Developments in the Oxidation Mechanism of **Aromatic Hydrocarbons**

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Aromatic HCs: some facts

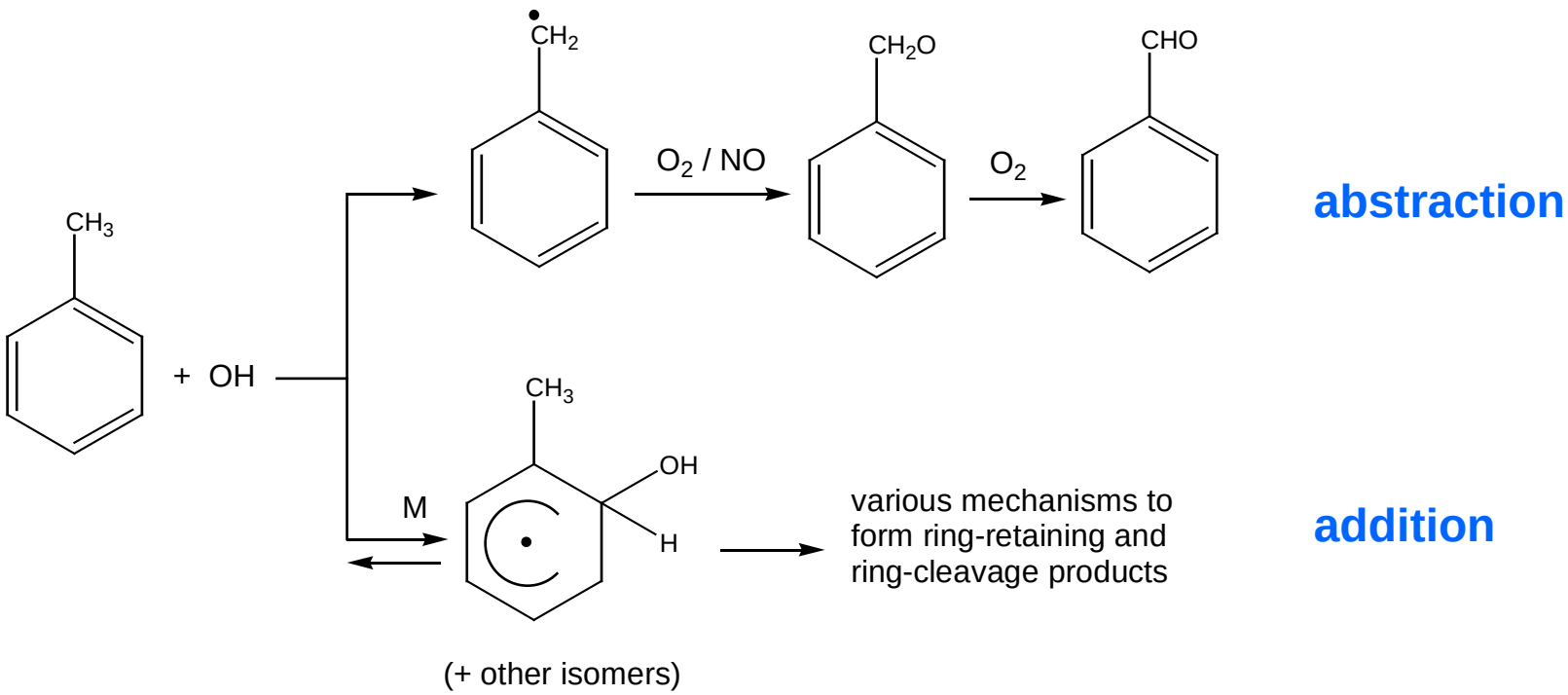
- major sources are combustion systems and solvent use
- Typical ambient concentrations of alkylated benzenes in cities:
    - low 25 ppbC high 590 ppbC
- Aromatic hydrocarbon photooxidation is alledged to make a significant contribution to secondary organic aerosol (SOA) formation in urban air

Aromatic HCs: some facts

- Significant impact on photooxidant formation in urban areas (Derwent *et al*. 90/98)
- 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

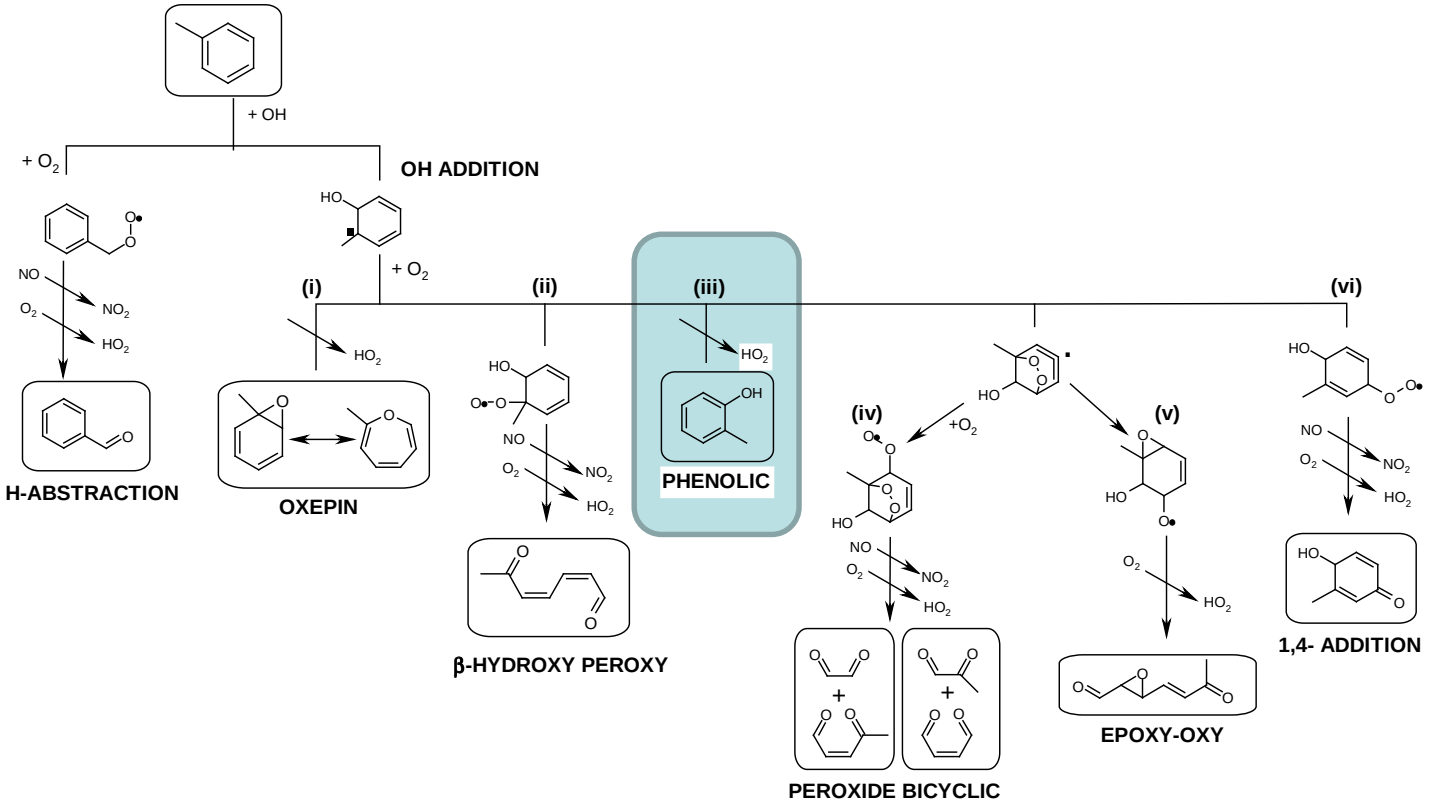
Primary oxidation steps

BTX: benzene, toluene, xylene isomers



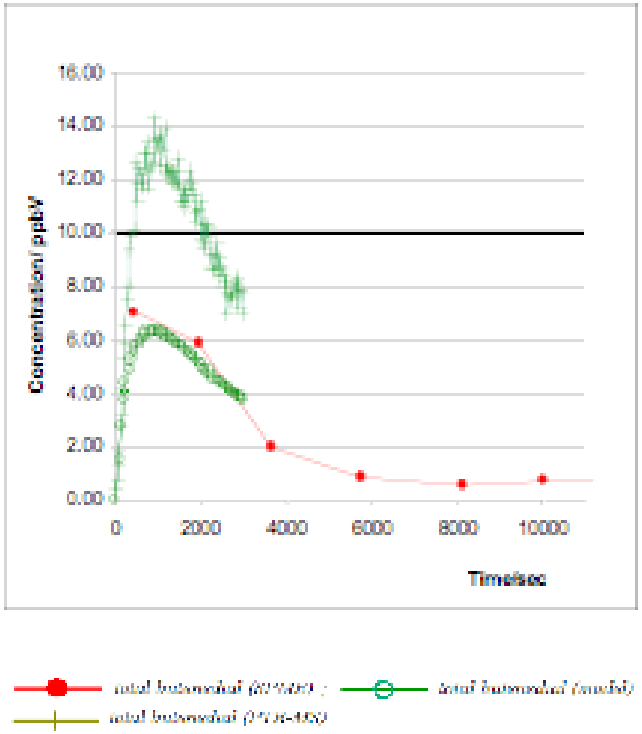
Recent review of the kinetics of aromatic-OH-adducts with O_2 and NO_2 in:
R. Koch, R. Knispel, M. Elend, M. Siese und C. Zetzsch, *Atmos. Chem. Phys. Discuss*. **2006**, *6*, 7623

Gas phase OH radical photooxidation of aromatic hydrocarbons

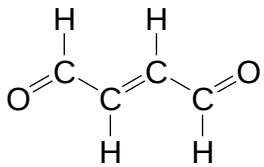


Simplified photooxidation mechanism from the „EXACT“ final report

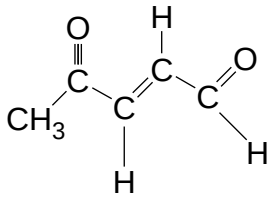
Formation of Unsaturated γ-Dicarbonyls (dicarbonyl route)



Yields of butenedial from experiment (EUPHORE) determined using PTRMS and SPME and from the MCM



butenedial



4-oxo-2-pentenal

have now been detected and quantified in the oxidation of benzene and toluene by FTIR, PTRMS and SPME (EUPHORE and Leipzig)

(Berndt and Böge, PCCP **2006**, *8*, 1205-1214)

- yields of butenedial match MCM prediction but those of 4-oxo-2-pentenal do not.

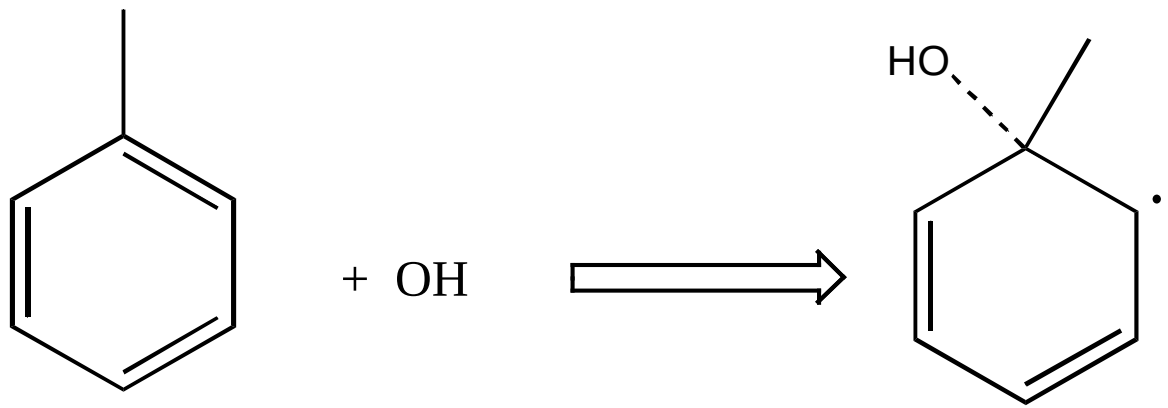
- yields associated with high error

IPSO addition of OH to the AH ring

- addition of OH occurs preferably to a non-substituted position

- ipso addition of OH, i.e. addition to a substituted position, always thought to be unimportant

- examples of OH addition to non-fully substituted aromatics in the liquid phase (e.g. Schuler *et al*., J. Phys. Chem. A, 106, 12178-12183 (2002))

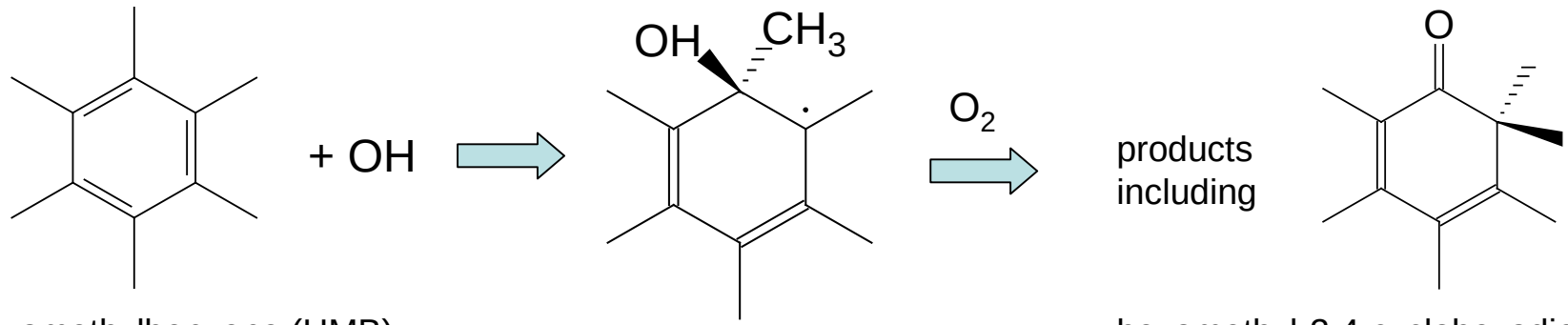


possible IPSO OH radical addition to toluene

IPSO addition of OH to the AH ring

• Evidence is emerging that OH radical ipso addition to non-fully substituted aromatics occurs in the gas phase

See for example:
Berndt and Böge, Int. J. Chem. Kinet., 33, 124-129 (2001)
Johnson *et al*., J. Photochem. Photobiol. A, 176, 98-106 (2005)
Koch *et al*., Atmos. Chem. Phys., 7, 2057-2071 (2007)



Hexamethylbenzene (HMB)
(Koch *et al*., 2007)

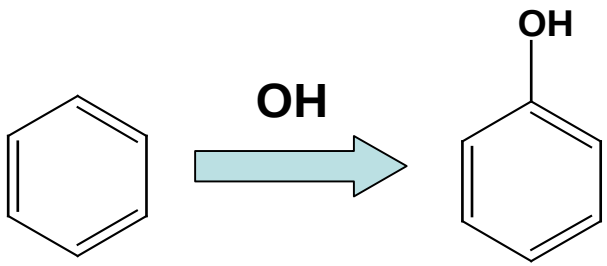
hexamethyl-2,4-cyclohexadienone
(Berndt and Böge, 2001)

Reaction of OH-adduct with O_2: $k = 1.2 \times 10^{-13}$ cm^3 s^{-1}
~200 times faster than O_2 with toluene-OH adduct
Demonstrates fast initial reaction
(k_{OH} (295 K) = 1.13×10^{-10} cm^3 s^{-1} : Berndt and Böge, 2001)

IPSO addition of OH to the AH ring

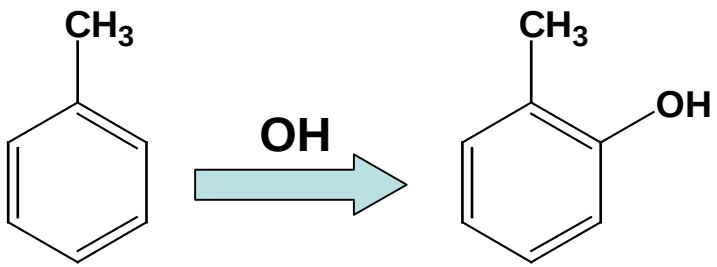
- HMB results show that ipso addition occurs for fully substituted aromatics
- the results imply that ipso addition may occur for less substituted aromatics
- implications of results need further assessment

OH oxidation of benzene / toluene – ring-retaining hydroxylated products



50-60%*

*(Berndt and Böge, *Phys. Chem. Chem. Phys*., **2006**, *8*, 1205-1214)



+ isomers

16-18%

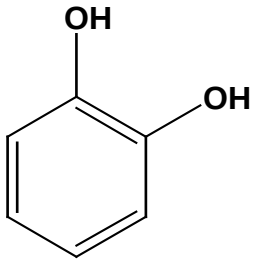
OH oxidation products of phenol and cresols

Reactant	Product	Yield (% molar)	Yield (lit)
phenol	1,2-dihyroxybenzene 1,4-benzoquinone 2-nitrophenol	78.1 ± **4.4** 4.6 ± **2.4** 5.2 ± **1.1**	 6.7 ± **1.5**
o-cresol	1,2-dihyroxy-3-methylbenzene methyl-1,4-benzoquinone 6-methyl-2-nitrophenol	60.8 ± **6.2** 10.5 ± **1.4** 5.5 ± **1.1**	 5.1 ± **1.5**
m-cresol	1,2-dihyroxy-3-methylbenzene methyl-1,4-benzoquinone 3-methyl-2-nitrophenol 5-methyl-2-nitrophenol	70.0 ± **5.2** 17.2 ± **2.3** - 4.2 ± **1.5**	 1.6 ± **0.1** **1.6** ± **0.1**
p-cresol	1,2-dihydroxy-4-methylbenzene 4-metyl-2-nitrophenol	64.1 ± **8.7** 7.6 ± 2.1	 10 ± **4**

Olariu et al. *Atmos. Environ.*, **2002**, *36*, 3685-3697

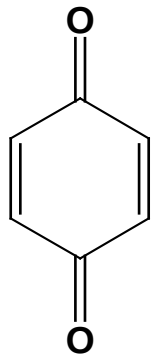
Major products are

1,2-dihydroxybenzenes

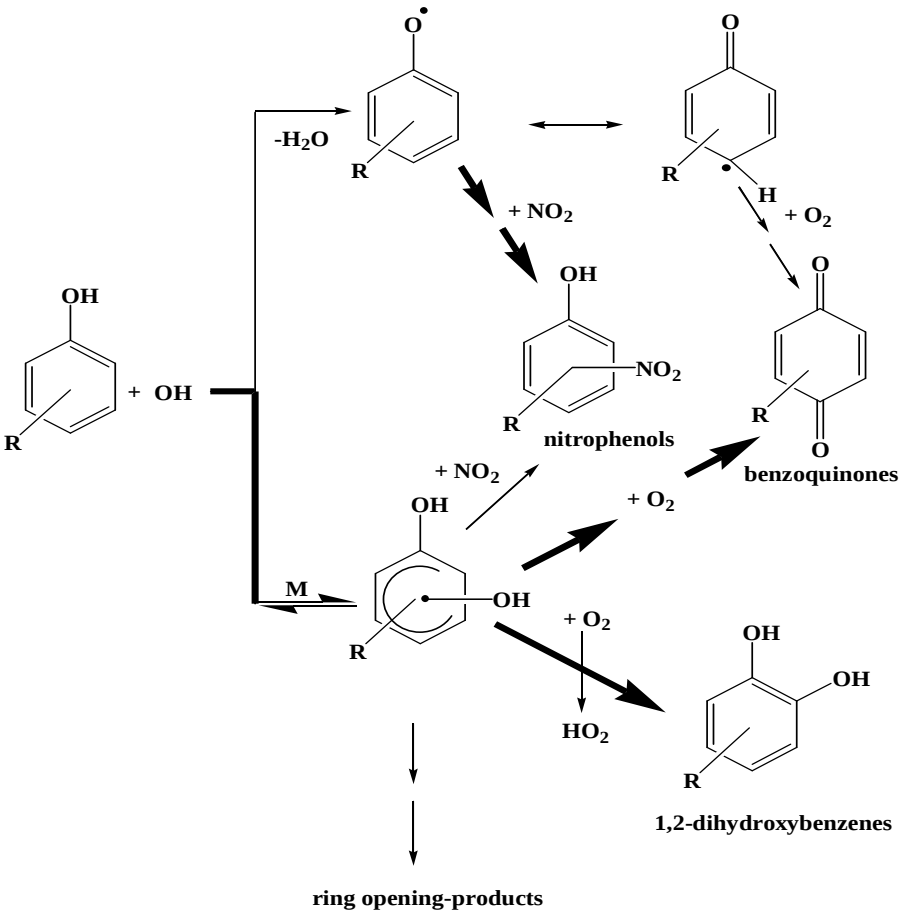


and

benzoquinones



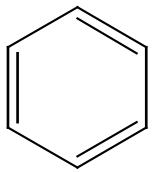
Simplified mechanism for the reaction of phenol/cresols with OH

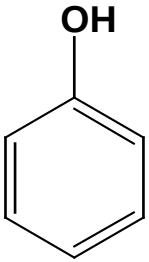


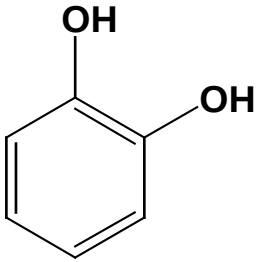
No evidence for the formation of small ring-fragmentation dicarbonyls such as glyoxal and methylglyoxal

IPSO OH-radical addition and formation of ring-retaining products could possibly be the reason

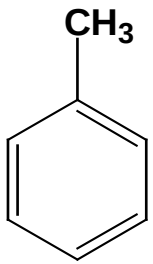
Rate data for hydroxylated aromatic compounds at 298 K

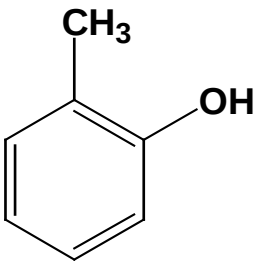


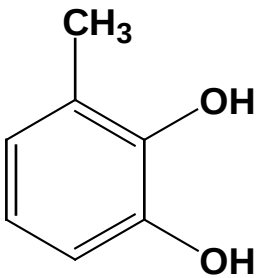




k(OH)	1.22×10^{-12}	2.7×10^{-11}	10.4×10^{-11}	$cm^3\ molecule^{-1}\ s^{-1}$
$k(O_3)$	$< 1 \times 10^{-20}$	not known	1×10^{-17}	$cm^3\ molecule^{-1}\ s^{-1}$
$k(NO_3)$	$< 3 \times 10^{-17}$	3.8×10^{-12}	9.8×10^{-11}	$cm^3\ molecule^{-1}\ s^{-1}$

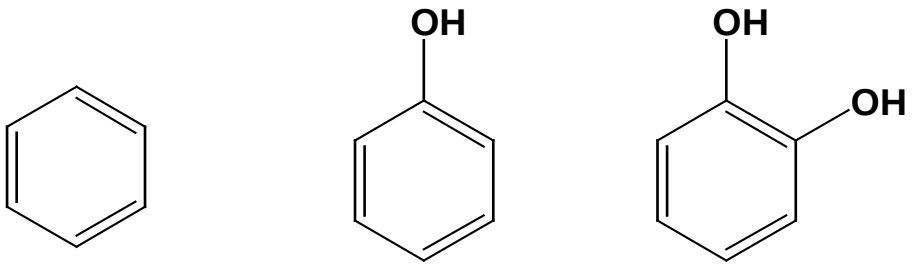






k(OH)	5.6×10^{-12}	4.1×10^{-11}	20.5×10^{-11}	$cm^3\ molecule^{-1}\ s^{-1}$
$k(O_3)$	$< 1 \times 10^{-20}$	3×10^{-19}	2.8×10^{-17}	$cm^3\ molecule^{-1}\ s^{-1}$
$k(NO_3)$	7×10^{-17}	1.4×10^{-11}	17×10^{-11}	$cm^3\ molecule^{-1}\ s^{-1}$

Lifetimes of aromatic compounds



τ(OH)	9.5 d	5.1 h	1.3 h
$\tau(O_3)$	>4.5 yr	-	1.7 d
$\tau(NO_3)$	>4 yr	8.8 min	**20.4 s**

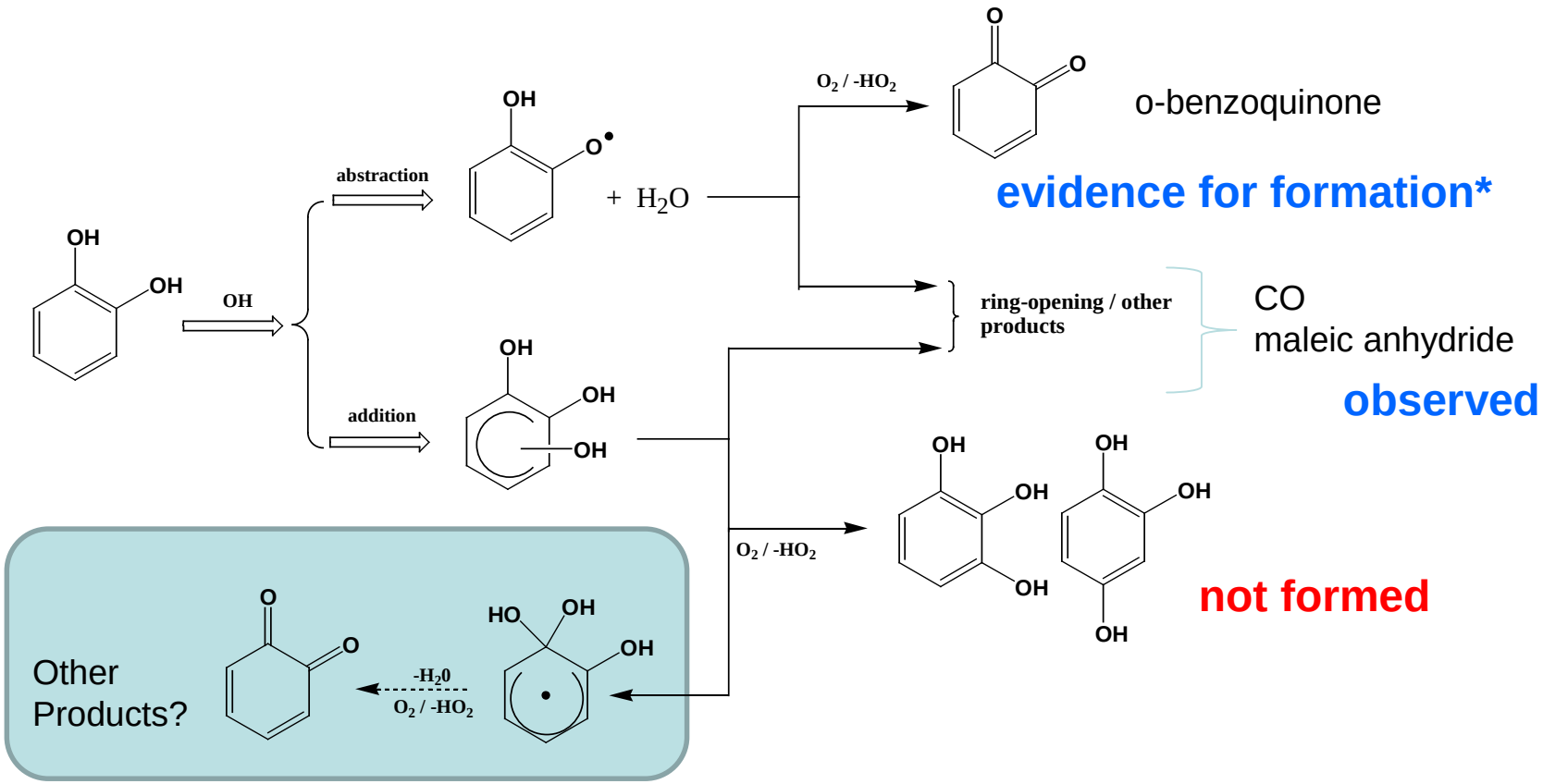
Atmospheric lifetimes calculated using:

[OH] a 12-h daytime average of 2 x 10^6 molecule cm^{-3}

[O_3] a 24-h average of 7 x 10^{11} molecule cm^{-3}

[NO_3] a 12-h nightime average of 5 x 10^8 molecule cm^{-3}

Dihydroxybenzene (catechol) OH oxidation products
(analysis with long path FTIR)



Ipso OH addition?

An intermediate „ketene“ absorption is observed

(*4-methyl-ortho-benzoquinone identified in OH + 4-methyl-1,2-dihydroxybenzene)

Dihydroxybenzene (catechol) OH oxidation products

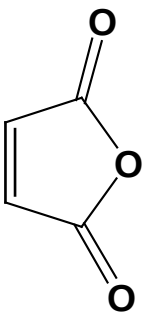
Main observations:

1,2,3-trihydroxybenzene and **1,2,4-trihydroxybenzene** **not formed**

An intermediate infrared absorption due to a **ketene** group (-C=C=O) is observed

Infrared evidence for the formation of **o-benzoquinone** (and methylated derivatives)

Positive identification of **maleic anhydride** (4-7%) (precursor butenedial ?)



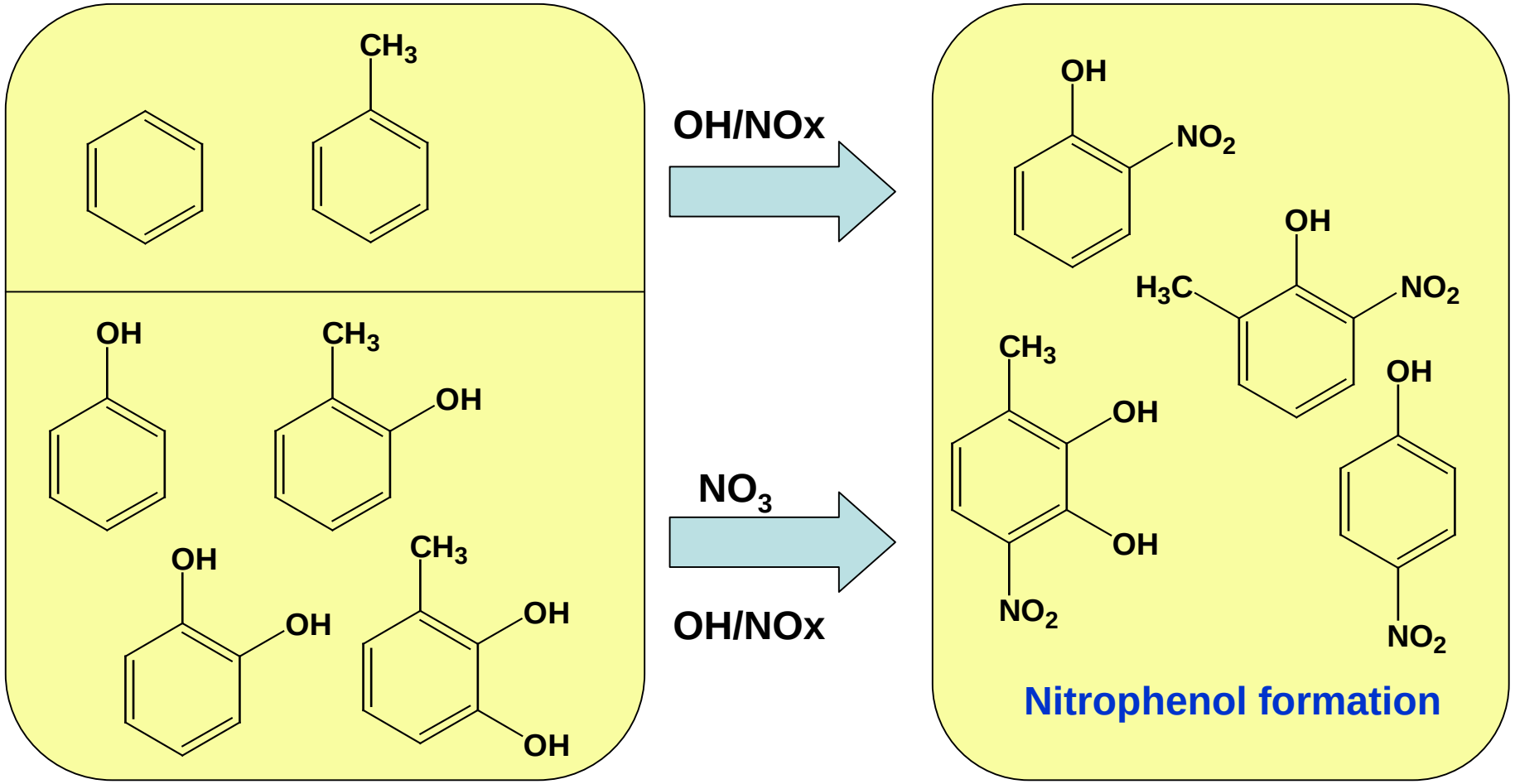
maleic anhydride

Formation of **CO** observed, yield increases with time,

Detection of CO shows ring opening is occurring
maleic anyhdride may also indicate ring-opening

Identification of **4-nitrocatechol**

Oxidation of aromatics to nitrophenols



Gas phase chemistry of nitrophenols

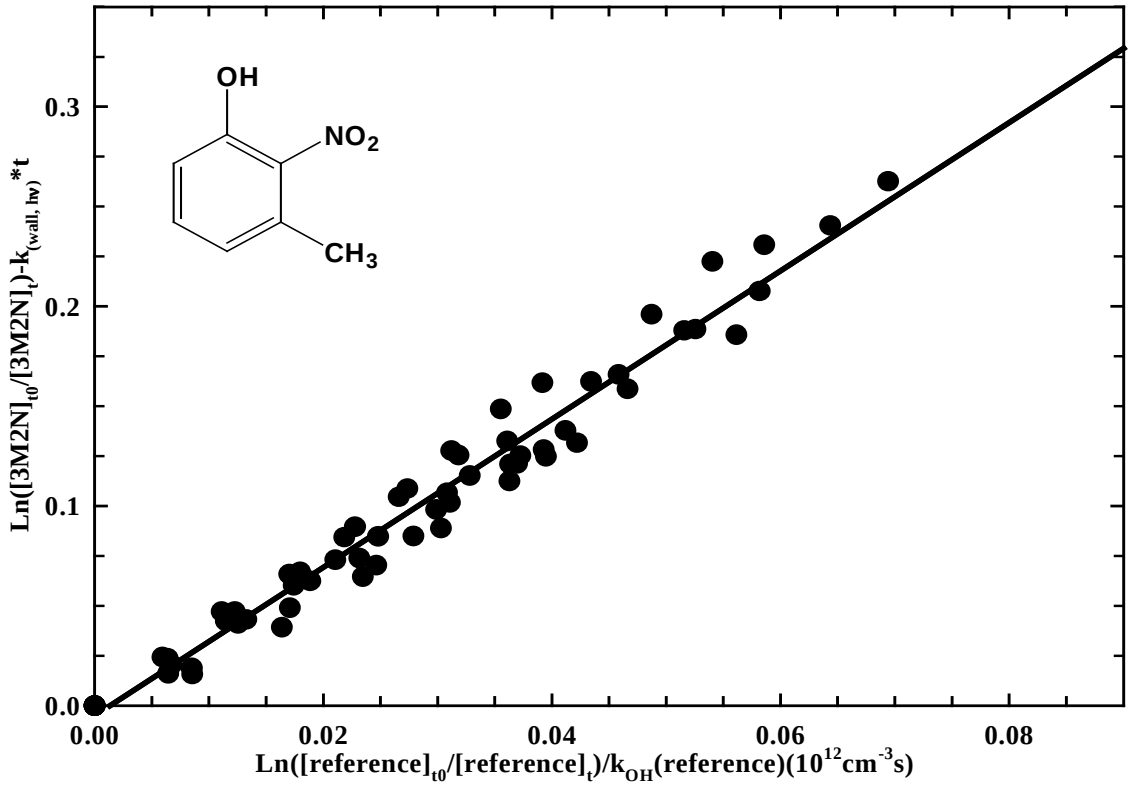
Status up to 2005:

Only a rate coefficient available for the reaction of OH with **2-nitrophenol** obtained by Zetzsch and coworkers (1985 Report) using FP-RF

Estimated rate coefficients for OH with **3-, 4-** and **5-methyl-2-nitrophenol**

Photolysis in solution was reported to be very slow

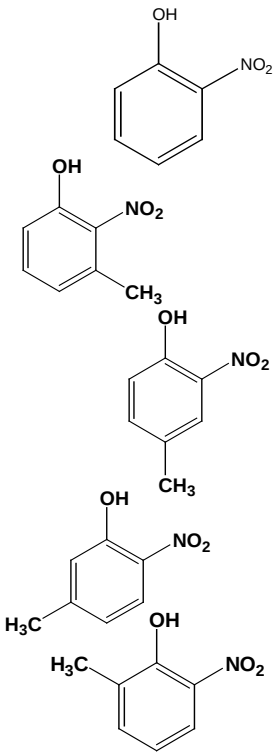
Plot of the kinetic data for the reaction of 3-methyl-2-nitrophenols (3M2N) with OH radicals



Data obtained at 1000 mbar total pressure of synthetic air by 298 K using with the relative kinetic technique and (•) ethene as reference hydrocarbon

Rate coefficients for the reactions of OH with 2-nitrophenols (NP) at 298 K obtained with the relative kinetic technique

(Bejan et al., *Phys. Chem. Chem. Phys.*, 2007, **DOI:** 10.1039/b709464g)

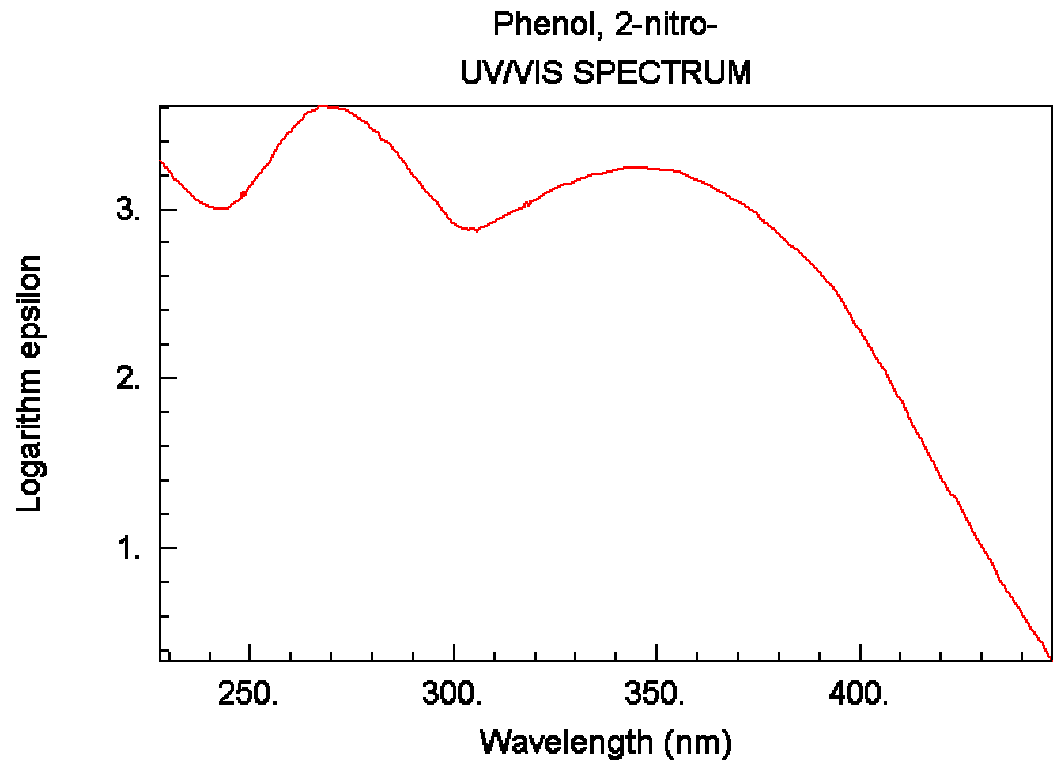


Compound	k_{OH} (10^{-12} cm^3 s^{-1})	k (literature) (10^{-12} cm^3 s^{-1})
NP	**~ 1**	0.9[a]
3M2NP	**(3.69±0.16)**	11.2[b]
4M2NP	**(3.46±0.18)**	5.38[b]
5M2NP	**(7.34±0.52)**	11.2[b]
6M2NP	**(2.70±0.17)**	-

a) Zetzsch and coworkers using FP-RF;

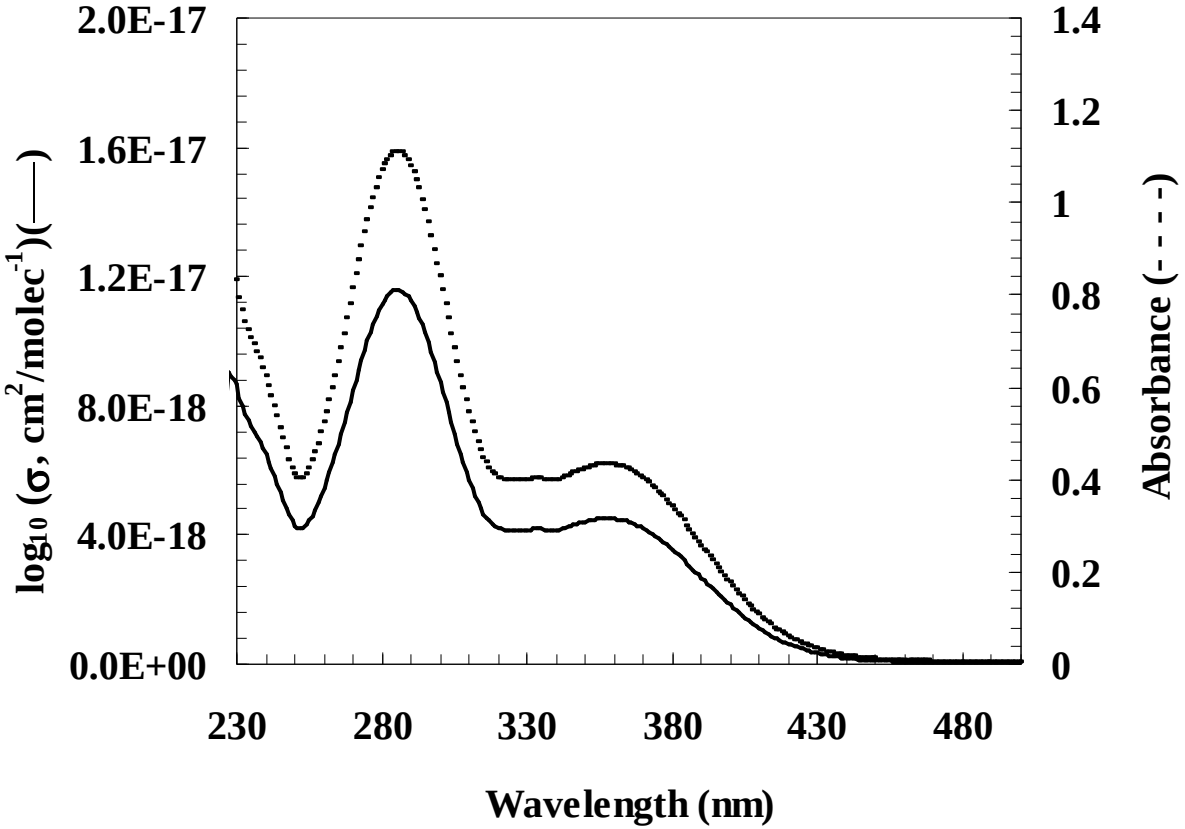
b) computer estimate by Meylan and Howard, *Chemosphere*, **1993**, *26(12)* 2293-2299.

UV spectra of 2-nitrophenols

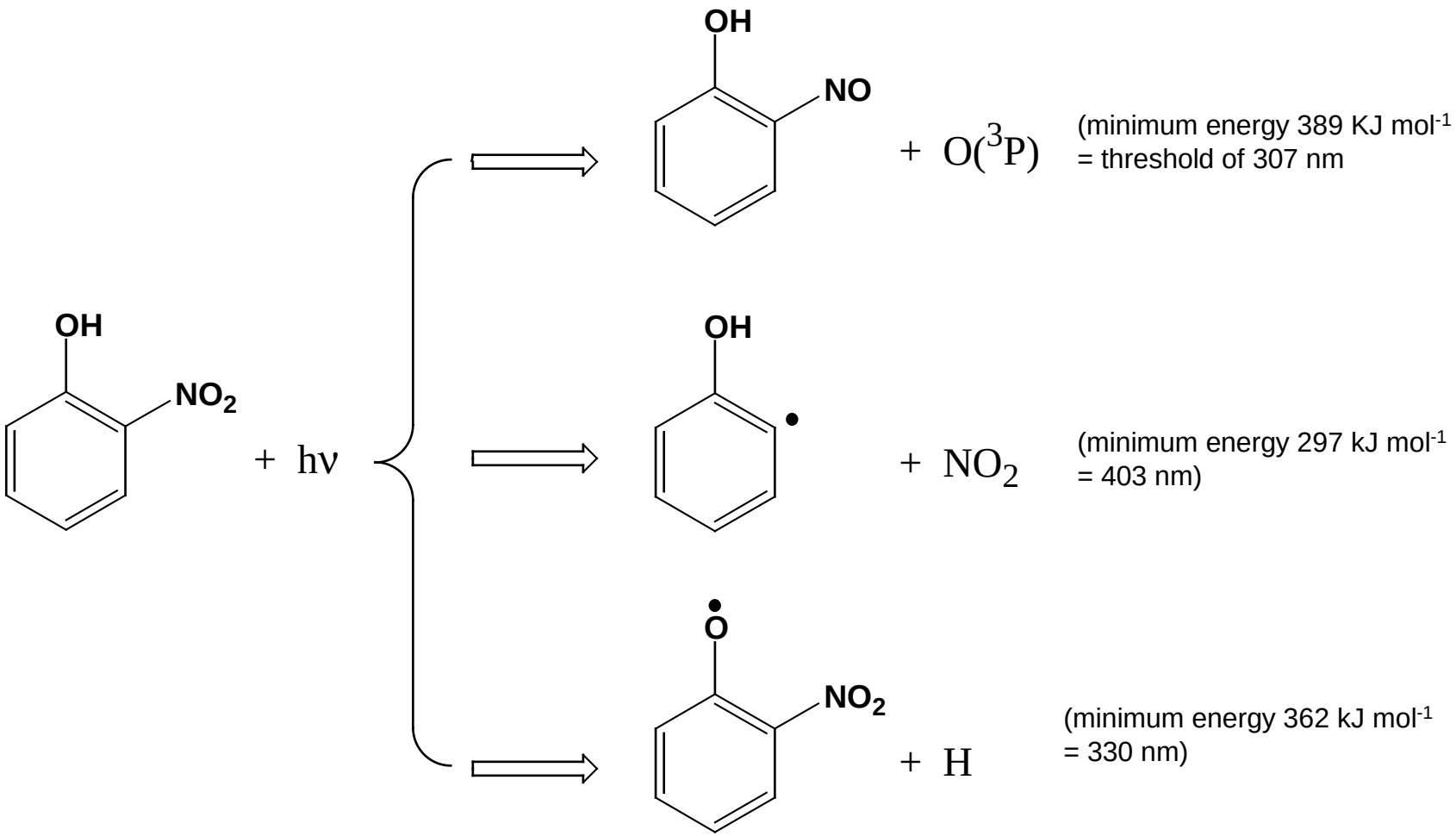


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

UV spectra of 3-methyl-2-nitrocresol

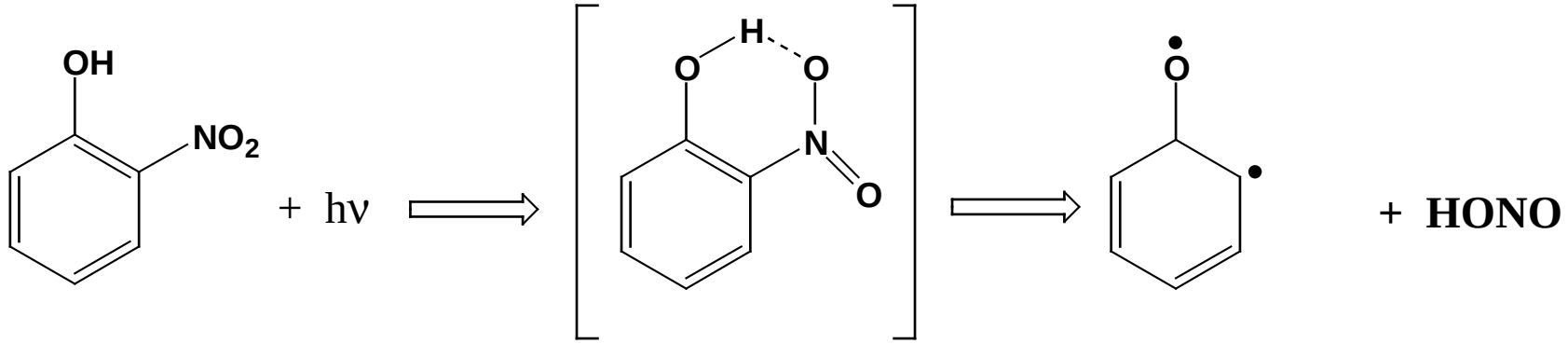


Proposed nitrophenol atmospheric photolysis pathways



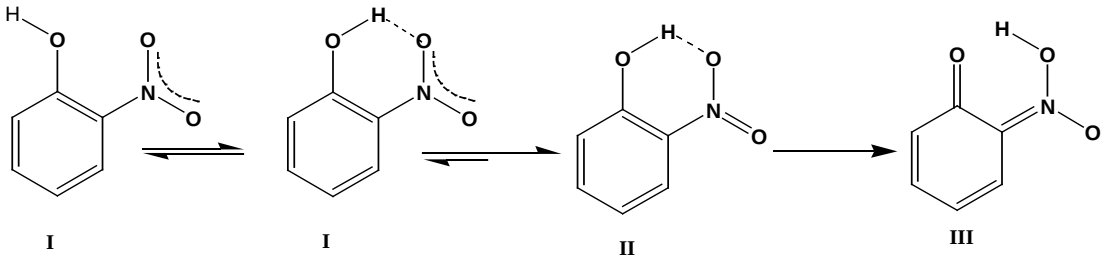
H-bonding in 2-nitrophenols

known strong intramolecular
H-bonding with NO_2



photolytic assisted H-atom transfer

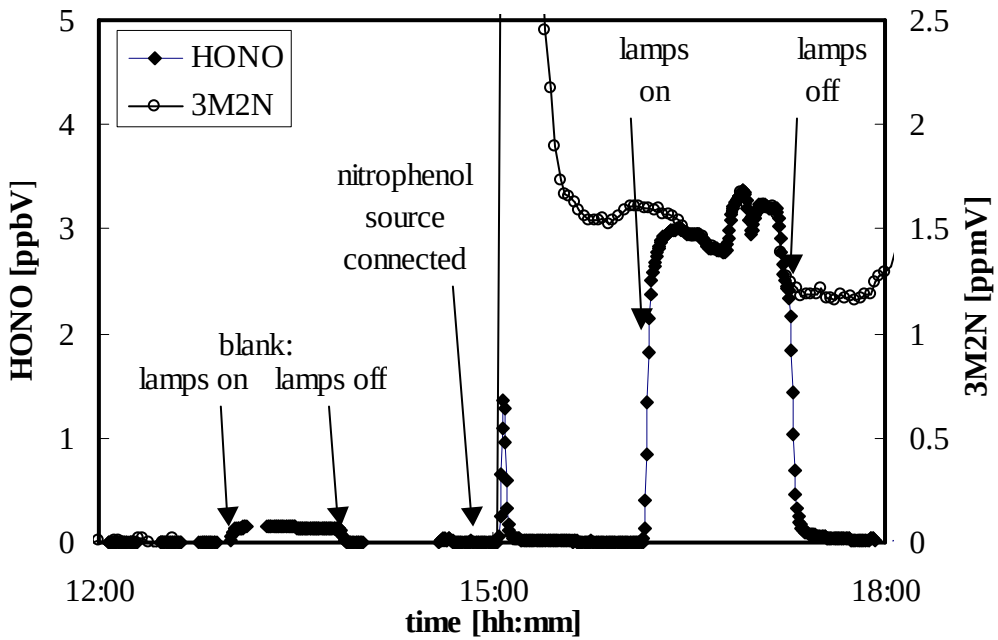
radical product + nitrous acid



Experiments on the photolysis of 2-nitrophenols

- experiments in a flow reactor using LOPAP for detection of HONO has shown that the photolysis of 2-nitrophenols forms HONO

(Bejan, et al., J. *Phys. Chem. Chem. Phys*., **2006** 8, 2028-2035)



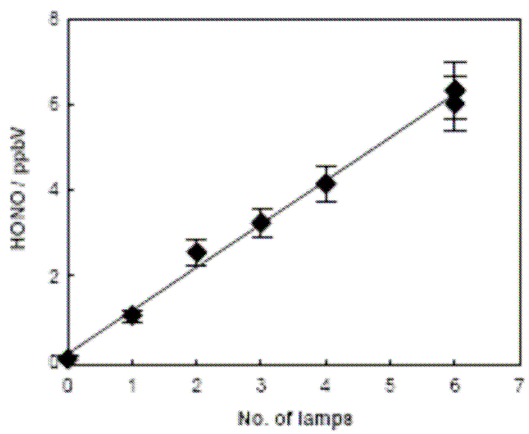
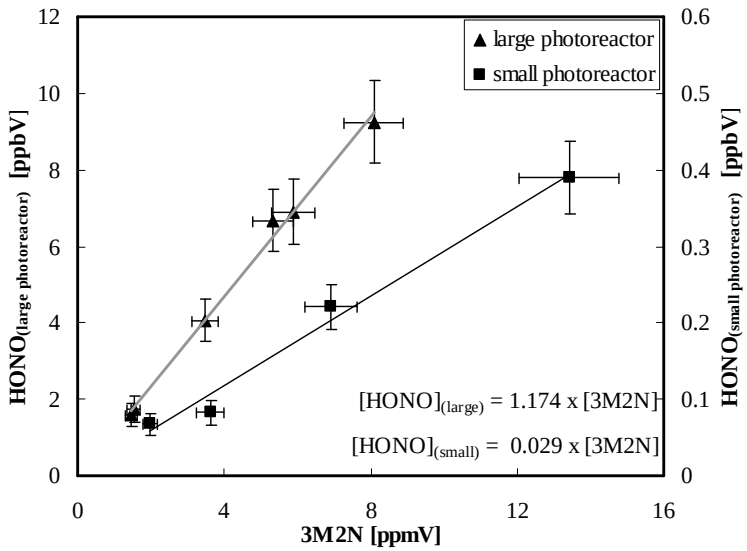


Fig. 4 HONO formation during the photolysis of 3M2NP in the large photoreactor as a function of the number of operating lamps ($t_{reac\,(large)}$ = 26.7 s).

Photolysis of 2-nitrophenols

Extensive tests performed to test mechanism of HONO formation



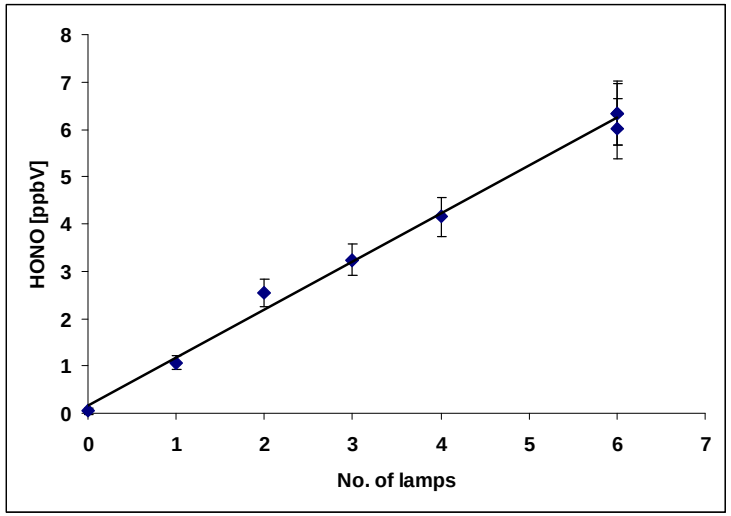
Tested effects of:

Number of photolysis lamps

Concentration of the nitrophenols

Change in surface to volume ratio

Bath gas (Ar, N_2, O_2, syn air)



Photolysis of 2-nitrophenols

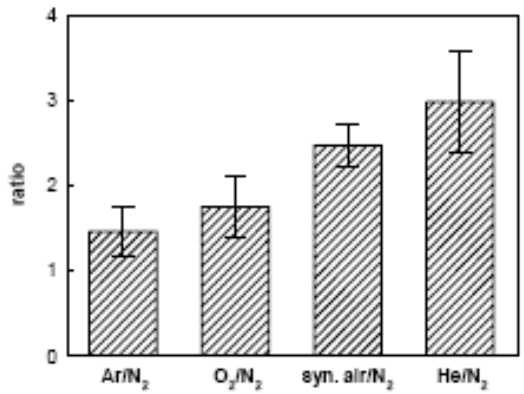
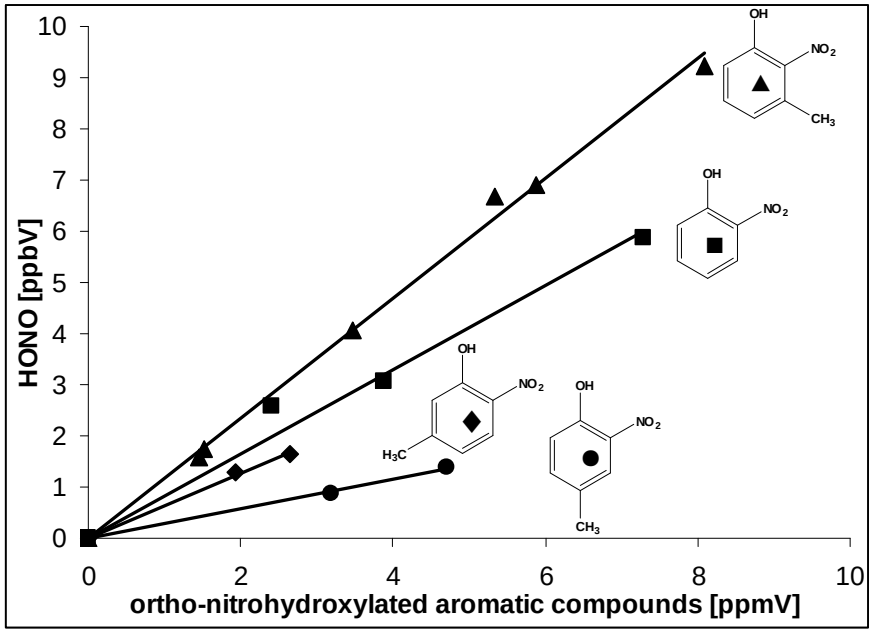


Fig. 6 Ratio of the HONO formation during the irradiation of 3M2NP in a certain buffer gas to the formation in pure nitrogen normalized to the same concentration of 3M2NP.

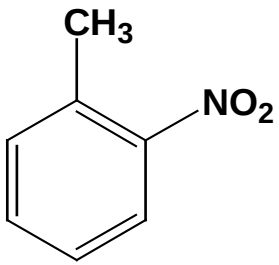


All observations are in line with a purely photolytic production of HONO

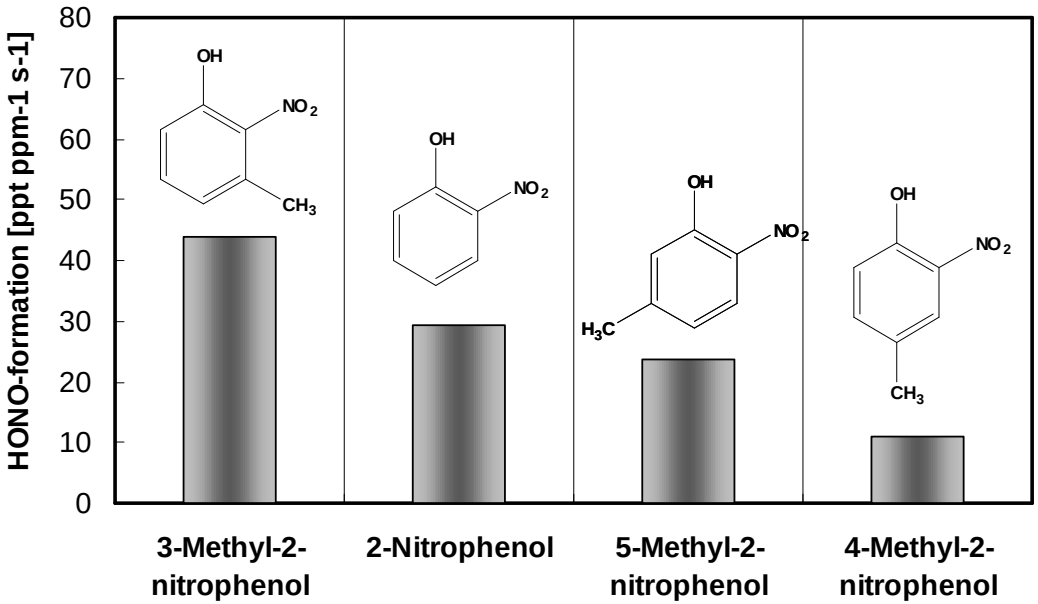
No formation of NO_2 observed

O_2 is not only a quench gas but appears to be active in the mechanism

Photolysis of 2-nitrophenols

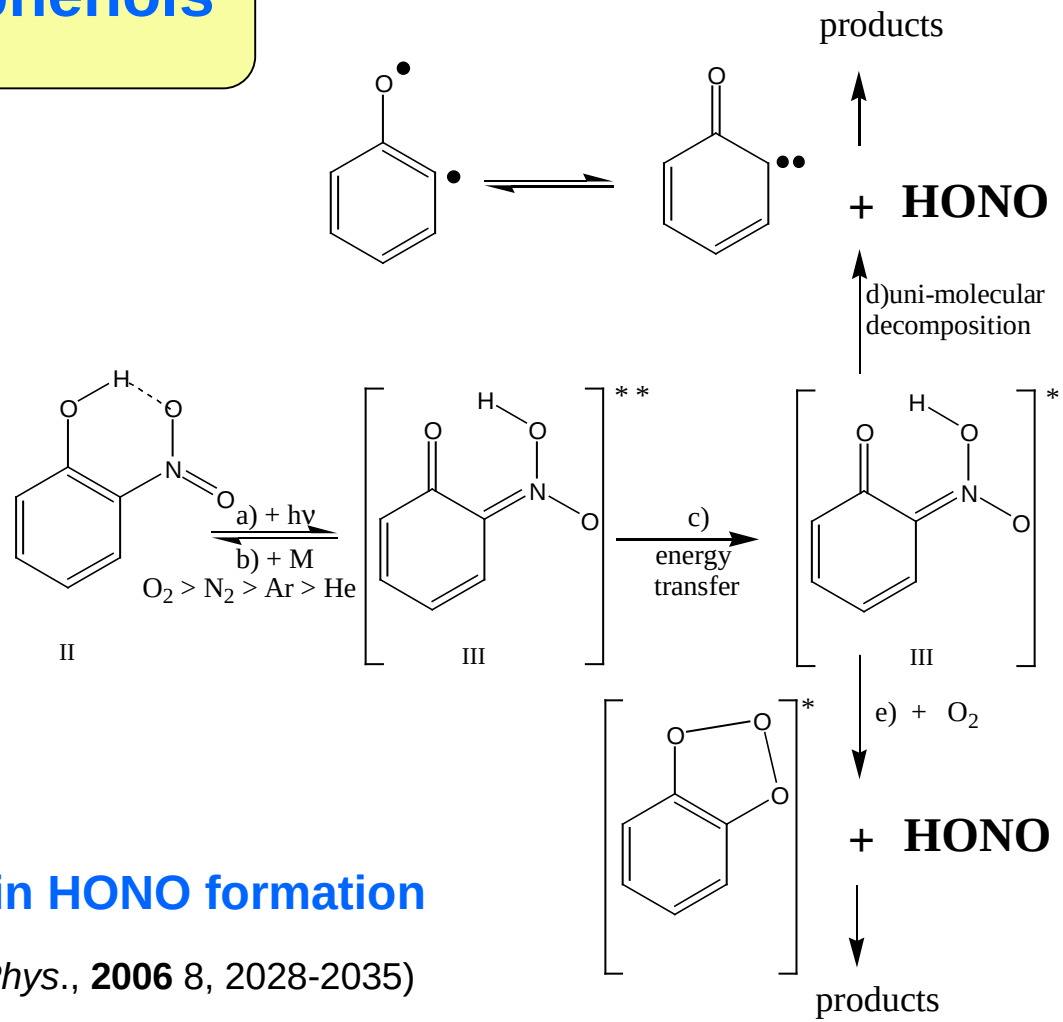


Photolysis of nitro-toluene and other alkyl nitro aromatics also observed to produce HONO



HONO formation rate (ppt ppm^{-1} s^{-1}) from different ortho-nitrohydroxylated monoaromatic compounds observed in a flow system (Bejan *et al*., 2006).

Photolysis of 2-nitrophenols



Mechanism proposed to explain HONO formation

(Bejan, et al., J. *Phys. Chem. Chem. Phys*., **2006** 8, 2028-2035)

Atmospheric lifetimes of 2-nitrophenols

Approximate atmospheric lifetimes of the 2-nitrocresols with respect to photolysis and reaction with OH radicals.

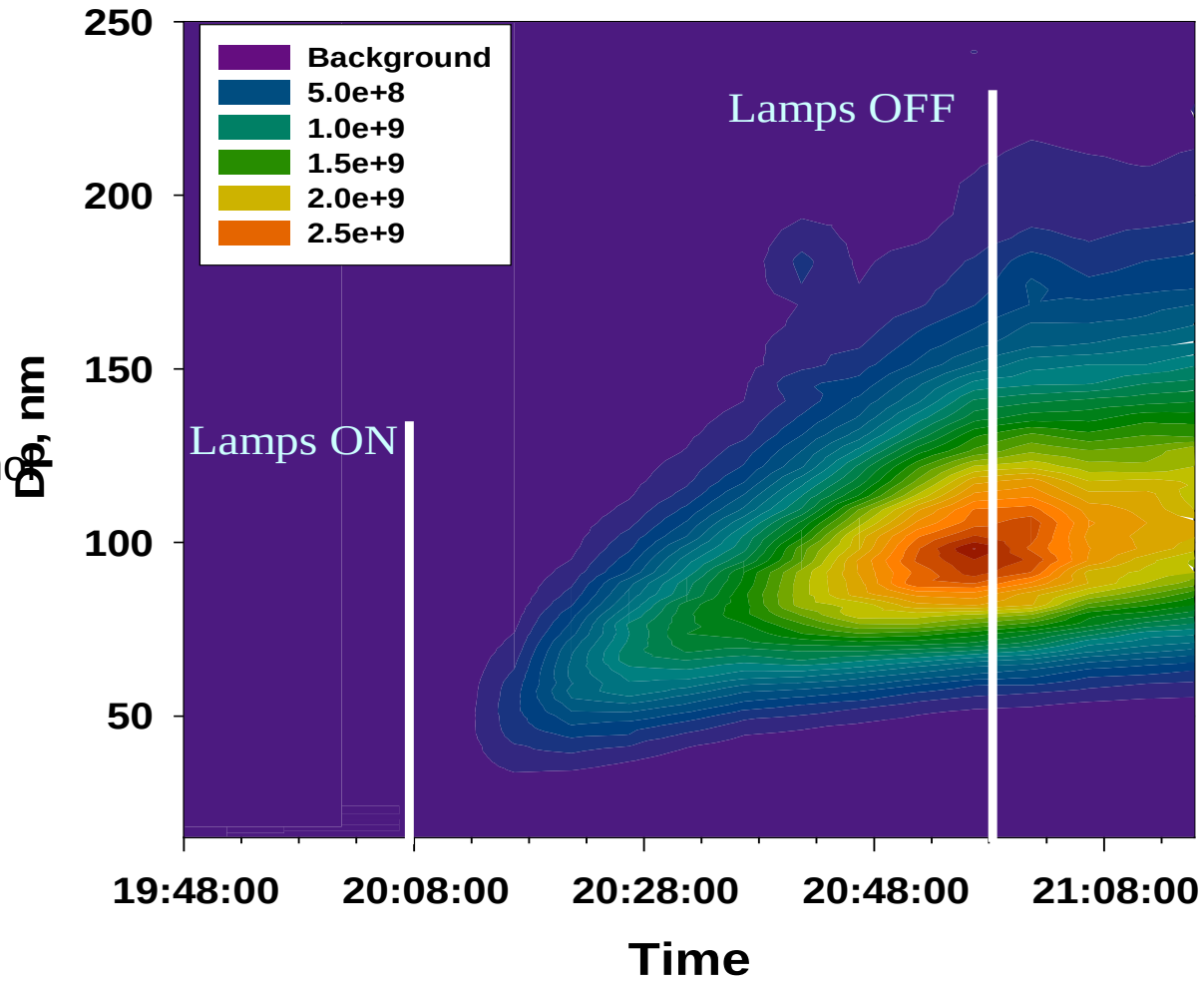
compound	2-nitrophenol	3-methyl-2-nitrophenol	4-methyl-2-nitrophenol	5-methyl-2-nitrophenol
$\tau_{h\nu}^{(a)}$ (min)	~ 64 min	~ 64 min	~ 4 h	~ 118 min
$\tau_{OH}^{(b)}$	7.2 d	~ 47 h	~ 50 h	~ 24 h

(a) Based on measured J's in EUPHORE for July from: P. Bardini, PhD UCC 2005 and new measurements 2007.

(b) Daily average OH = 1.6 x 10^6 cm-3 (Prinn *et al*., 1995).

Atmospheric chemistry of 2-nitrophenols

Time dependence of the aerosol size distribution measured during a typical photolysis experiment on 2-nitrophenol



Conversion of very low concentrations (1 ppb) results in aerosol formation

Atmospheric chemistry of 2-nitrophenols

- the photolysis frequency J(nitrophenol $\rightarrow$ HONO) is less than the total photolysis frequency J(nitrophenol)

- product channels other than HONO formation must be operative

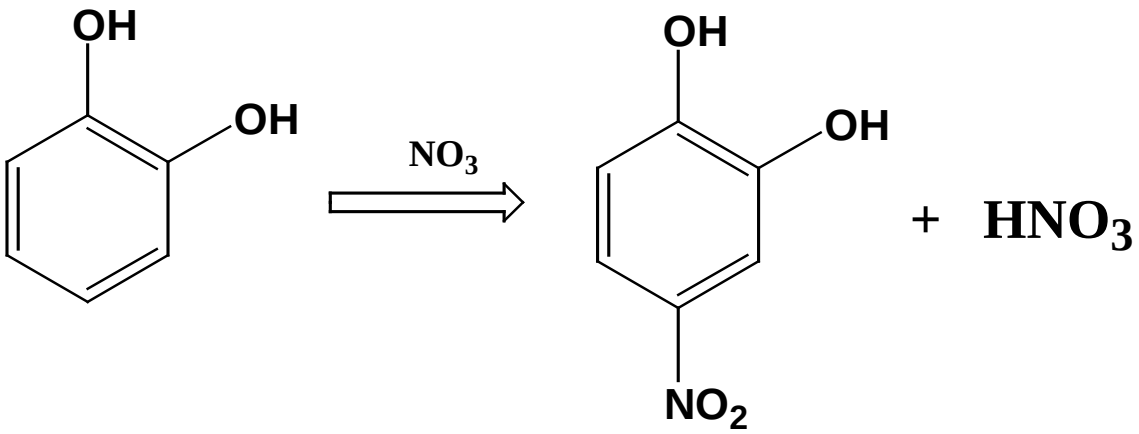
- the photolysis is very efficient in producing aerosol

- although the HONO channel may contribute to the aerosol formation it is not the major contributor

- studies are underway to better quantify the photolysis freqencies of nitrophenols and identify the source of the SOA formation

Dihydroxybenzene (catechol) - NO_3 reaction products

(work 2006)



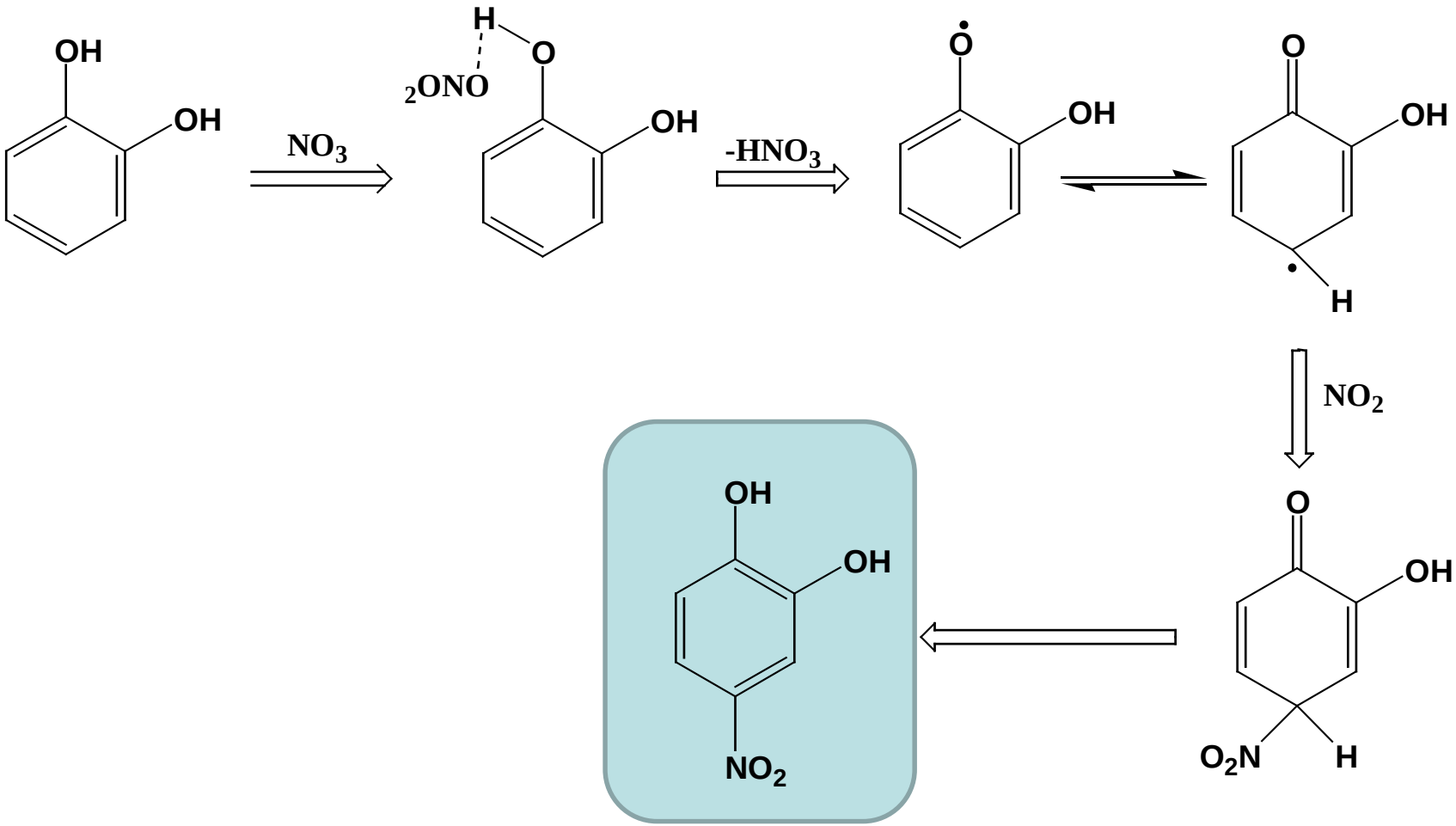
Only observe **4-nitro-1,2-dihydroxybenzene** and **nitric acid** as gas phase products

No indication of other products in the residual infrared spectrum

Aerosol is formed – still to be quantified

Dihydroxybenzene (catechol) - NO_3 reaction Mechanism?

(work 2006)



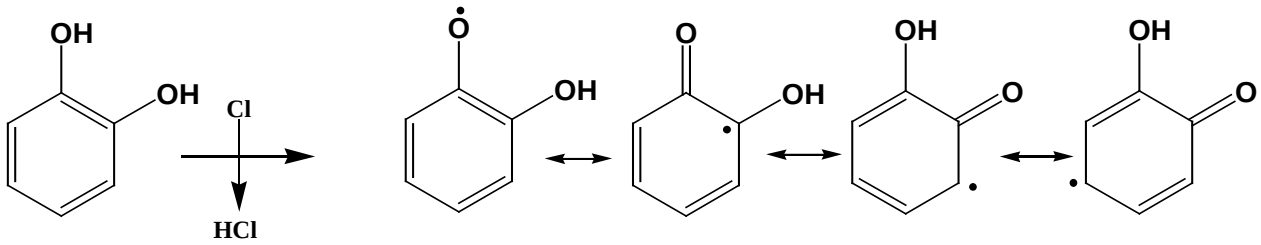
THANKS FOR YOUR ATTENTION

Assuming 1 ppb total 2-nitrophenols in the atmosphere

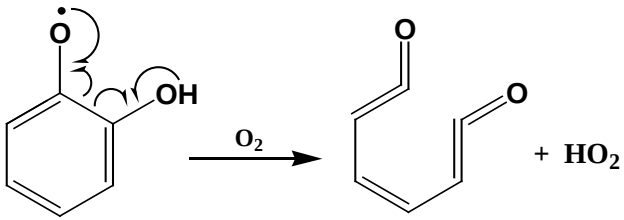
and a $J(NO_2)$ of 10^{-2} s^{-1}

would support a gas phase HONO product rate of 100 pptv/h

Ketene identity?

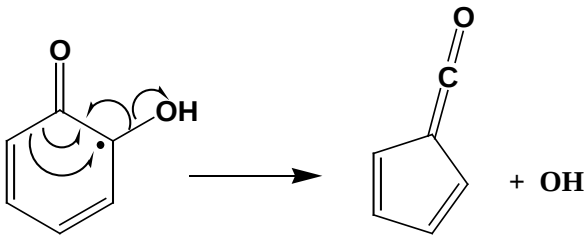


ring opening



2-butene-1,4-diketene

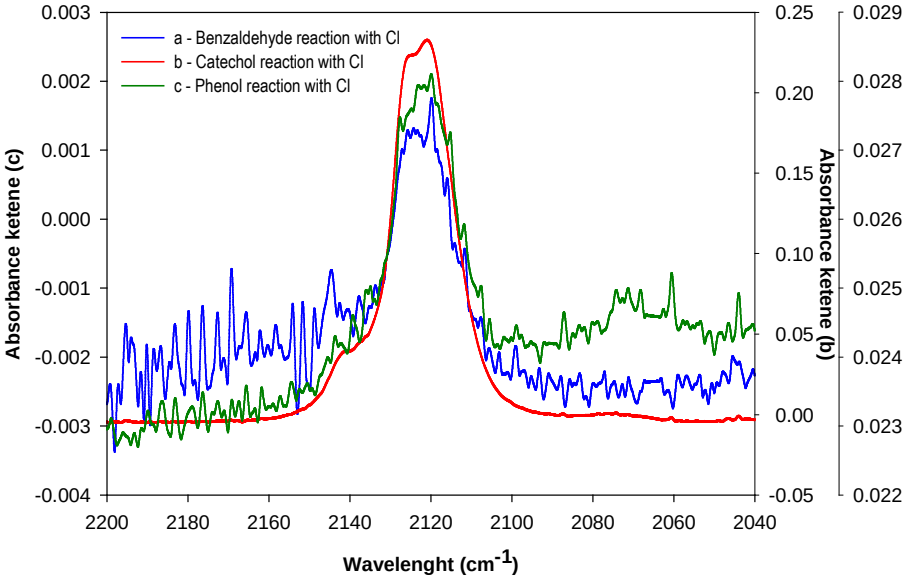
ring size reduction

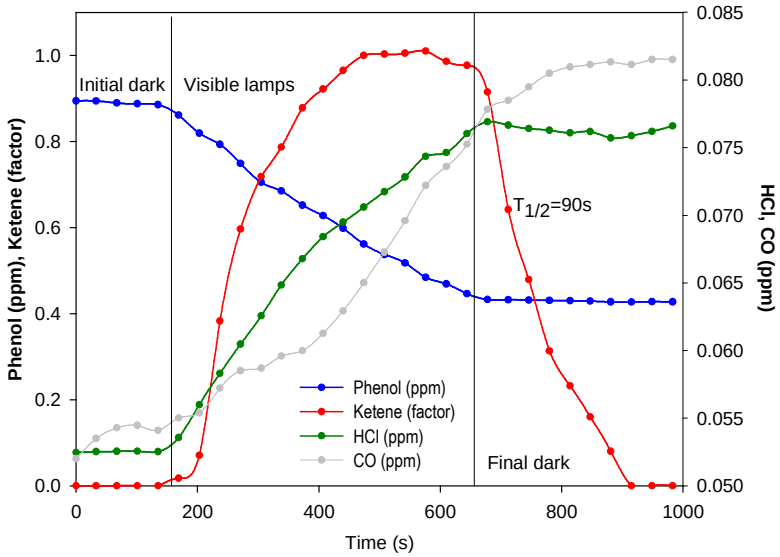


1,4-cyclopentadienyl-5-ketene

Observation of intermediate ketene absorptions

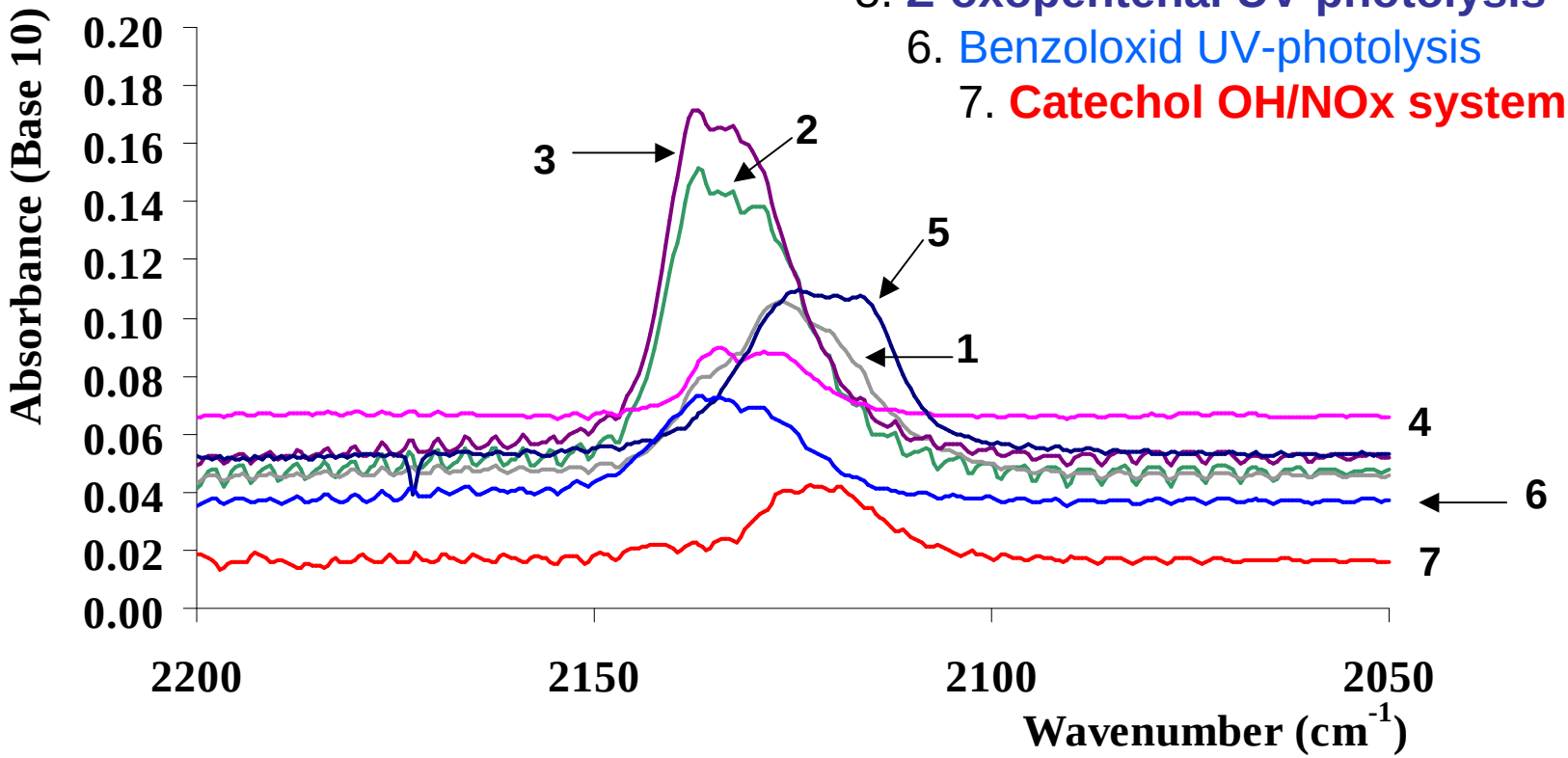
Phenoxy radicals generated from benzaldehyde, phenol and catechol by reaction with Cl atoms



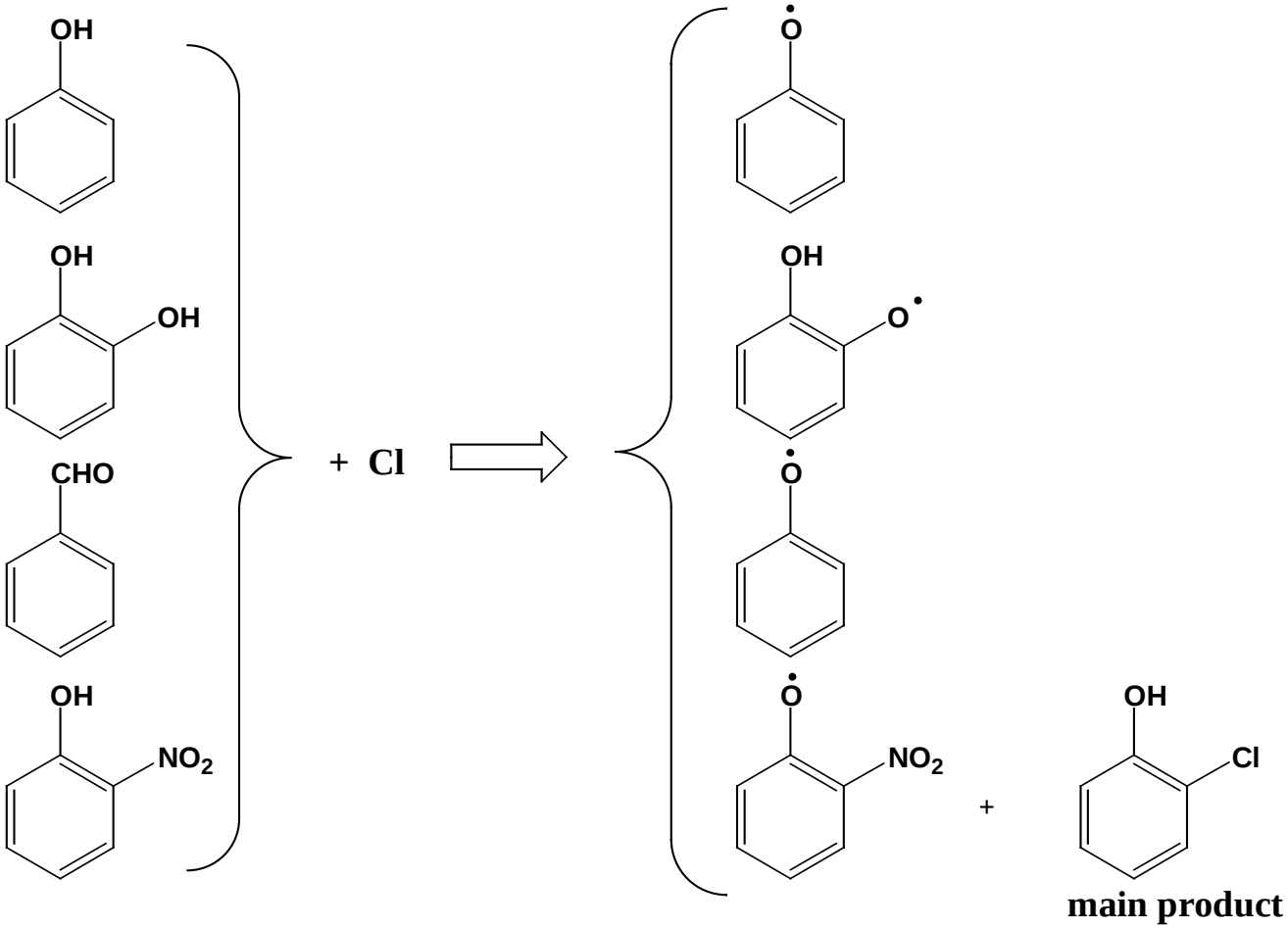


Ketene identity?

Ketene formation from:
1. **E,E-2-Methyl-2.4-hexadiendial UV-photolysis**
2. E,E-2.4-hexadiendial UV-photolysis
3. E.Z-2,4-hexadiendial UV-photolysis
4. Benzene oxid-oxepin VIS-photolysis
5. **Z-oxopentenal UV-photolysis**
6. Benzoloxid UV-photolysis
7. **Catechol OH/NOx system**



Generation of phenoxy radicals



Laboratory photolysis rates and steady-state OH radical concentrations observed for 2-nitrophenols in a photoreactor.

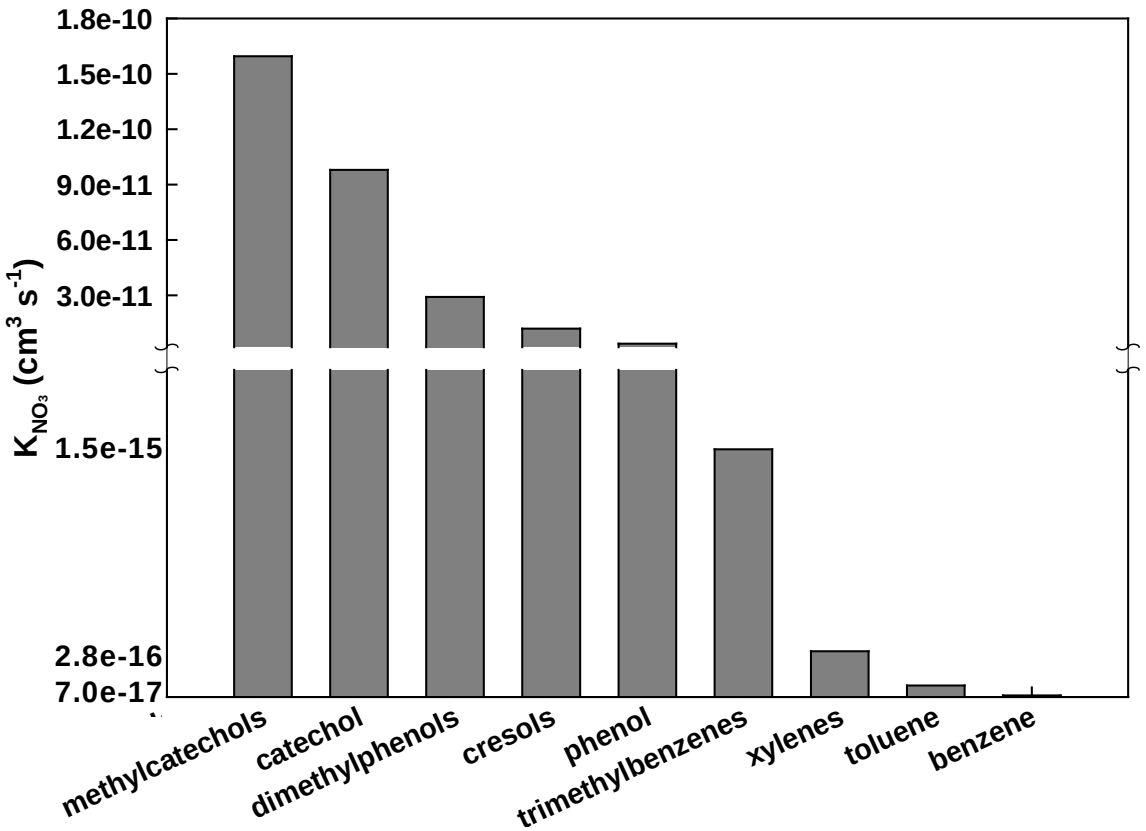
Compound	2-nitrophenol	3-methyl-2-nitrophenol	4-methyl-2-nitrophenol	5-methyl-2-nitrophenol
Photolysis[(a)] (s^{-1})	$(1.5 \pm 0.5) \times 10^{-4}$	$(1.67 \pm 0.11) \times 10^{-4}$	$(8.86 \pm 1.07) \times 10^{-5}$	$(1.07 \pm 0.14) \times 10^{-4}$
OH concentration (cm^{-3})	$\sim 3 \times 10^{5}$	$\sim 3 \times 10^{5}$	$\sim 2 \times 10^{5}$	$\sim 3 \times 10^{5}$

(a) Values for the photolysis rate obtained in the 1080 L quartz glass reactor.

Lamps: Philips TL05 – 40W superactinic lamps, emit in the range 320 – 480 nm and have a maximum intensity at 360 nm.

Value for 2-nitrotoulene 7.3×10^{-5} s^{-1})

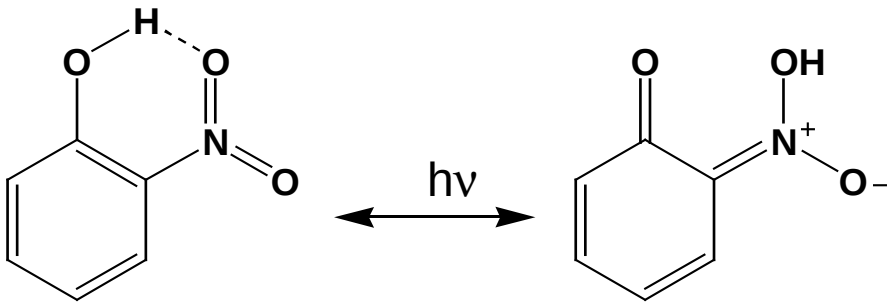
Trend of rate coefficients for the reaction of methylated hydroxyaromatic compounds with NO_3 radicals



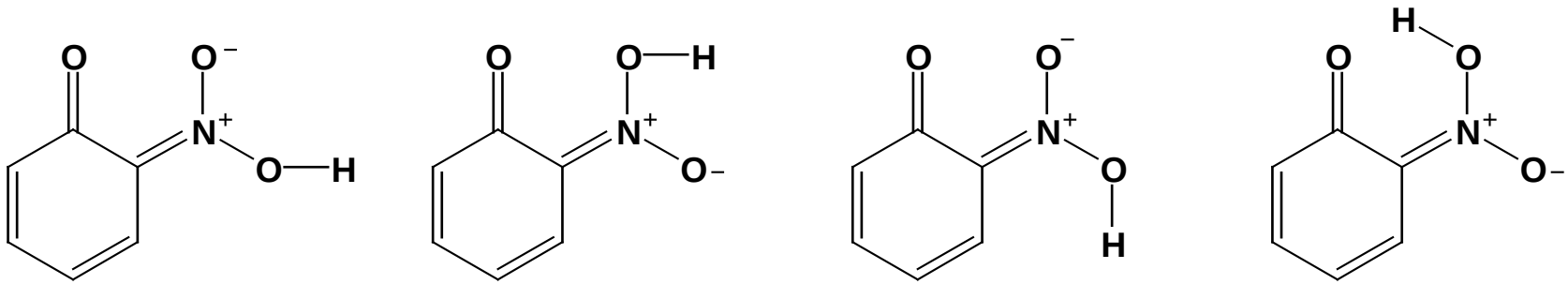
For the isomers an average of the rate coefficients has been used.
For benzene an upper limit of $k_{NO3} = 3 \times 10^{-17}$ cm^3 s^{-1} has been used.

Identification of the aci-nitro form of 2-nitrophenol

(Nagaya, Kudoh and Nakata, *Chem. Phys. Letter*, **2006**, *427*, 67-71)

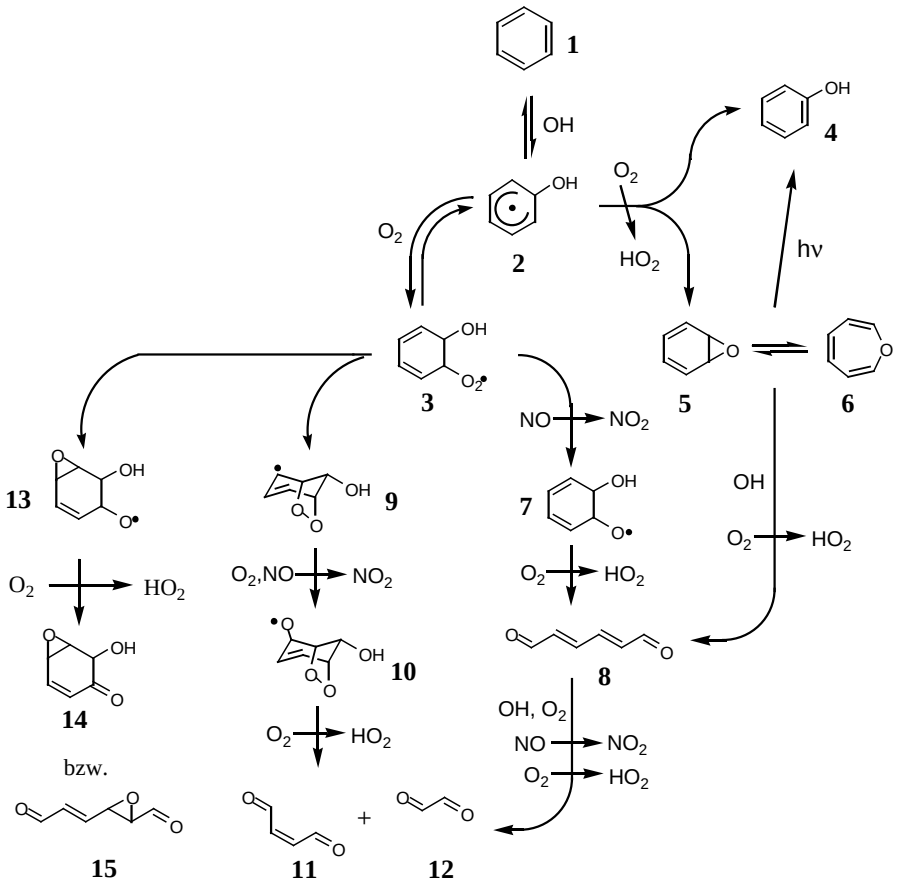


Matrix-isolation infrared spectroscopy in combination with density Function (DFT) calculations



CC **TC** **CT** **TT**

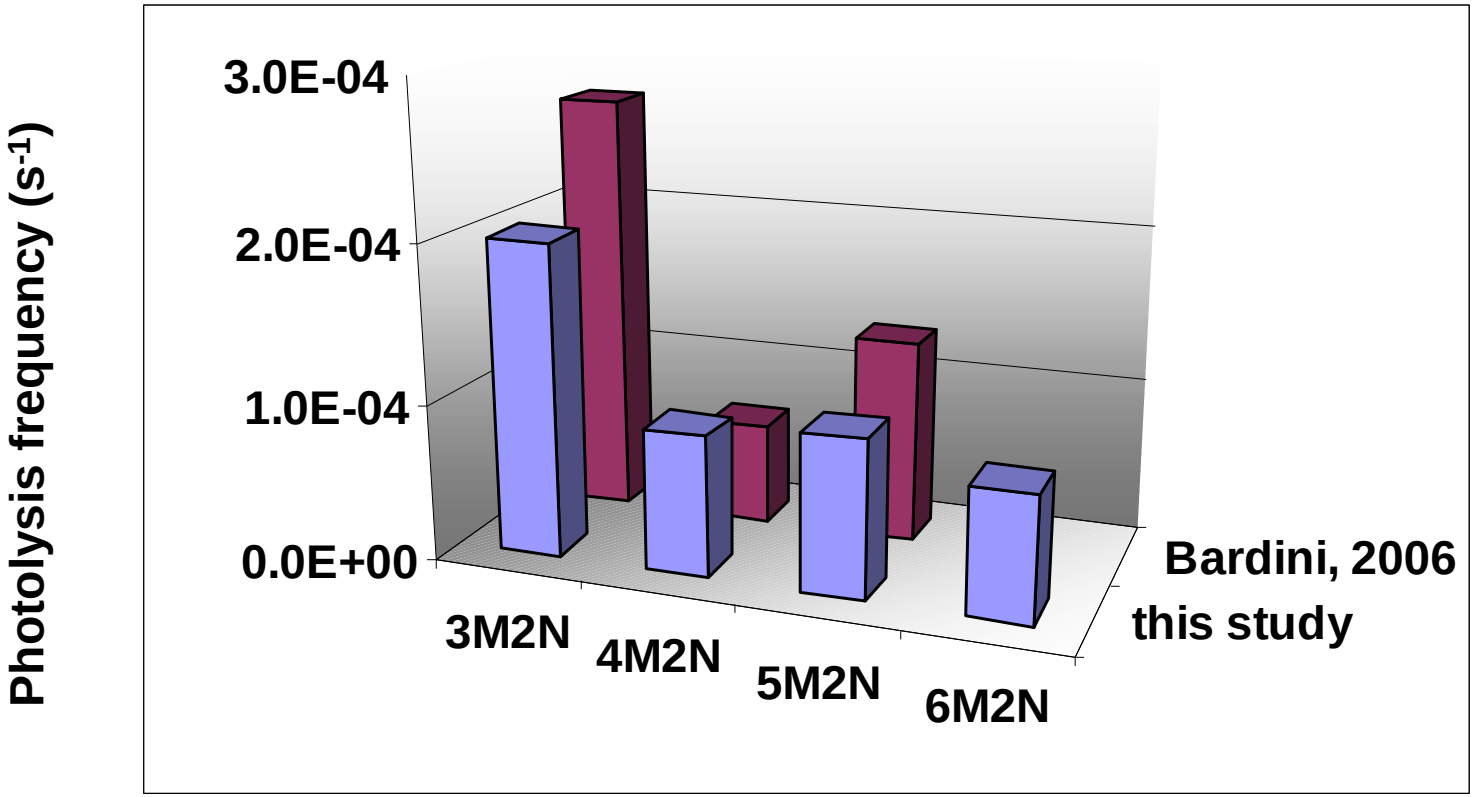
Primary oxidation products

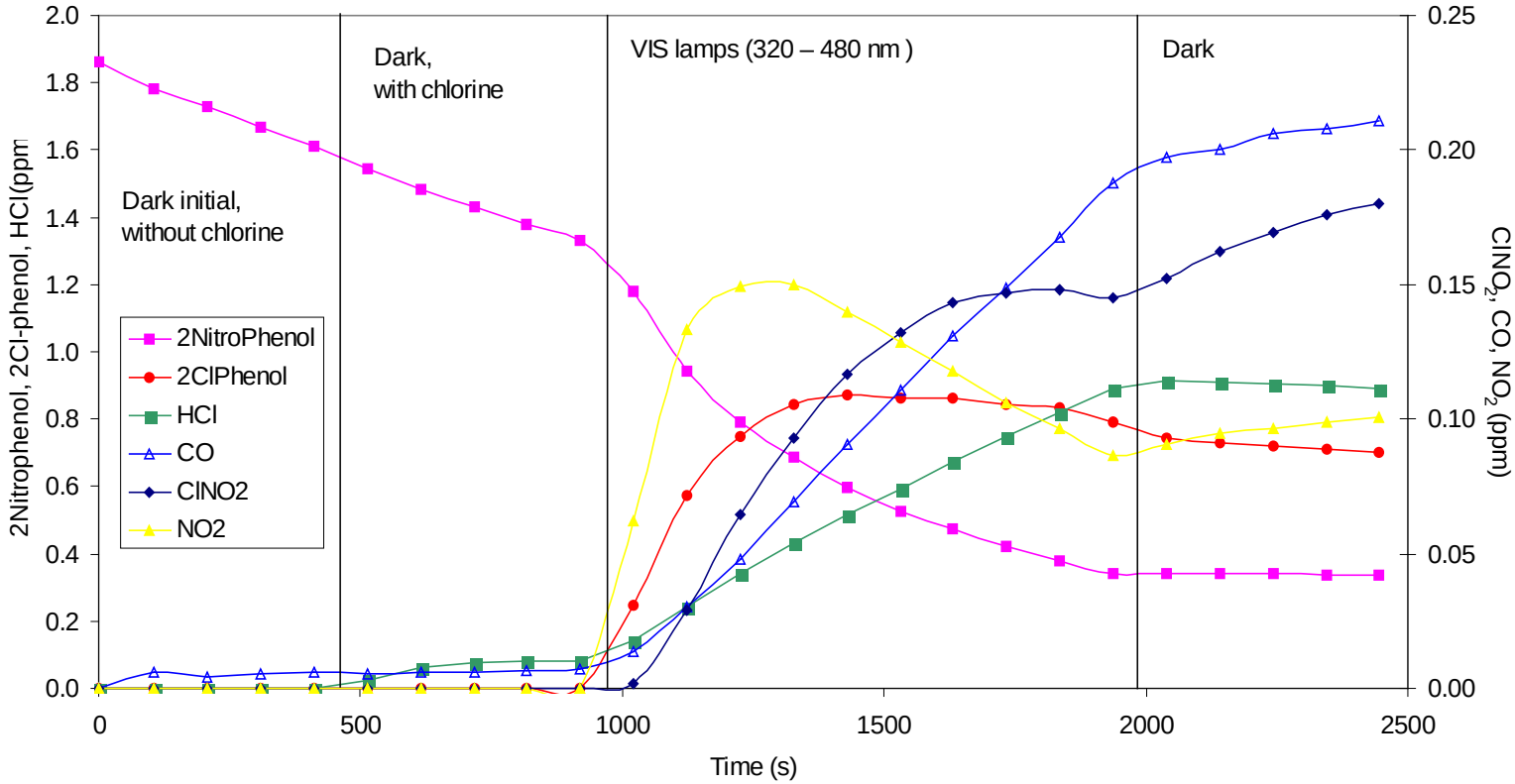


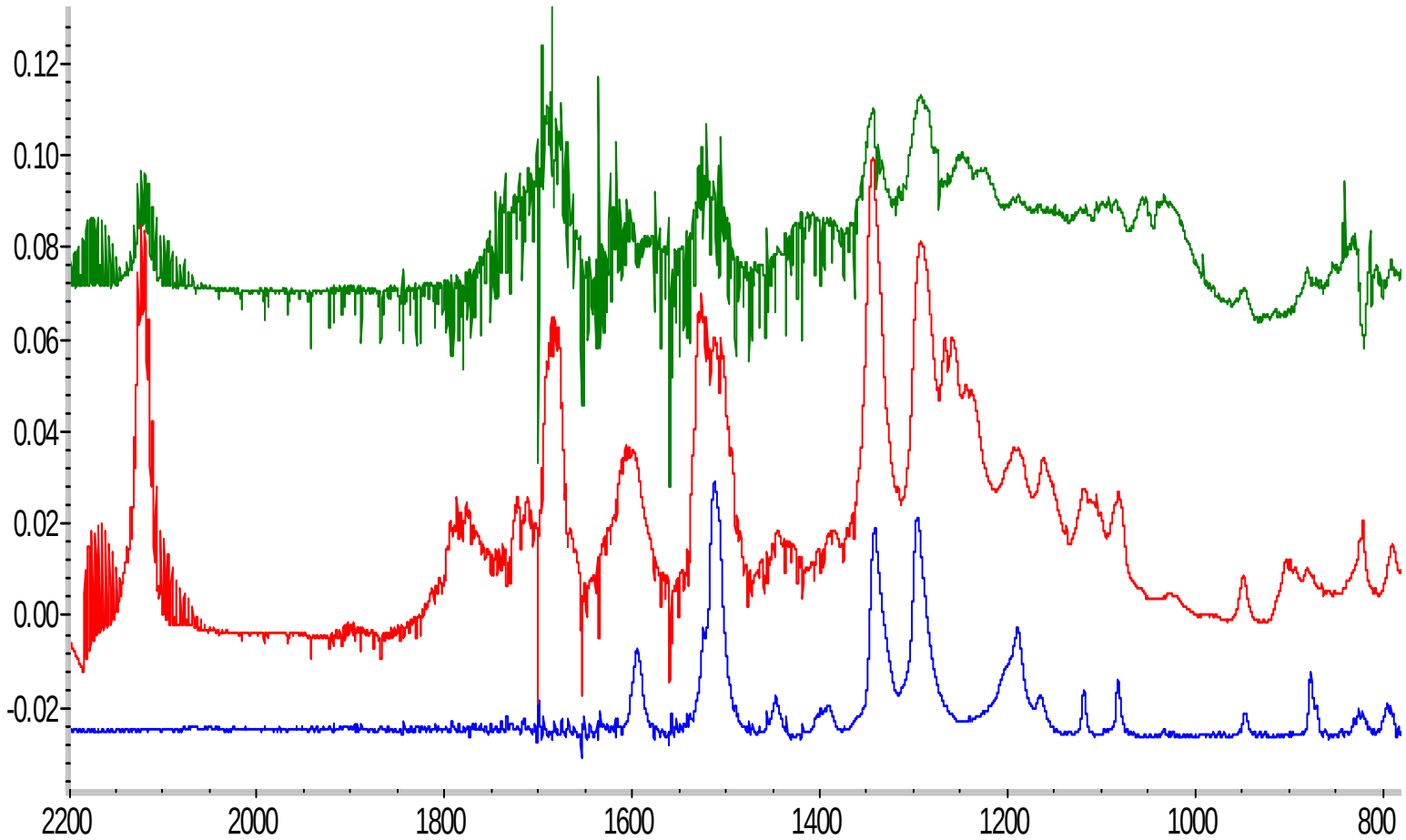
Recent quantification of dienedials by IFG and EUPHORE

(Berndt and Böge, PCCP **2006**, *8*, 1205-1214)

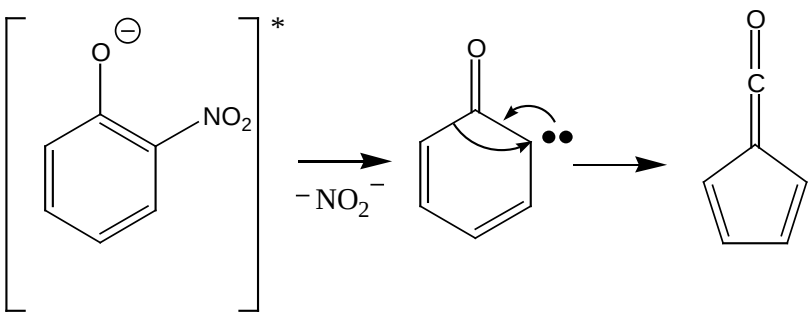
Comparison of estimated atmospheric J-values for 2-nitrocresols with those measured by Bardini (2006) in the EUPHORE chamber, Valencia, Spain.




Dark initial,
without chlorine
Dark,
with chlorine
VIS lamps (320 – 480 nm)
Dark
2NitroPhenol
2ClPhenol
HCl
CO
ClNO2
NO2
2Nitrophenol, 2Cl-phenol, HCl(ppm
ClNO2, CO, NO2 (ppm)
Time (s)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0.00
0.05
0.10
0.15
0.20
0.25
0
500
1000
1500
2000
2500



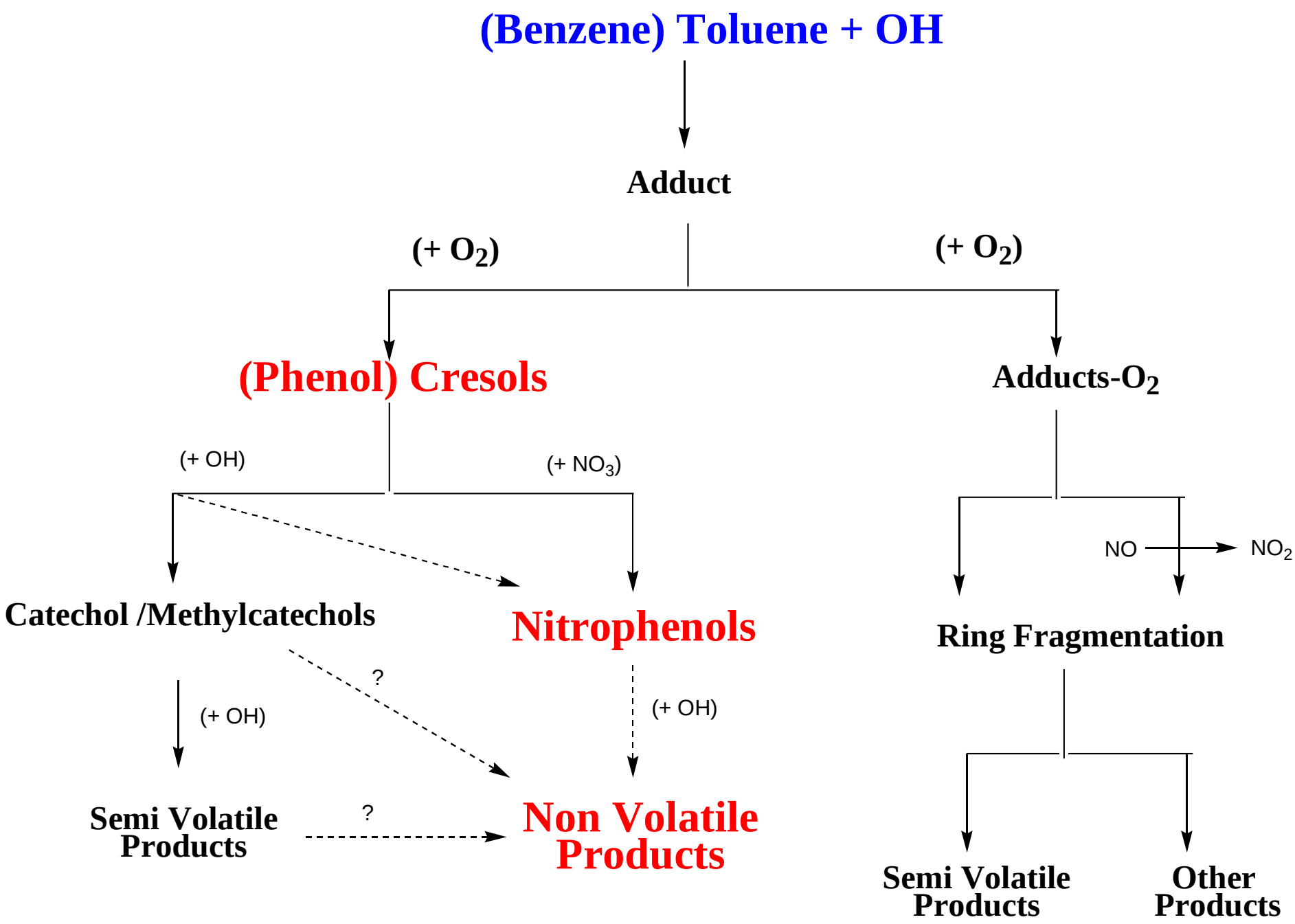
Comparison between the product spectrum obtained from the reaction of catechol with chlorine atoms with that from the reaction with OH radicals. The lower trace is a spectrum of 4-nitrocatechol identified as product.



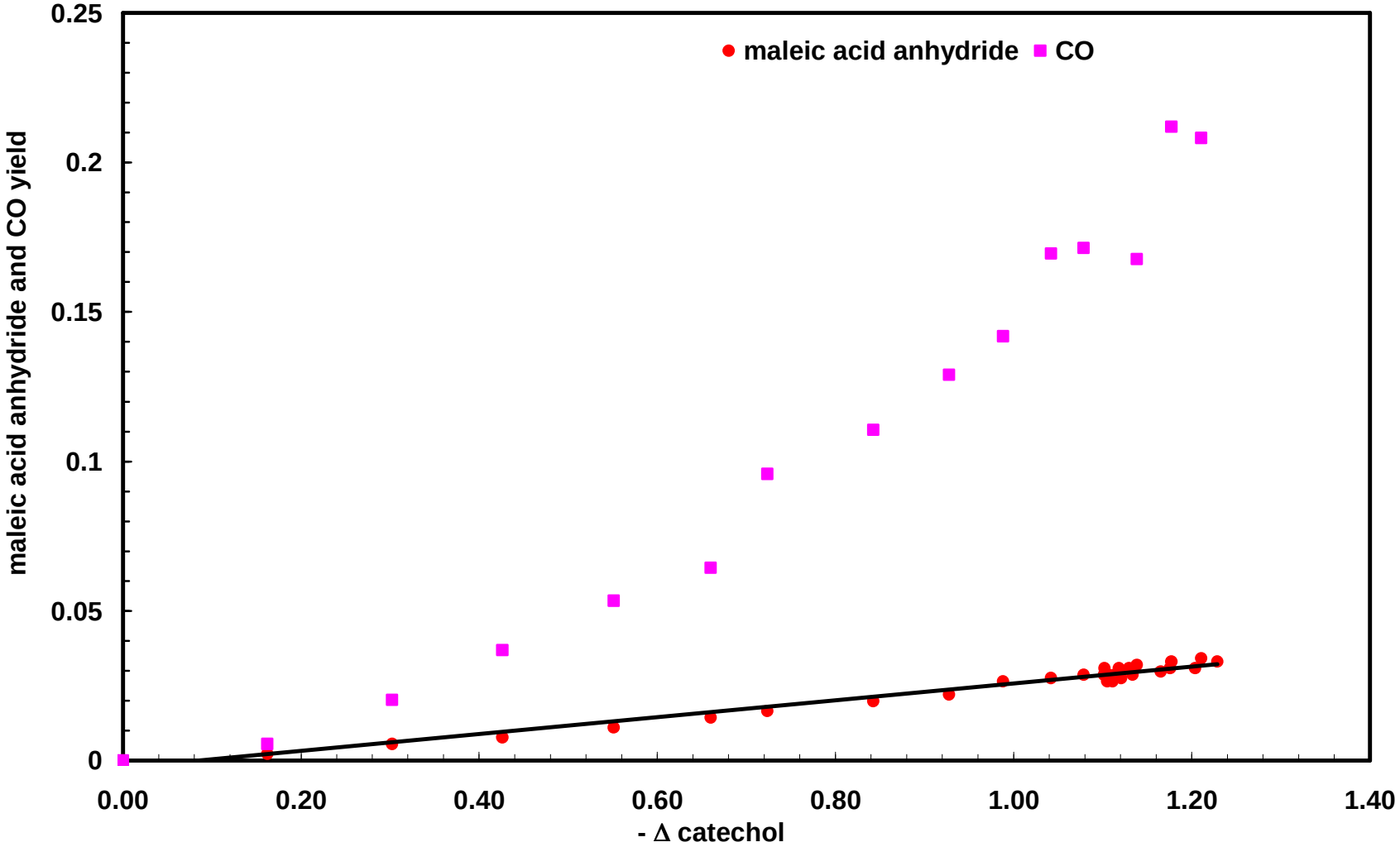
Formation of cyclopentadiene ketene from the phototransformation of 2-nitrophenol in aqueous solution (Alif *et al*., 1991)

Aerosol yields from the ozonolysis of dihydroxybenzenes (DHB)

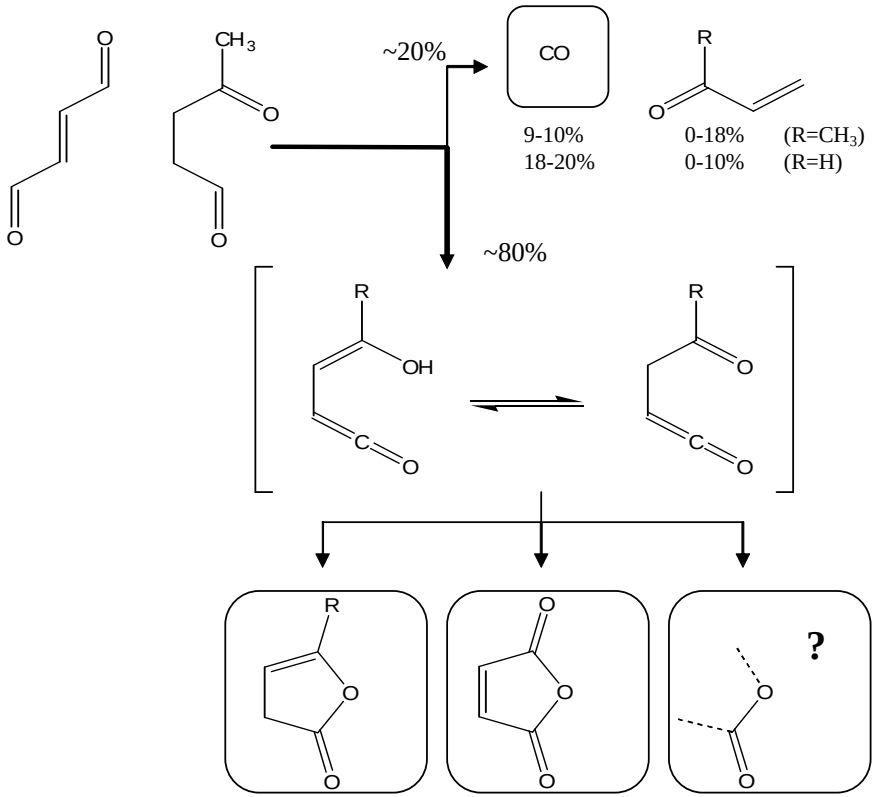
Reaction	Mass catechol reacted (mg m3)	Mass aerosol (mg m3)	**Aerosol yield (%)**
1,2-DHB (cyclohexane) + O_3	279	44.3	**19.9**
1,2-DHB (cyclohexane) + O_3	229	44.7	**24.8**
1,2-DHB + O_3	1308	299.6	**27.6**
1,2-DHB + O_3	422	85.3	**23.7**
1,2-DHB + O_3	158	54.5	**33.6**
3M-1,2-DHB (cyclohexane) + O_3	613	117	**21.8**
3M-1,2-DHB + O_3	891	197	**26.1**
4M-1,2-DHB (cyclohexane) + O_3	1024	1727	**18.1**
3M-1,2-DHB + O_3	1490	282	**21.0**


(Benzene) Toluene + OH
Adduct
(+ O2)
(+ O2)
(Phenol) Cresols
Adducts-O2
(+ OH)
(+ NO3)
NO
NO2
Catechol /Methylcatechols
Nitrophenols
Ring Fragmentation
?
(+ OH)
(+ OH)
Semi Volatile Products
?
Non Volatile Products
Semi Volatile Products
Other Products

Dihydroxybenzene (catechol) OH oxidation products
(CO and maleic anhydride)



Photolysis of butenedials



Z-4-oxo-pent-2-enal system (R= CH_3)
E-butendial system (R = H)

α-Angelicalactone 31-35%
(3H)-Furan-2-one 45-55%

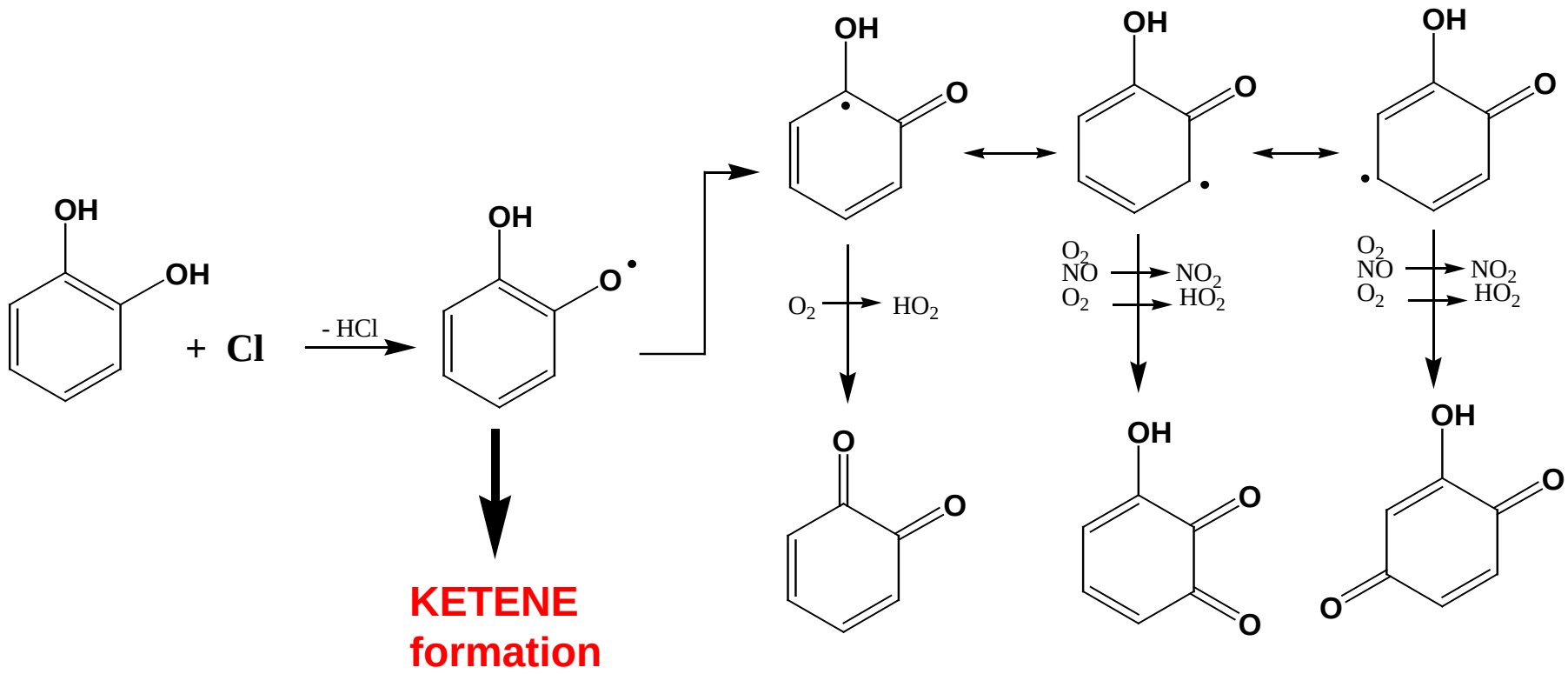
Maleic Anhydride 4-5%
Maleic Anhydride 20-21%

Unknown C=O 20%
Unknown C=O 6-14%

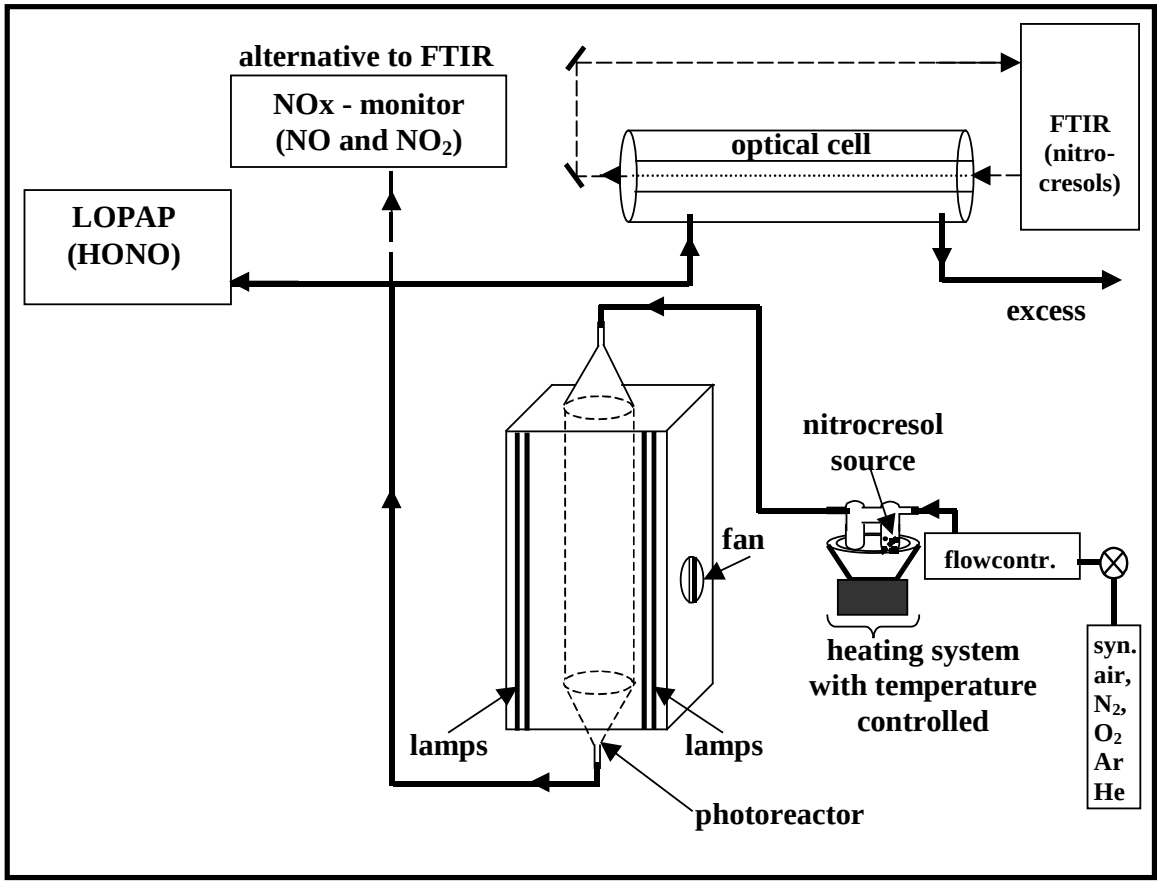
From:
Thüner, Rea and Wenger
4th EUPHORE Report 2001

Ketene and benzoquinone formation

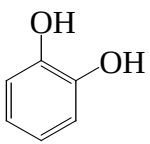
work on Cl + catechols has shown H-atom abstraction from an OH group
Is a major channel to ketene and benzoquinone formation

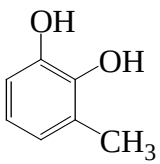


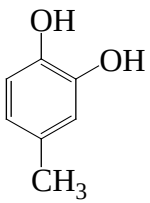
Flow system used for study of nitrophenol photolysis



Rate coefficients for the reactions of OH radicals with dihydroxybenzenes and benzoquinone
(Relative kinetic technique at 298 K)

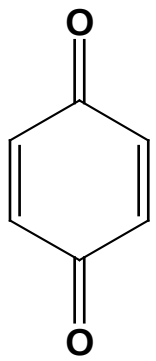




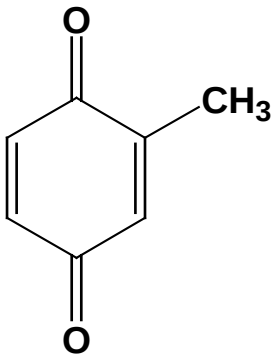


Compound	k (10^{-11} cm^3 s^{-1})	τ_i = 1/k[OH]
1,2-dihydroxybenzene	**10.4 ± 2.1**	100 min
1,2-dihydroxy-3-methylbenzene	**20.5 ± 4.3**	51 min
1,2-dihydroxy-4-methylbenzene	**15.6 ± 3.3**	67 min

(Olariu et al. *Int. J. Chem. Kinet.*, **2000**, *32*, 696-702)

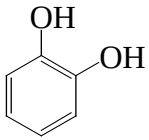
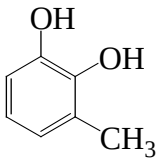
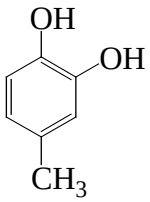


1,4-benzoquinone
(k = (0.46 ± 0.09) x 10^{-11})
(37 h)



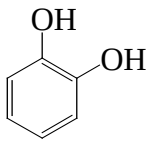
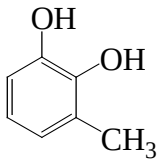
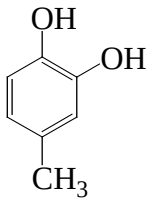
methyl-1,4-benzoquinone
(k = (2.35 ± 0.47) x 10^{-11})
(7.4 h)

Rate coefficients at 298 K for the reactions of NO_3 radicals with dihydroxybenzenes

	Compound	1080 l reactor k (10^{-11} cm^3 s^{-1})	EUPHORE k (10^{-11} cm^3 s^{-1})	**k(average) (10^{-11} cm^3 s^{-1})**
	**1,2-dihydroxybenzene**	9.03 ± 3.7	10.6 ± 4.3	**9.8 ± 5.0**
	**1,2-dihydroxy-3-methylbenzene**	17.3 ± 5.6	17.1 ± 4.8	**17.2 ± 5.6**
	**1,2-dihydroxy-4-methylbenzene**	16.0 ± 5.2	13.4 ± 5.0	**14.7 ± 6.5**

(Olariu et al. *Int. J. Chem. Kinetics*, **2004**,*36*, 577–583)

Rate coefficients at 298 K for the reactions of O_3 with Dihydroxybenzenes
(relative kinetic technique at 298 K)

	Compound	k (10^{-17} cm^3 s^{-1})
	1,2-dihydroxybenzene	0.96 ± 0.0
	1,2-dihydroxy-3-methylbenzene	2.80 ± 0.13
	1,2-dihydroxy-4-methylbenzene	2.63 ± 0.34

(Tomas et al, *Int. J. Chem. Kinet.*, **2003**, *35*, 223-230)