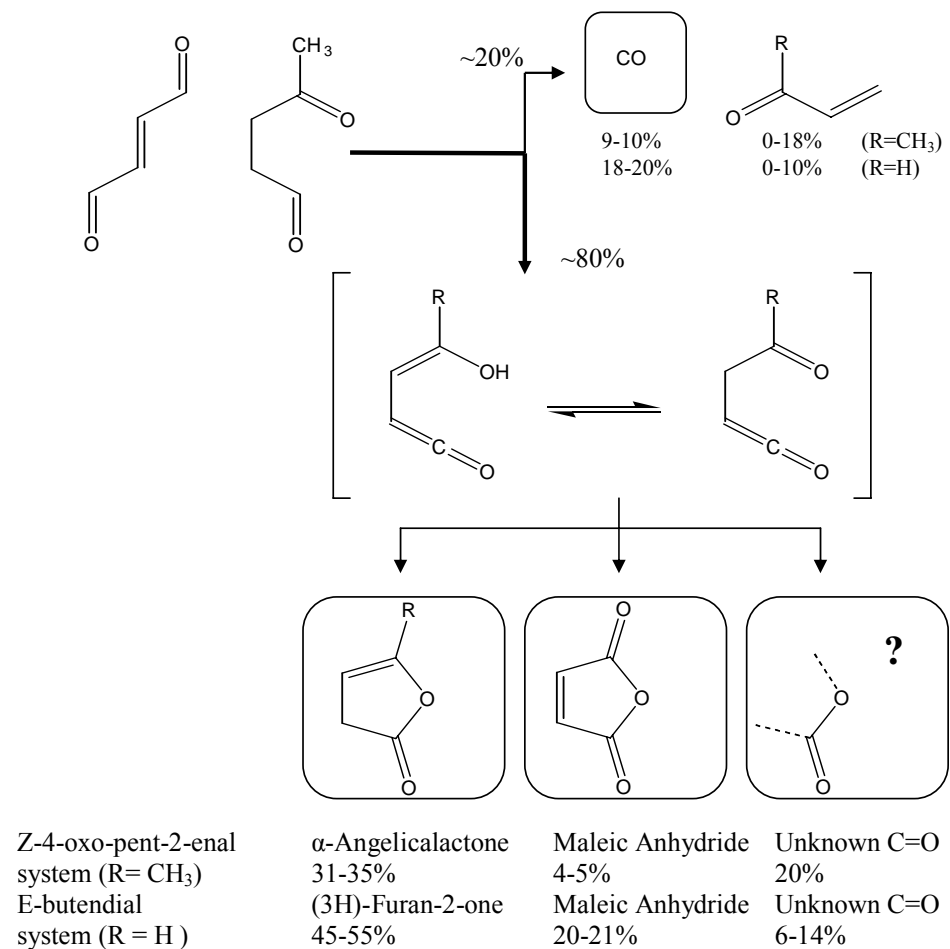
Xiang *et al.* J. Phys. Chem. A **2007**, 111,9025

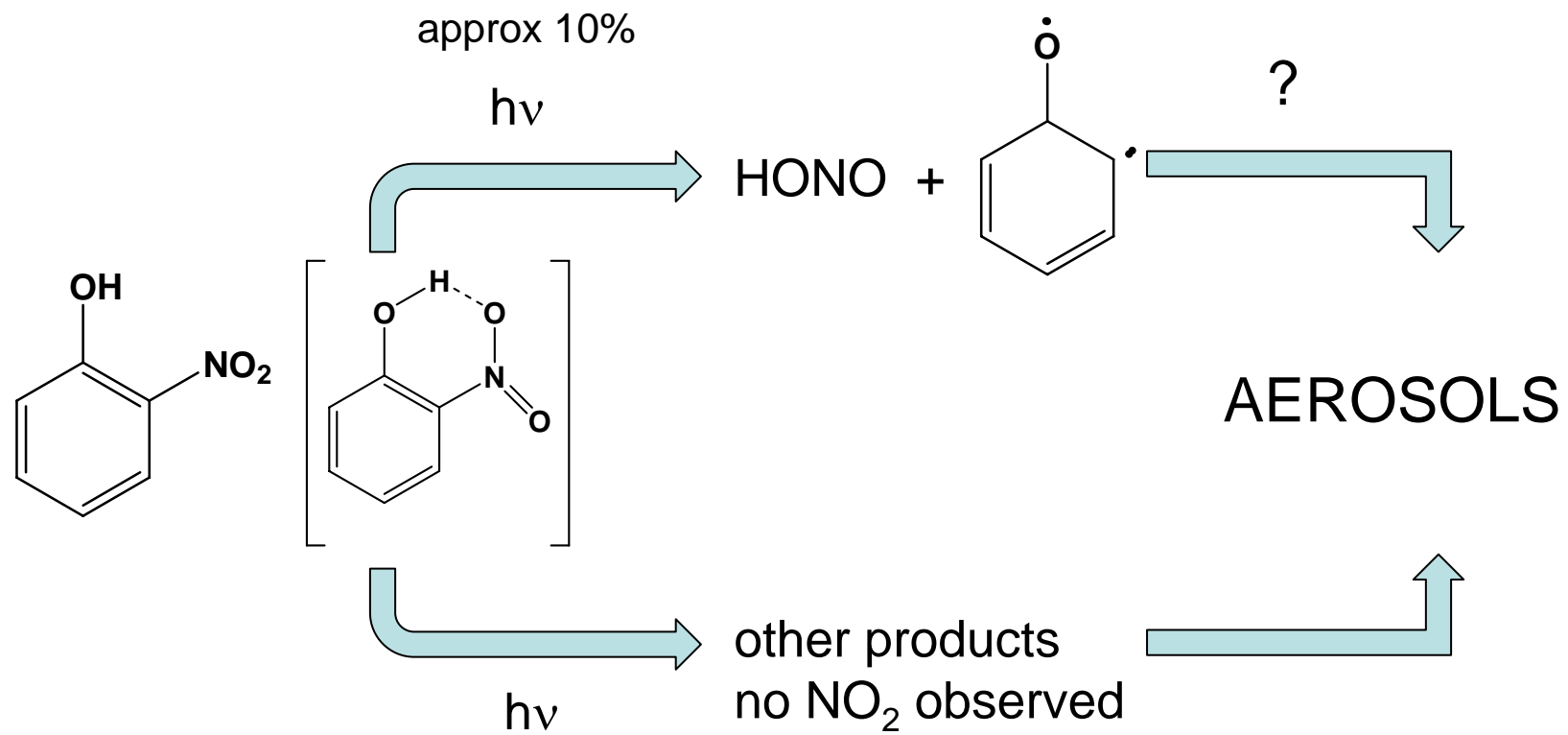
- Photolysis studied at 193, 248, 308, 351nm
- Observed ethane, methyl vinyl ketone and 5-methyl-3H-furan2-one
- Suggested pathways:

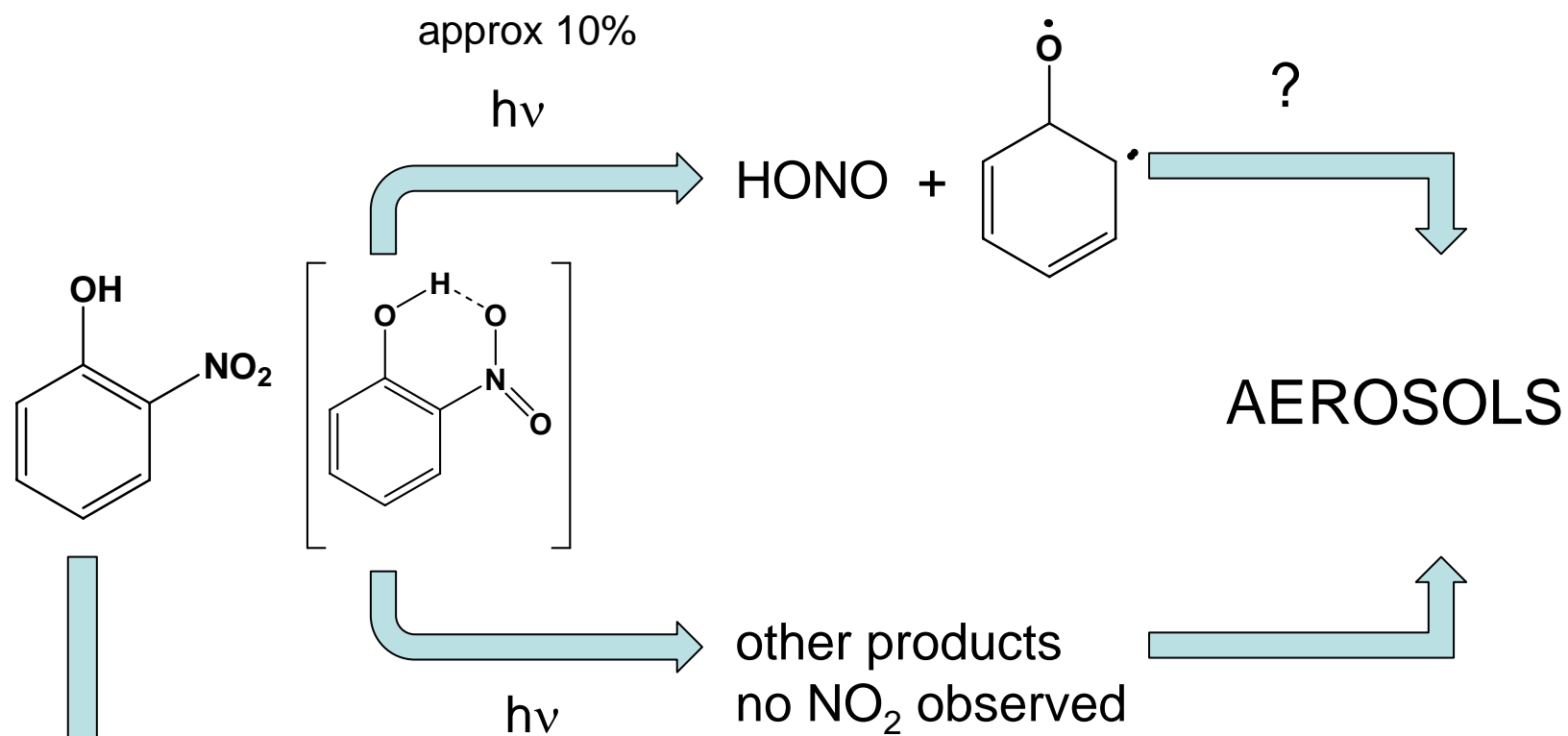


Earlier studies: (Bierbach *et al.* Environ. Sci. Technol. **1994**, 28, 715; Liu *et al.* Environ. Sci. Technol. **1999**, 33, 4212; Thüner *et al.* EUPHORE Report 2001, 41-46)

Possible photolysis pathways for unsaturated dicarbonyls (Thüner et al. 2001)







Photodissociation study
at 266 and 355 nm

- formation of nascent OH
observed at both wavelengths
- yield not quantified

(Wei et al. Chem. Phys. Lett. 463 (2008) 340-344)

Photolysis frequencies of nitrophenols in natural sunlight verified

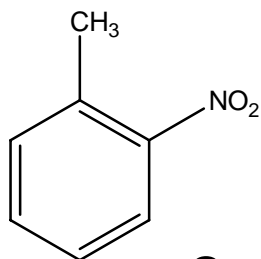
Valencia

Latitude: 39° 29'North Longitude: 0° 24'West

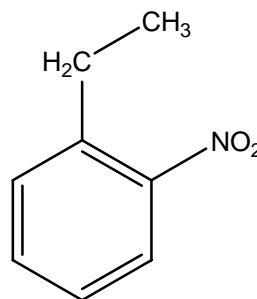
$J_{\text{nitrophenol}} \sim 3 \times 10^{-4} \text{ s}^{-1}$ (July 2007)

- Aerosol yield variable (30-60%)
- Density also variable 0.8 – 1.2 g cm⁻³

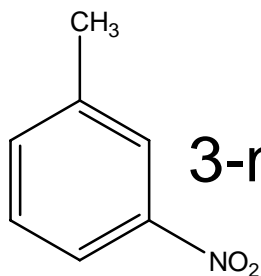
HONO formation observed for the photolysis of nitrotoluenes



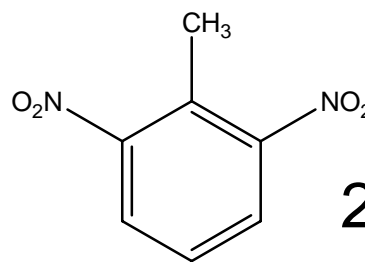
2-nitrotoluene



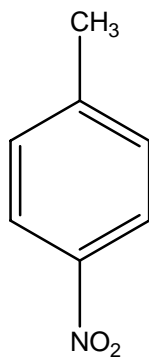
2-ethylnitrobenzene



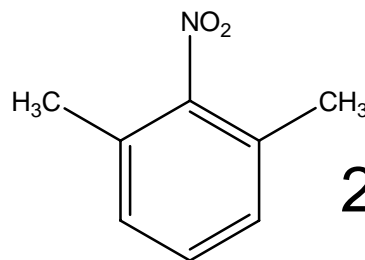
3-nitrotoluene
very low



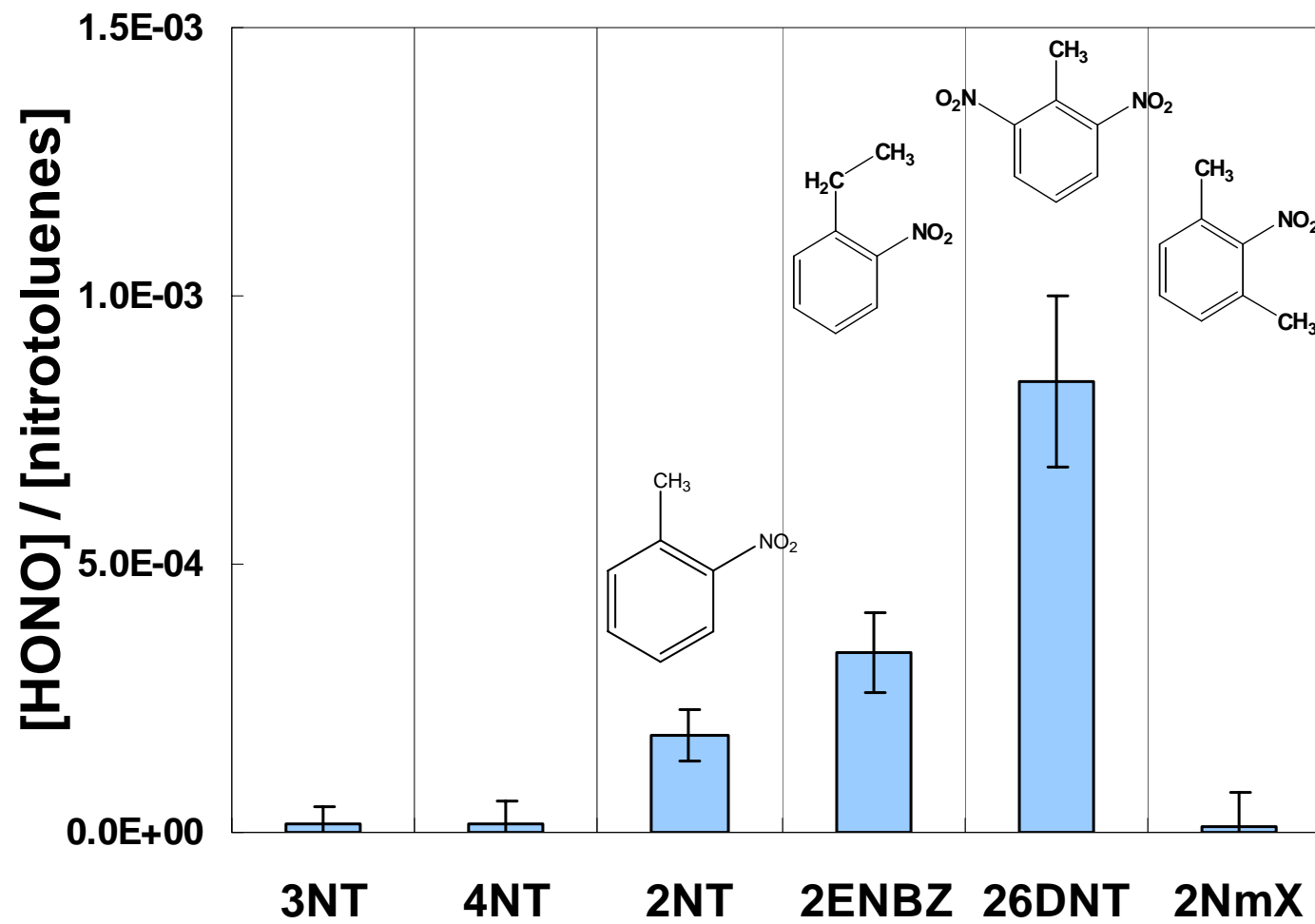
2,6-dinitrotoluene



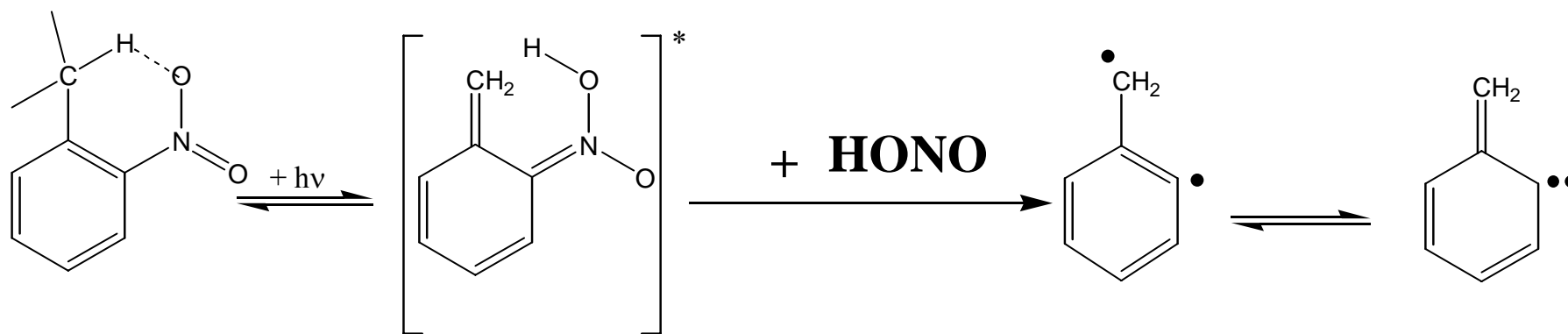
4-nitrotoluene
very low



2-nitro -*m*-xylene
very low

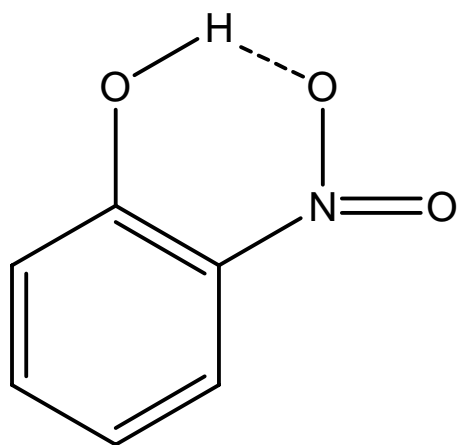
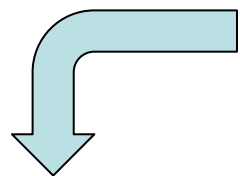


Proposed mechanism (speculative)

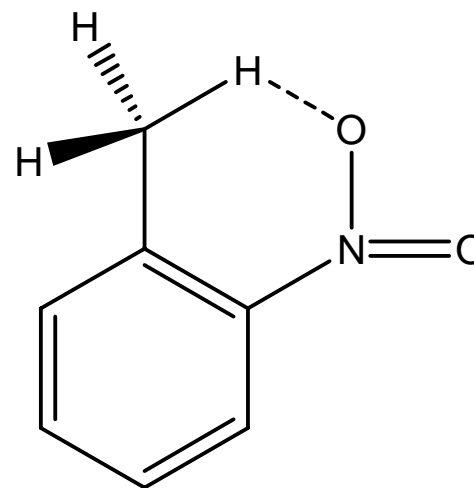


HONO formation not as high as that observed for nitrophenols

stronger intramolecular H-bonding



nitrophenol



nitrotoluene

Aromatic SOA formation - effect of NO_x

- SOA yields under low-NO_x conditions substantially exceed those obtained under high-NO_x conditions
- Suggests the importance of peroxy radical chemistry in SOA formation

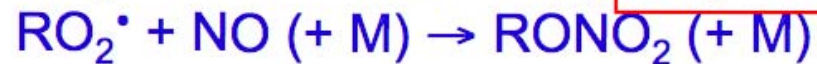
Sources: Song *et al.* Environ. Sci. Technol. **2005**, 39, 3143

Ng *et al.* Atmos. Chem. Phys. **2007**, 7, 3909

Sato *et al.* J. Phys. Chem. A **2007**, 111, 9796

Reactions of organic peroxy radicals, RO_2^\bullet

- In the presence of sufficient NO:



- At low NO concentrations:



Aromatic SOA formation - effect of light intensity

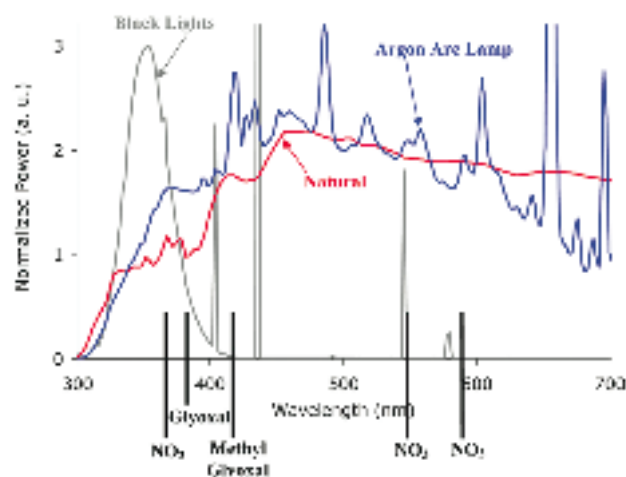


FIGURE 1. Natural, argon arc lamp, and black light source spectrums normalized to the total NO_2 photolysis rate with the average photolysis wavelength for select compounds.

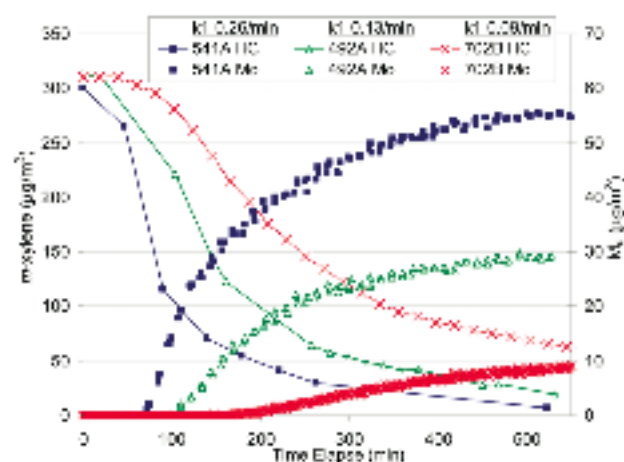


FIGURE 4. *m*-Xylene decay and aerosol formation (M_a) for three experiments with similar initial conditions conducted at different light intensities (k_1).

SOA formation increases significantly with light intensity
(measured as $k(\text{NO}_2)$ - 0.09 to 0.26 min^{-1})
Probably due to differing OH, HO_2 and RO_2 concentrations

Source: Warren *et al.* Environ. Sci. Technol. 2008

Aromatic SOA formation - effect of lamps

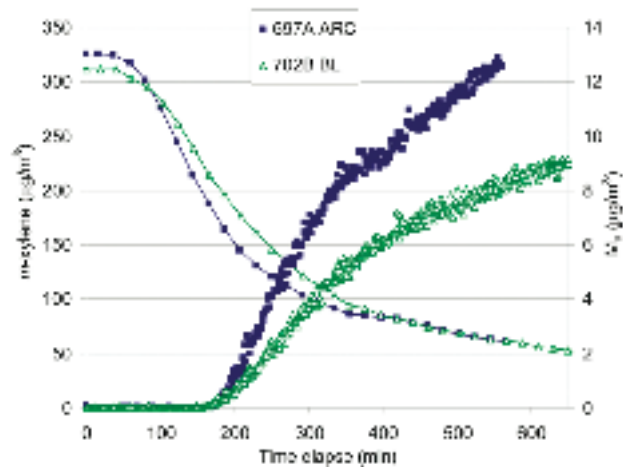


FIGURE 7. *m*-Xylene decay and aerosol formation (M_t) for experiments with similar initial conditions conducted at the same light intensity ($k_1 = 0.09 \text{ min}^{-1}$) that used different irradiation sources: an argon arc lamp (ARC) and black lights (BL).

Argon lamps produce 20% more SOA than black lights for $k(\text{NO}_2)=0.09 \text{ min}^{-1}$

Source: Warren *et al.* Environ. Sci. Technol. 2008

Global modeling of SOA from aromatic hydrocarbons

- Benzene has now been added to a global transport model
- Mechanism accounts for low and high-yield SOA pathways
- Aromatics yield more SOA when they react with OH in regions where $[\text{NO}]/[\text{HO}_2]$ is low
- Benzene is estimated to be the most important aromatic with regard to global SOA
- Total production nearly equal to that of toluene and the xylenes combined

(Henze *et al.* Atmos. Chem. Phys. 8, 2008, 2405)

THE END - THANKS