



Mechanism of the Photooxidation of Aromatic Hydrocarbons:

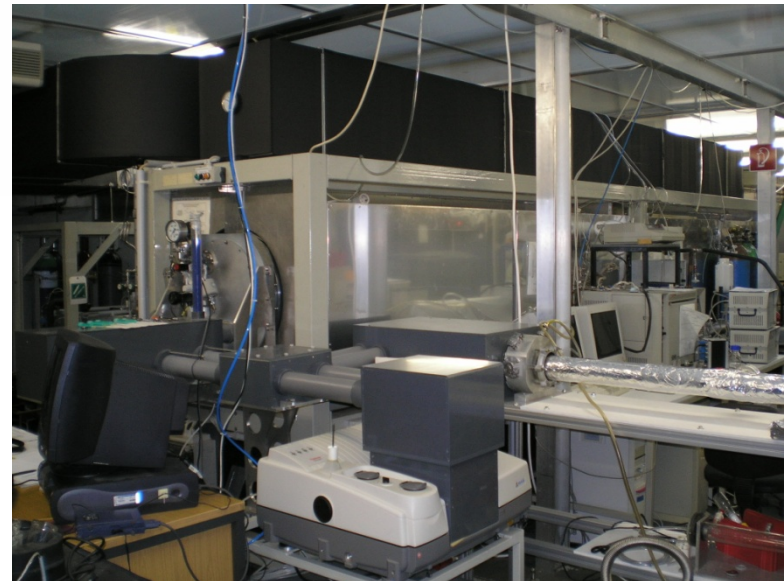
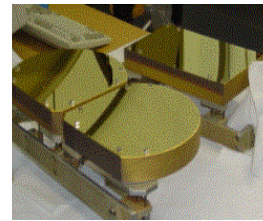
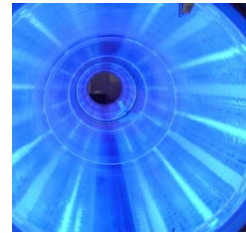
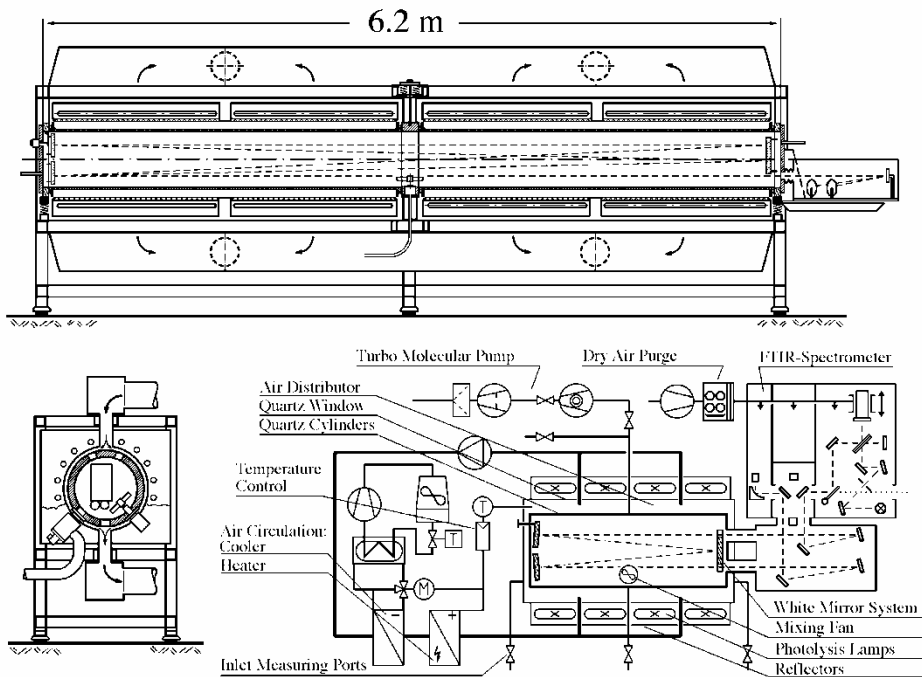
Chemistry of Ring-Retaining Products

I. Barnes

Bergische University Wuppertal



Photoreactor in Wuppertal Germany



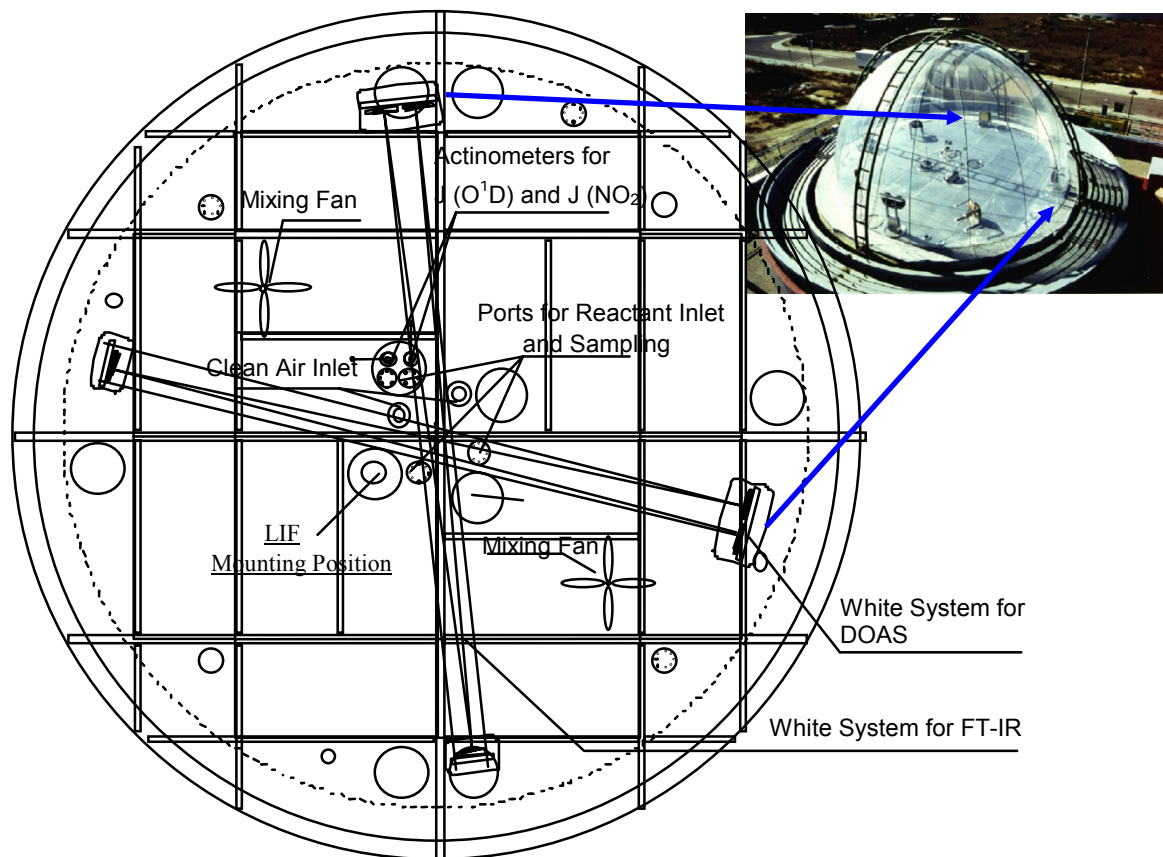
6 Meter or 1080 l reactor (~ 1990)

In situ FITR, GC and DMA

Base optical path 6 meter,

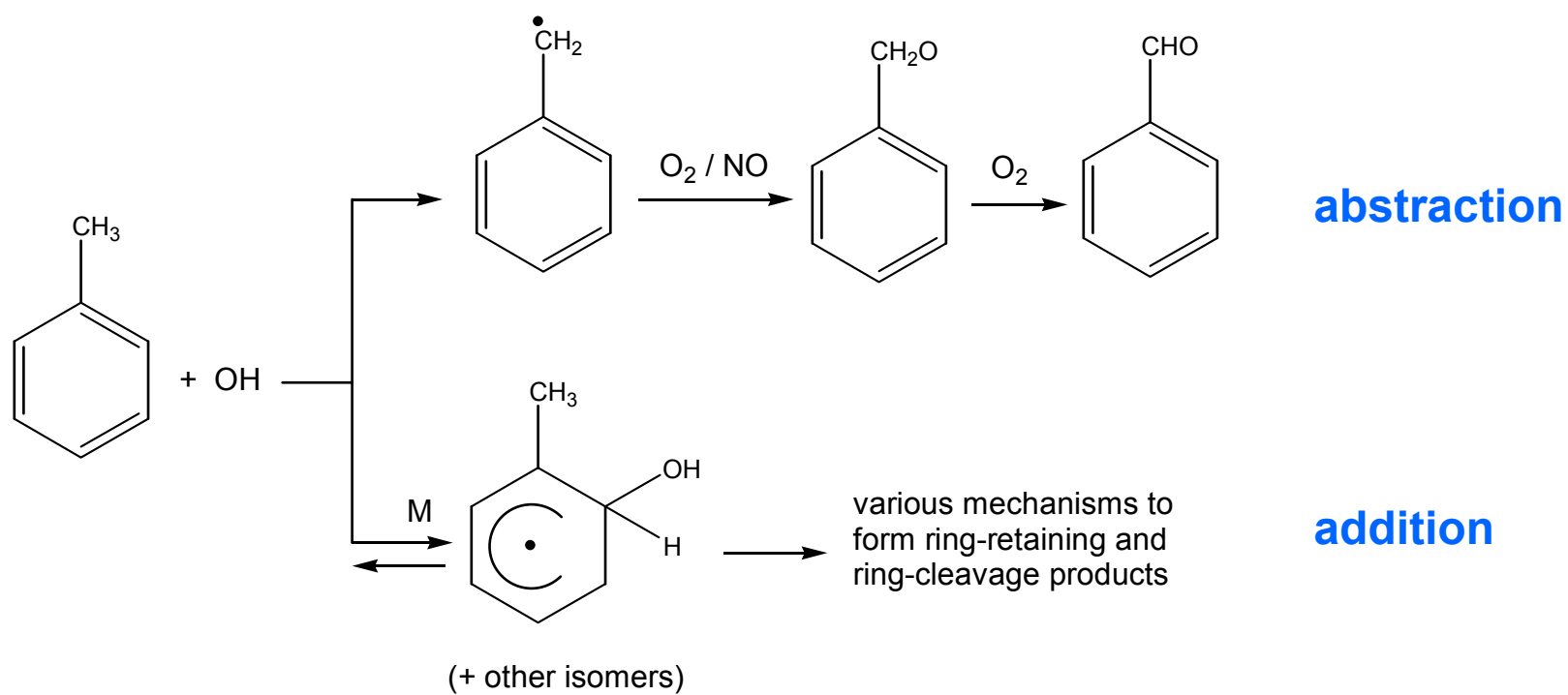
total optical path 484,7 m

Outdoor Photoreactor, Valencia, Spain



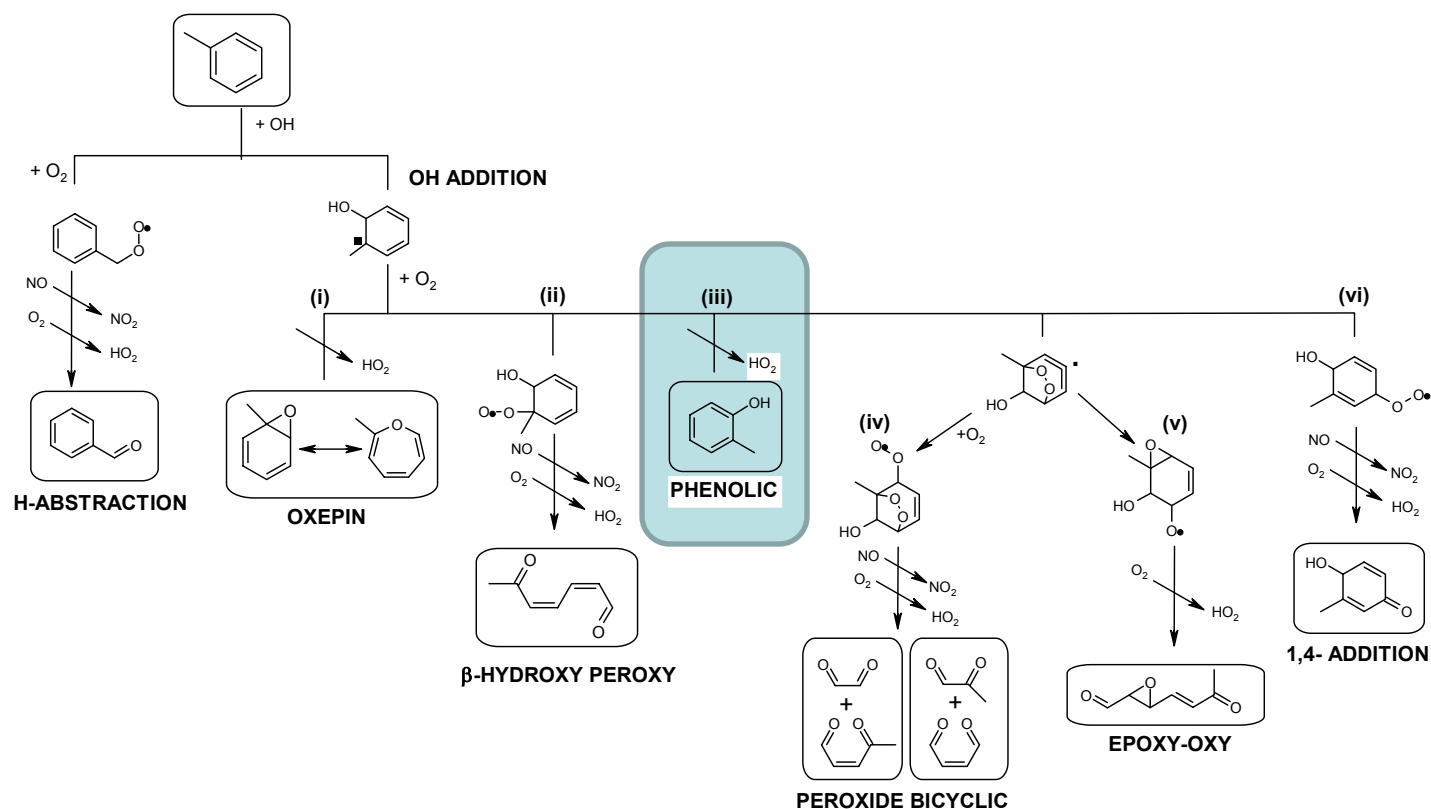
EUPHORE chamber at CEAM, Valencia, Spain

Primary oxidation steps



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

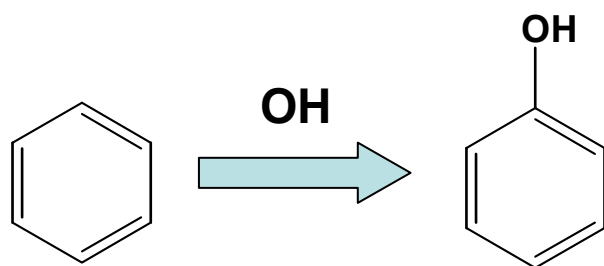


Simplified photooxidation mechanism from the „EXACT“ final report

Recent quantification of dienedials by IFG and EUPHORE

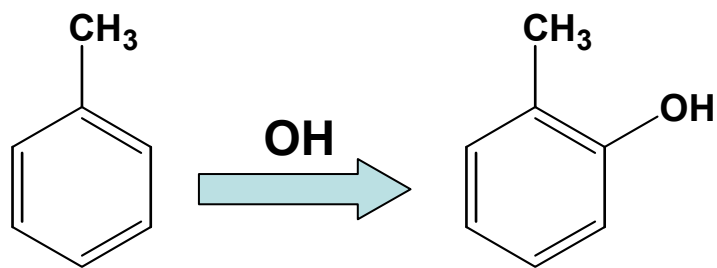
(Berndt and Böge, PCCP **2006**, 8, 1205-1214)

OH oxidation of benzene / toluene – Ring-retaining products



50-60%*

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



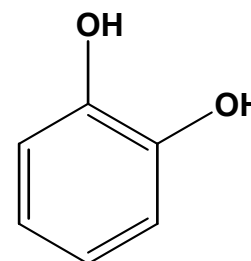
+ isomers

16-18%

OH oxidation products of phenol and cresols

Reactant	Product	Yield (% molar)	Yield (lit)
phenol	1,2-dihydroxybenzene 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-dihydroxy-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-dihydroxy-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-methyl-2-nitrophenol	64.1 ± 8.7 7.6 ± 2.1	10 ± 4

Major products are
1,2-dihydroxybenzenes



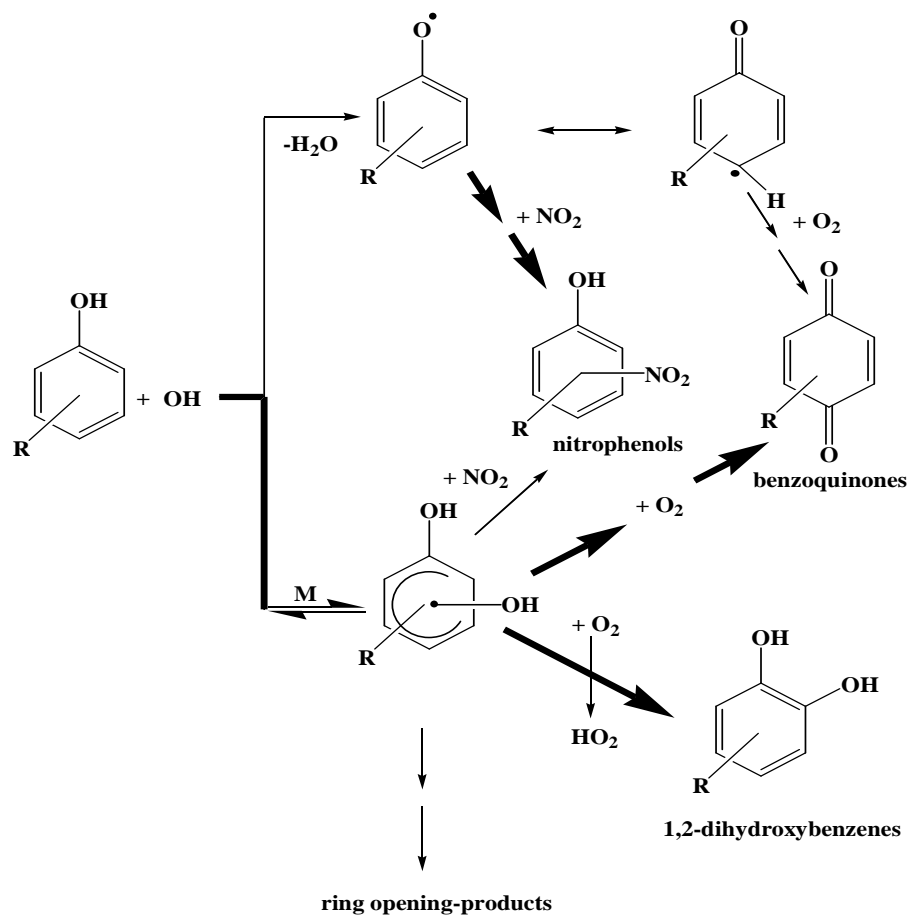
and



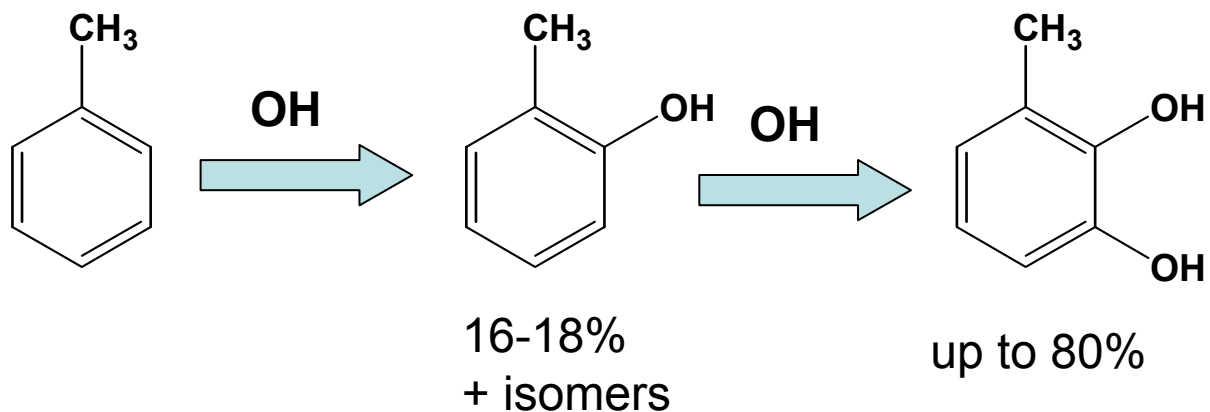
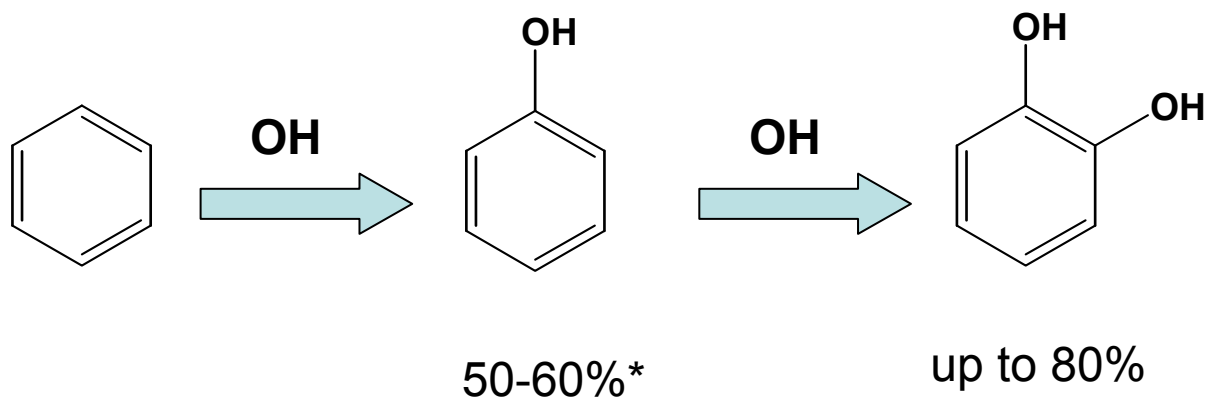
Olariu et al. *Atmos. Environ.*, **2002**, 36, 3685-3697

Product study OH + phenol: Berndt and Böge, *Phys. Chem. Chem. Phys.*, **2003**, 5, 342-350

Simplified mechanism for the reaction of phenol/cresols with OH



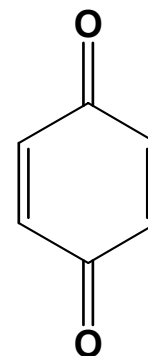
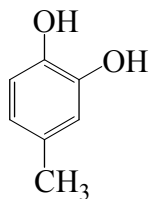
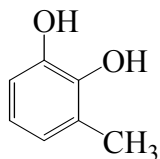
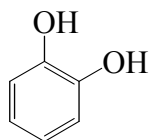
OH oxidation of benzene / toluene – Ring-retaining products



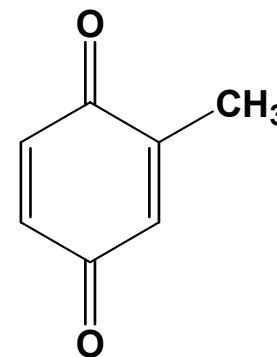
*(Berndt and Böge, *Phys. Chem. Chem. Phys.*, **2006**, 8, 1205-1214)

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

Compound	k ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)	τ_i = $1/k[\text{OH}]$
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



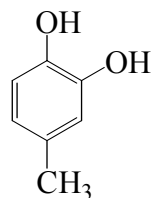
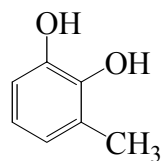
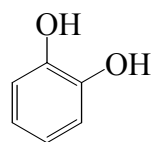
1,4-benzoquinone
($k = (0.46 \pm 0.09) \times 10^{-11}$)
(37 h)



methyl-1,4-benzoquinone
($k = (2.35 \pm 0.47) \times 10^{-11}$)
(7.4 h)

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

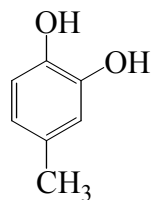
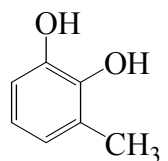
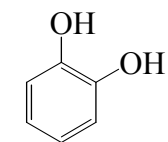
**Rate coefficients at 298 K for the reactions of O₃ with
Dihydroxybenzenes
(relative kinetic technique at 298 K)**



Compound	k (10⁻¹⁷ cm³ 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)

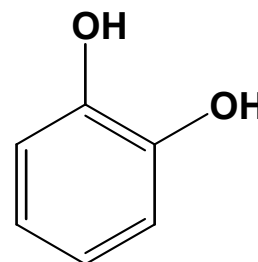
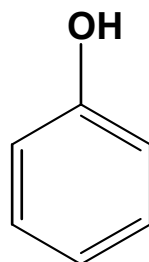
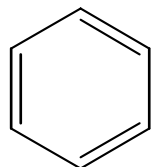
Rate coefficients at 298 K for the reactions of NO₃ radicals with dihydroxybenzenes



Compound	1080 l reactor	EUPHORE	k(average) (10 ⁻¹¹ cm ³ s ⁻¹)
	k (10 ⁻¹¹ cm ³ s ⁻¹)	k (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)

Lifetimes of aromatic compounds



$\tau(\text{OH})$	9.5 d	5.1 h	1.3 h
$\tau(\text{O}_3)$	>4.5 yr	-	1.7 d
$\tau(\text{NO}_3)$	>4 yr	8.8 min	20.4 s

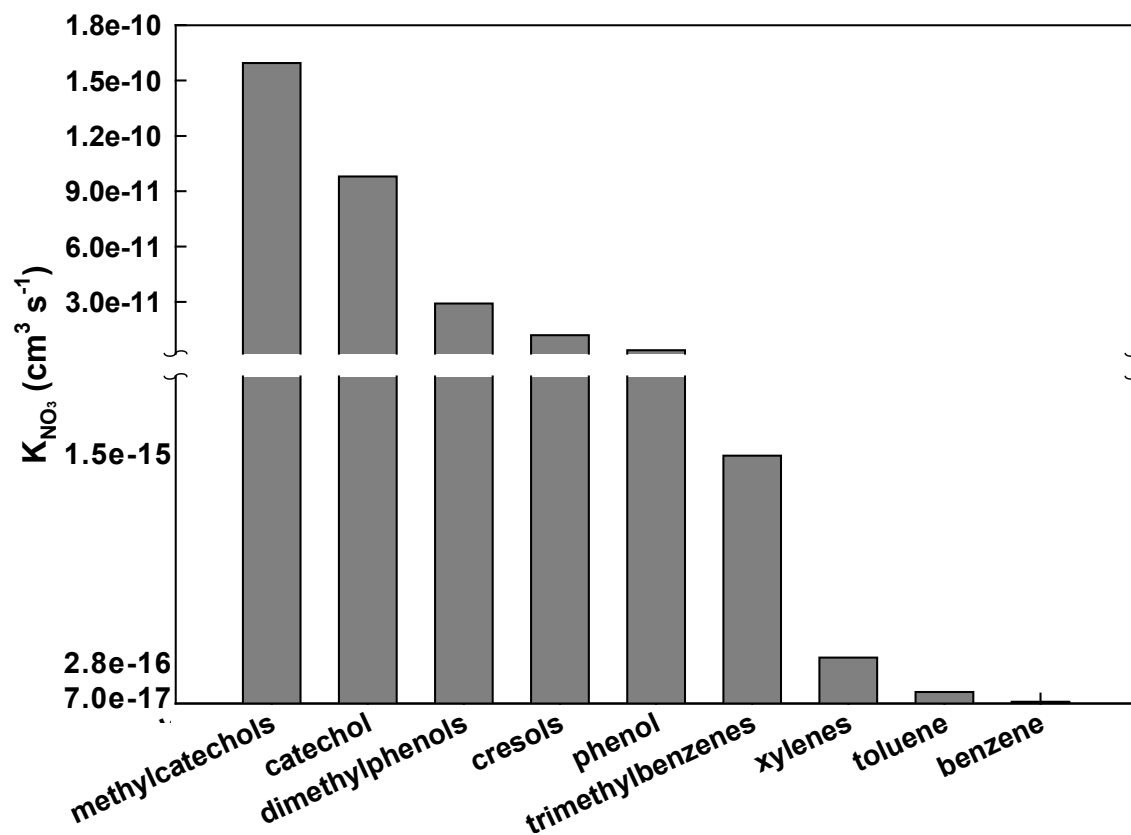
Atmospheric lifetimes calculated using:

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

[O₃] a 24-h average of 7×10^{11} molecule cm^{-3}

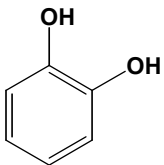
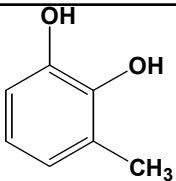
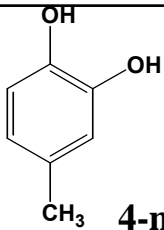
[NO₃] a 12-h nighttime average of 5×10^8 molecule cm^{-3}

Trend of rate coefficients for the reaction of methylated hydroxyaromatic compounds with NO₃ radicals.

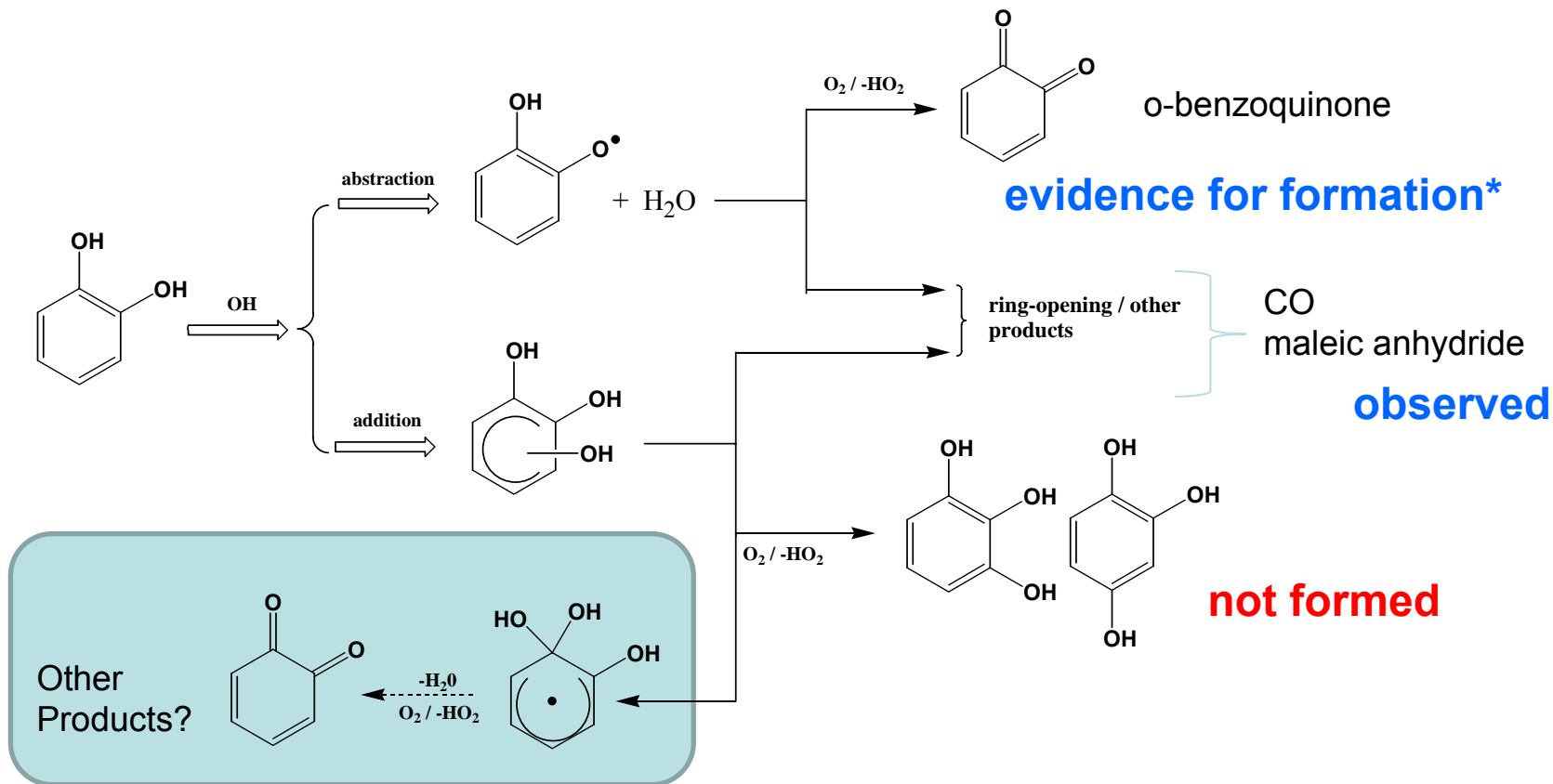


For the isomers an average of the rate coefficients has been used.
For benzene an upper limit of $k_{\text{NO}_3} = 3 \times 10^{-17}$ cm³ s⁻¹ has been used.

Rate coefficients for the reaction of Cl with catechols (relative kinetic technique at 298 K)

compound	reference	k_1/k_2	k_1 ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)	k_1 (average) ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)
 1,2-dihydroxybenzene	ethene	3.8 ± 0.1	6.8 ± 0.1	(6.6 ± 0.1)
	isoprene	1.8 ± 0.1	6.3 ± 0.1	
 3-methyl-1,2-dihydroxybenzene	ethene	3.7 ± 0.2	6.7 ± 0.3	(6.7 ± 0.8)
	isoprene	2.1 ± 0.3	7.0 ± 0.7	
 4-methyl-1,2-dihydroxybenzene	ethene	3.1 ± 0.5	6.2 ± 0.8	(6.2 ± 0.8)

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

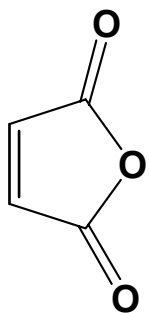
Main observations:

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

An intermediate infrared absorption due to a **ketene** group ($-\text{C}=\text{C}=\text{O}$) is observed

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

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



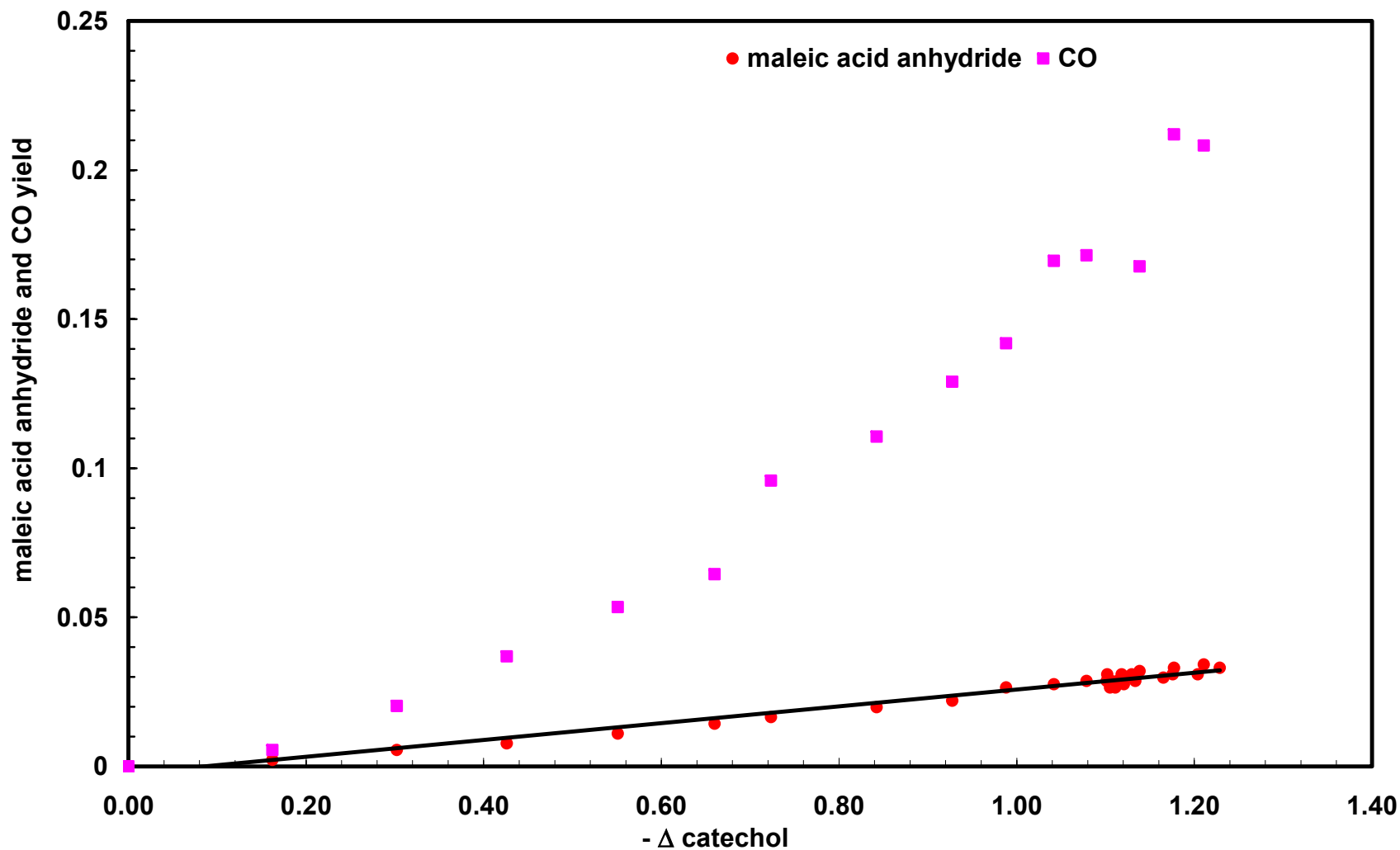
maleic anhydride

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

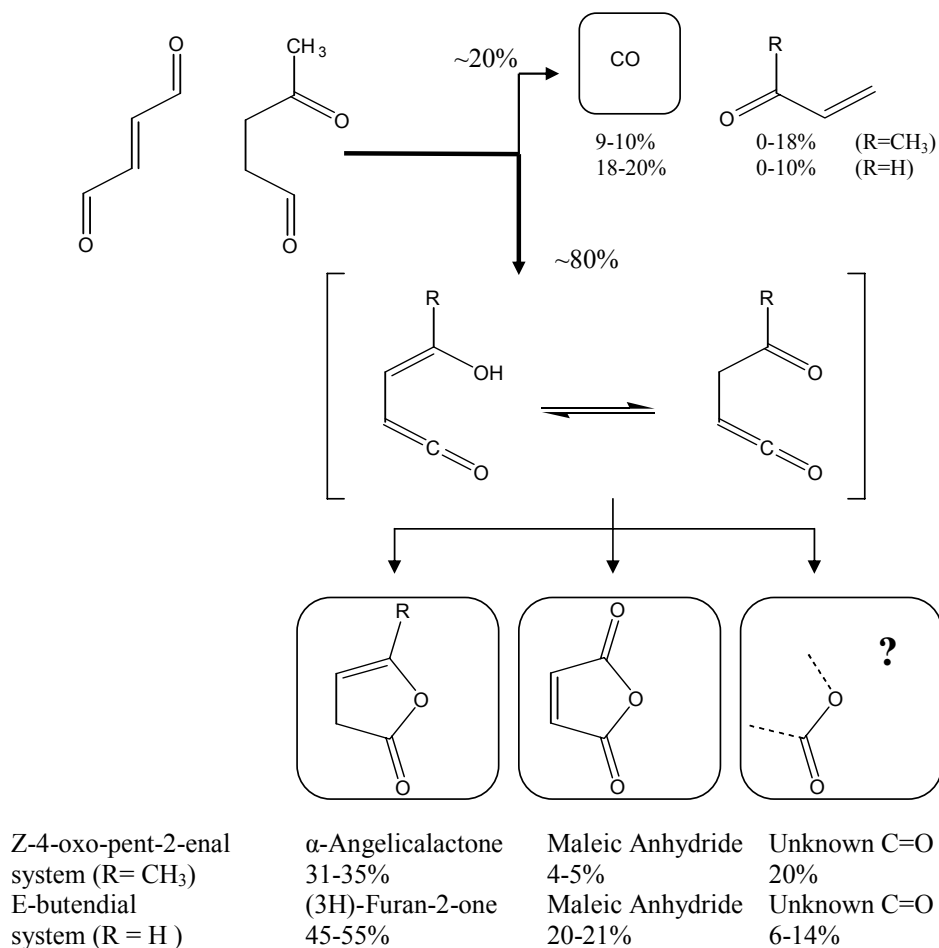
Detection of CO shows ring opening is occurring
maleic anhydride may also indicate ring-opening

Identification of **4-nitrocatechol**

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



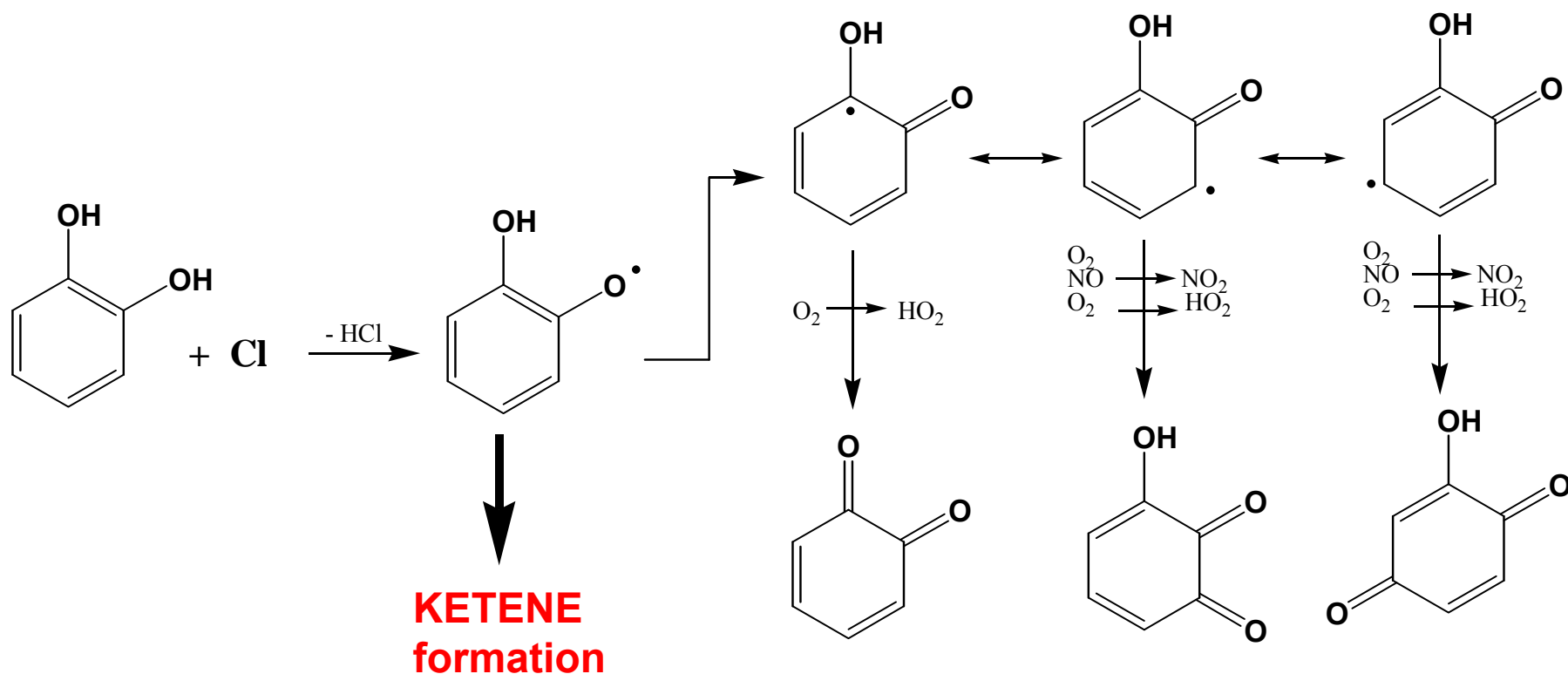
Photolysis of butenedials



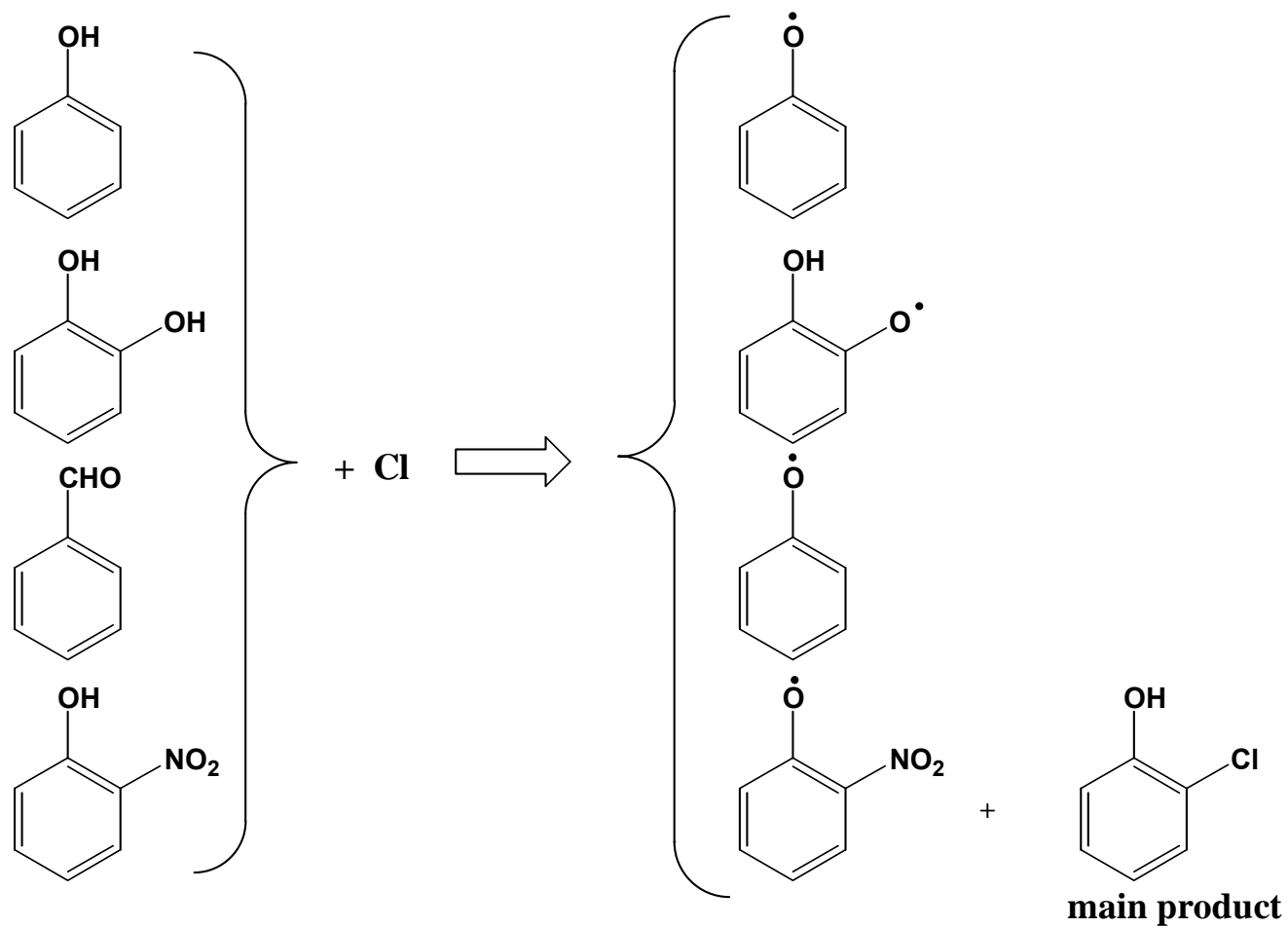
From:
Thüner, Rea and Wenger
4th EUPHORE Report 2001

Ketene and benzoquinone formation

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

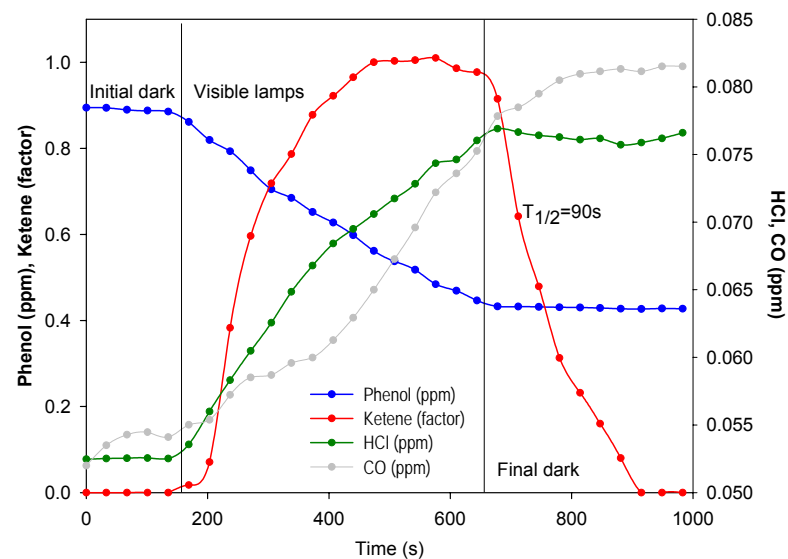
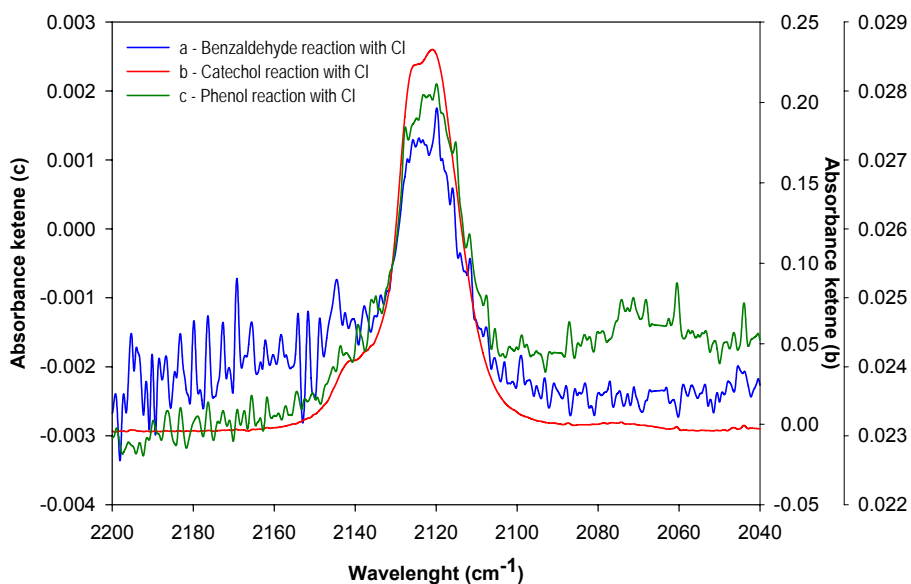


Generation of phenoxy radicals

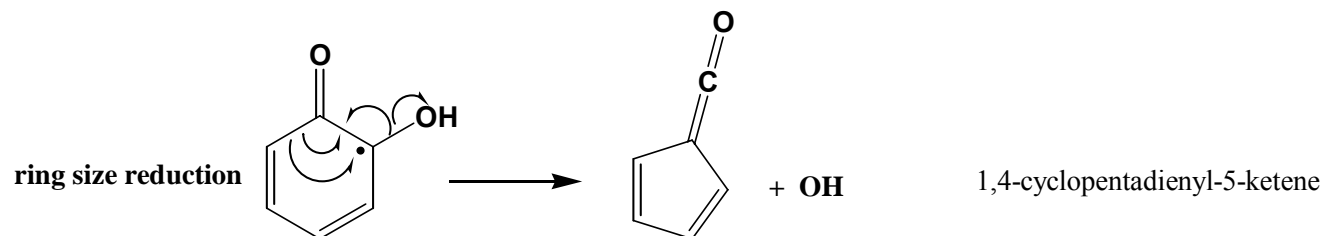
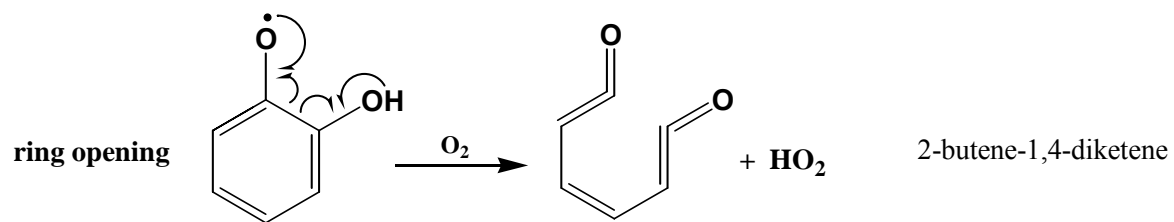
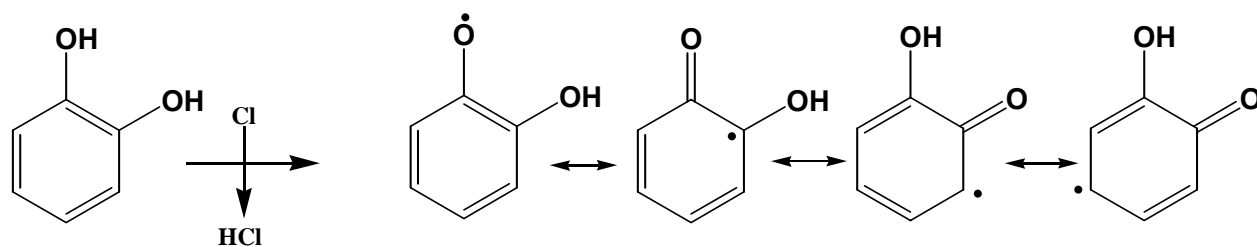


Observation of intermediate ketene absorptions

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

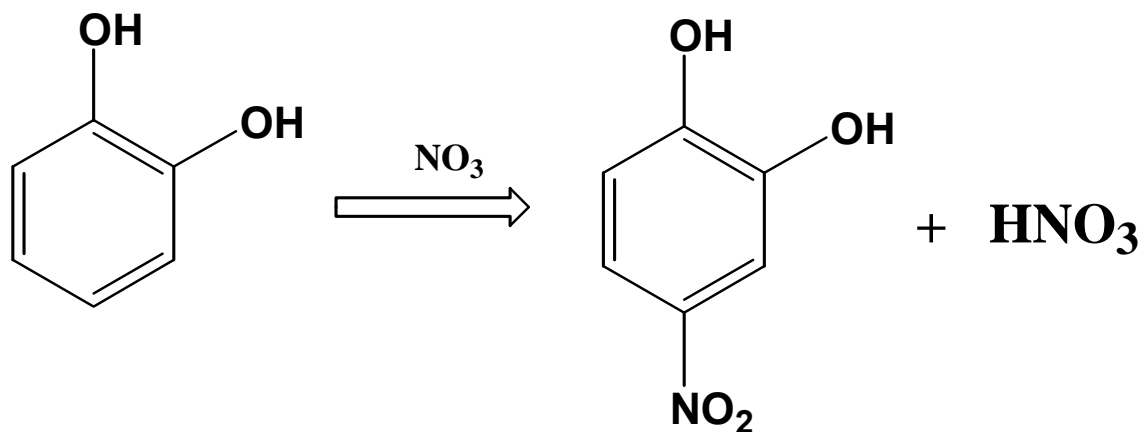


Ketene identity?



Dihydroxybenzene (catechol) - NO_3 reaction products

(work 2006)

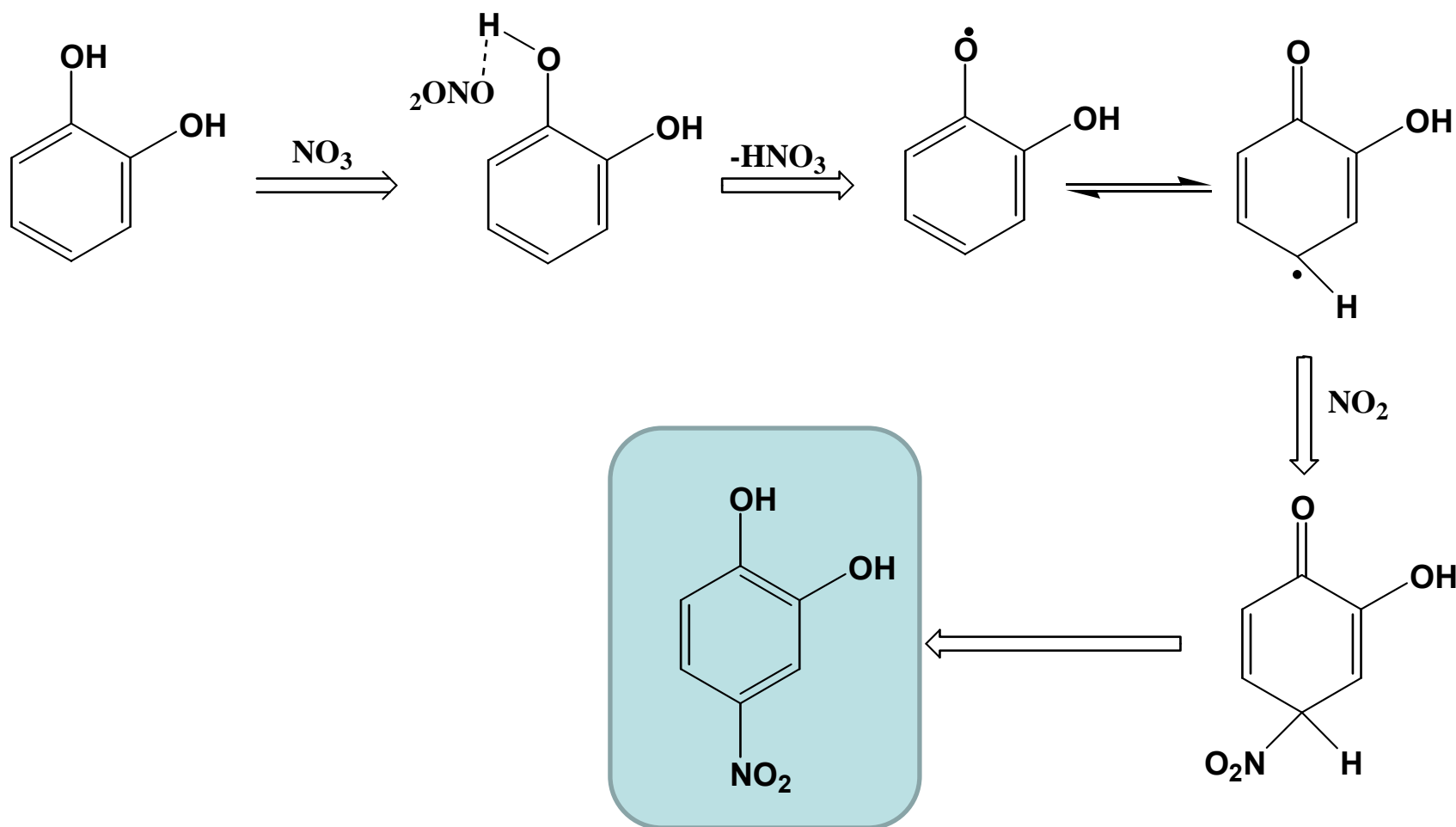


Only observe **4-nitro-1,2-dihydroxybenzene** and **nitric acid** as gas phase products

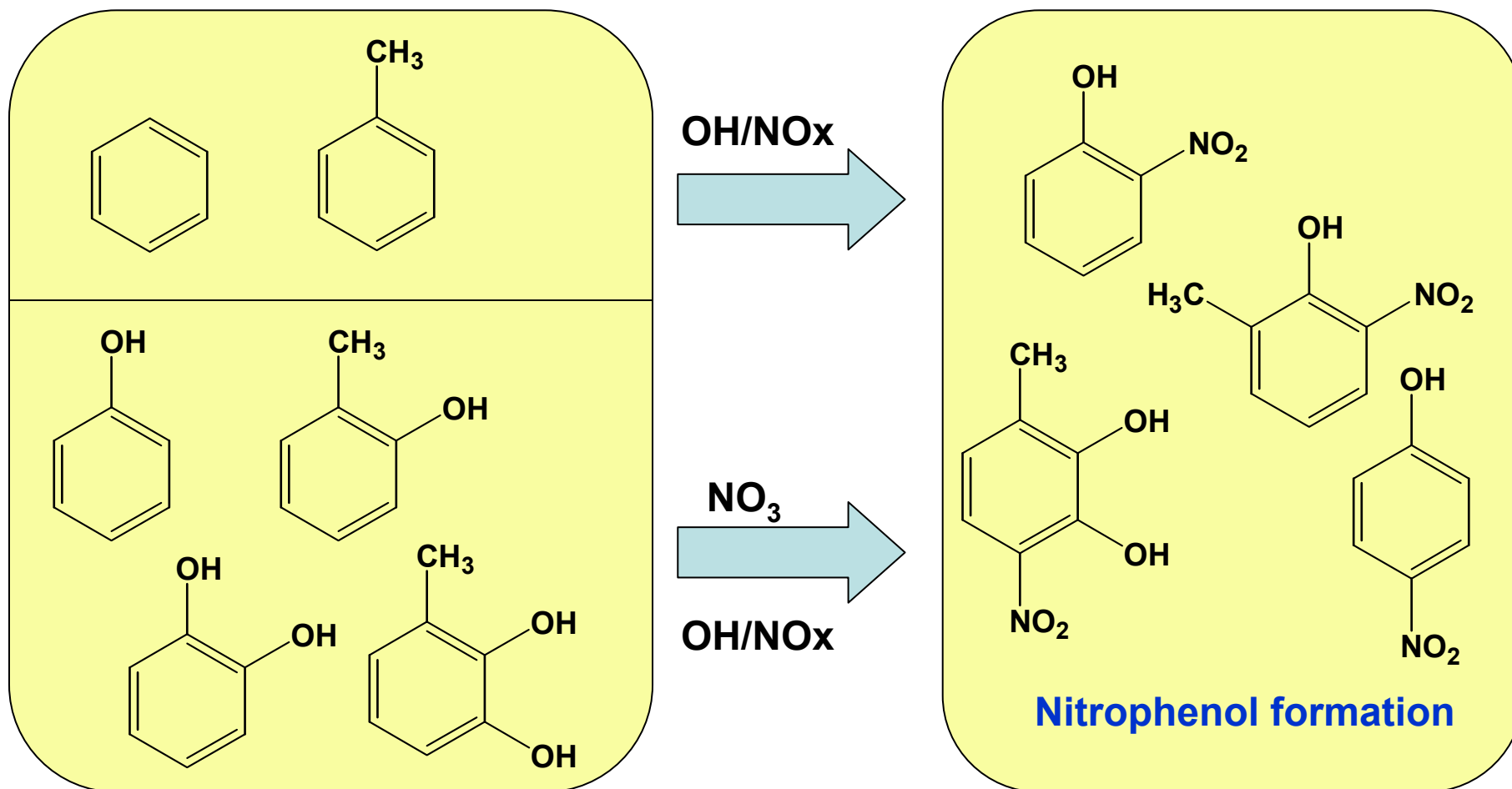
No indication of other products in the residual infrared spectrum

Aerosol is formed – still to be quantified

Dihydroxybenzene (catechol) - NO_3 reaction Mechanism? (work 2006)



Oxidation of aromatics to nitrophenols



Gas phase chemistry of nitrophenols

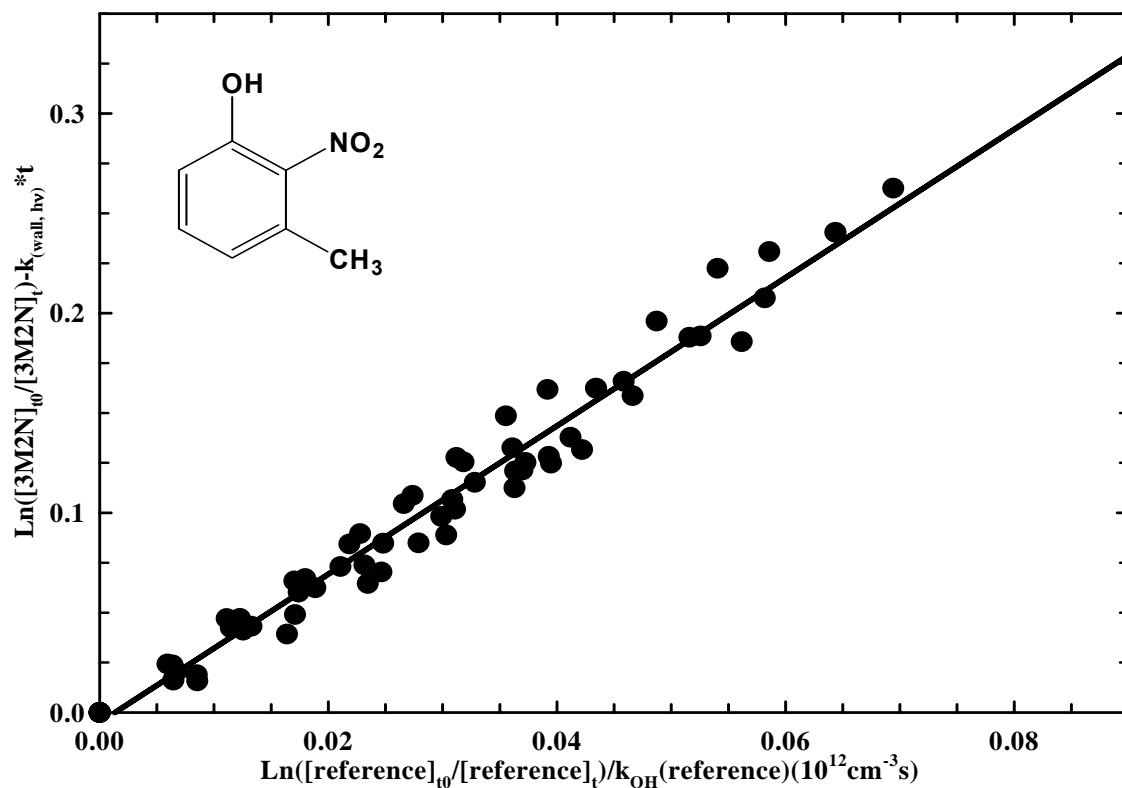
Status up to 2005:

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

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

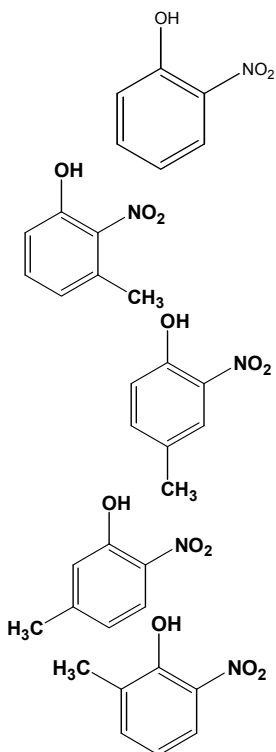
Photolysis in solution was reported to be very slow

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**

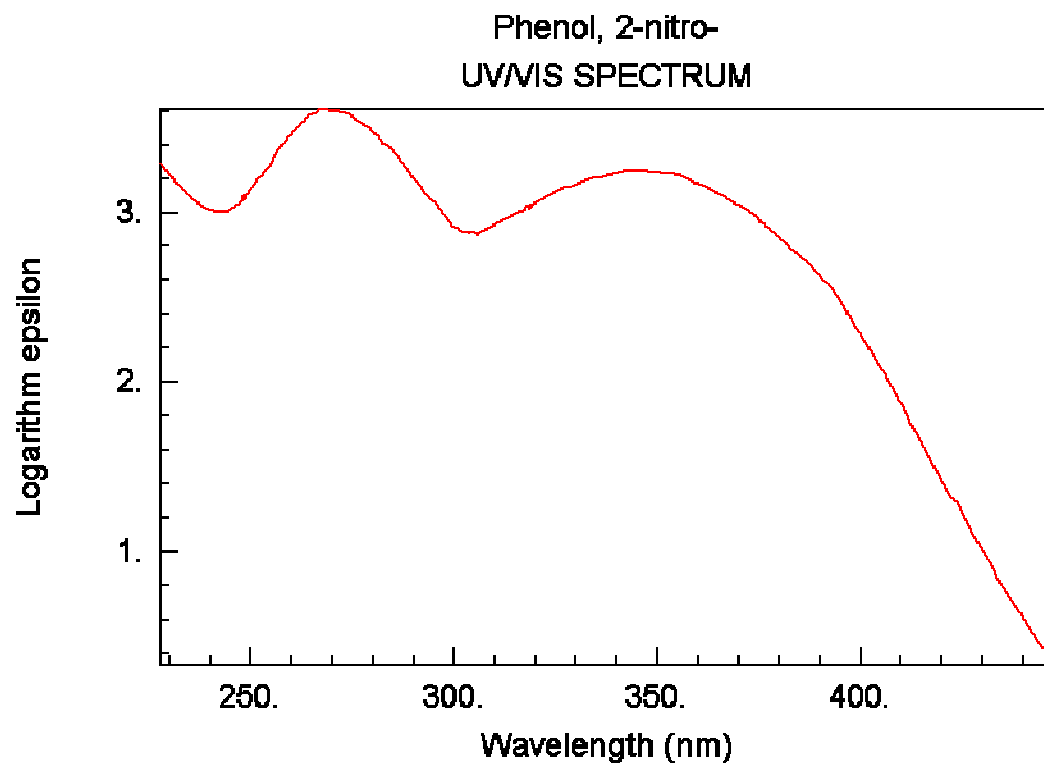


Compound	k_{OH} ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)	k (literature) ($10^{-12} \text{ cm}^3 \text{ s}^{-1}$)
NP	~ 1	0.9 ^a
3M2NP	(3.69±0.16)	11.2 ^b
4M2NP	(3.46±0.18)	5.38 ^b
5M2NP	(7.34±0.52)	11.2 ^b
6M2NP	(2.70±0.17)	-

a) Zetzsch and coworkers using FP-RF;

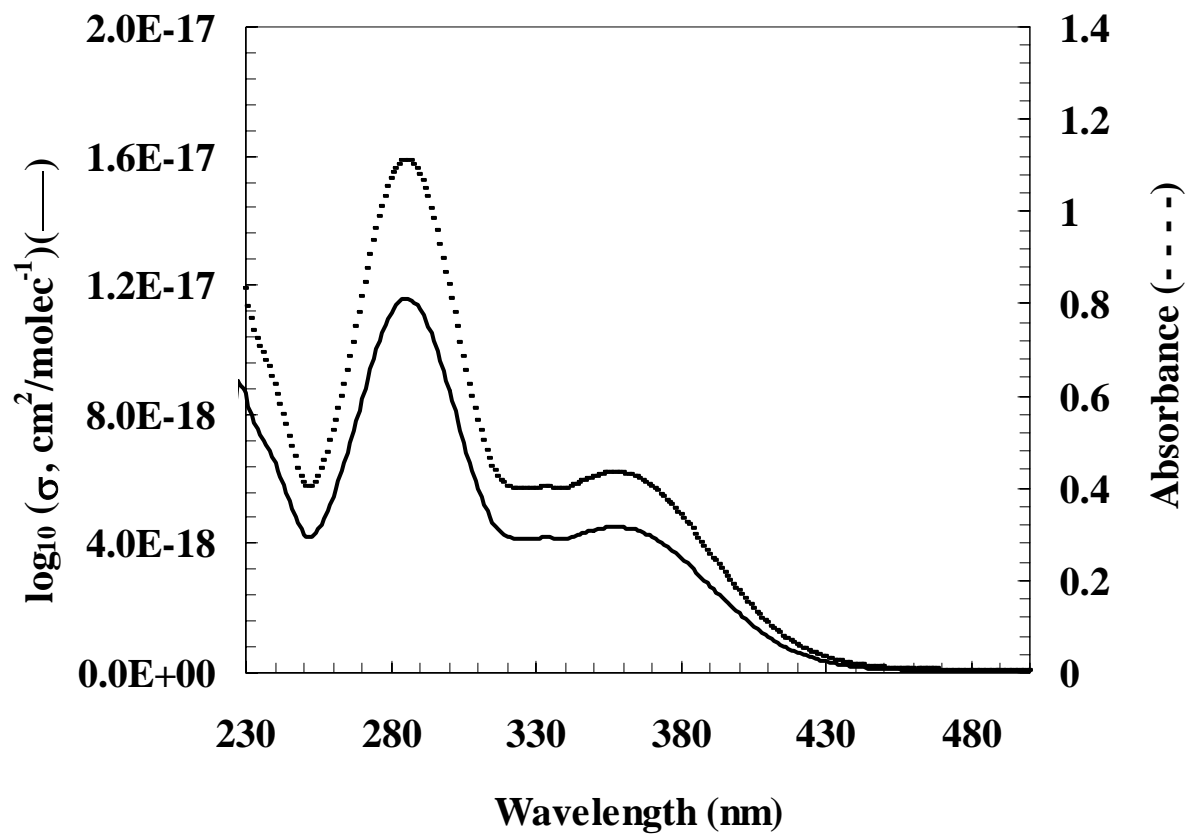
b) computer estimate by Meylan and Howard, *Chemosphere*, **1993**, 26(12) 2293-2299.

UV spectra of 2-nitrophenols

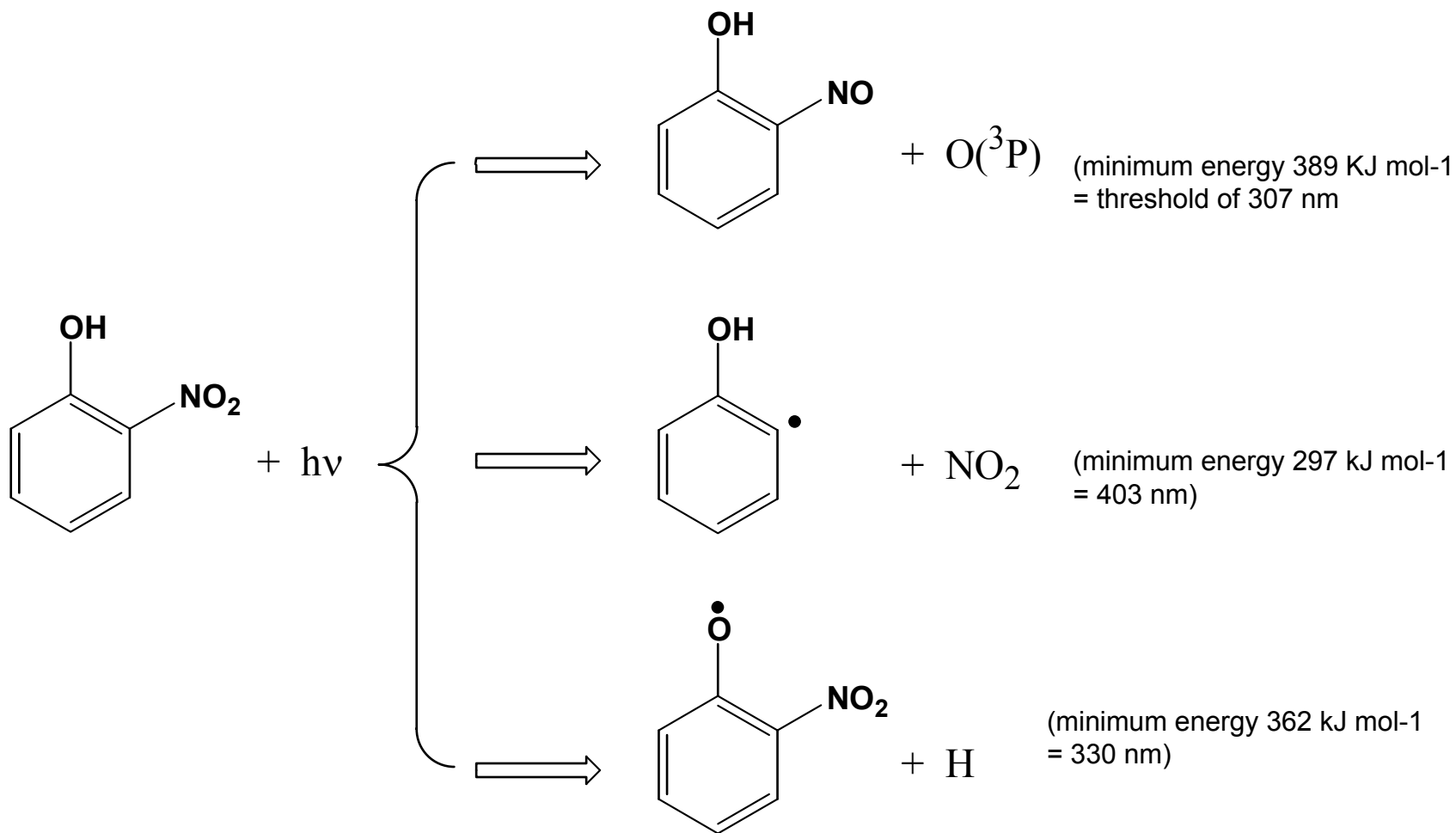


NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

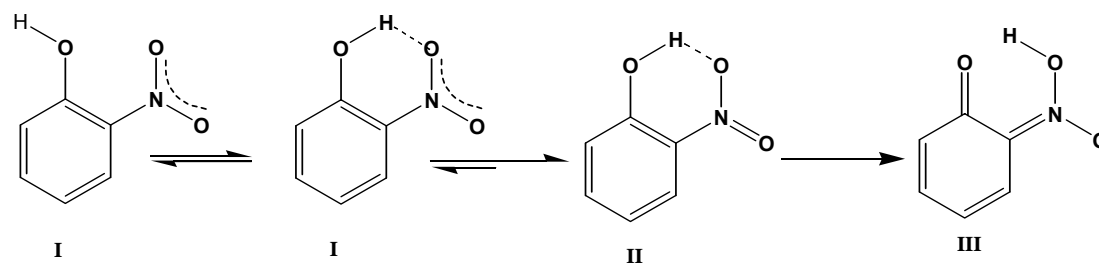
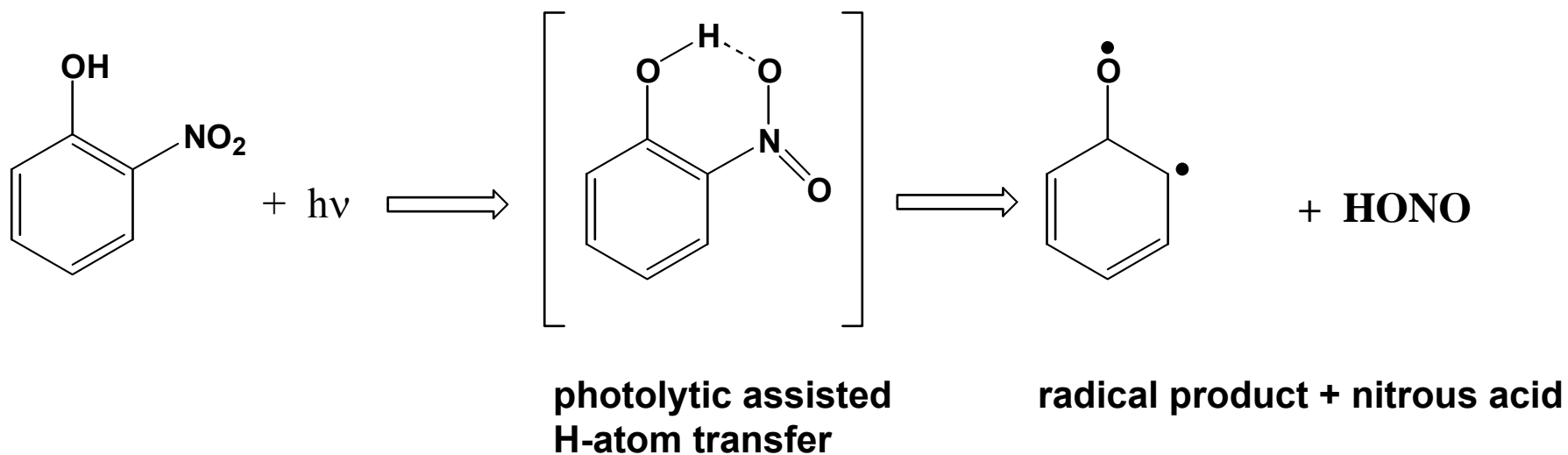
UV spectra of 3-methyl-2-nitrocresol



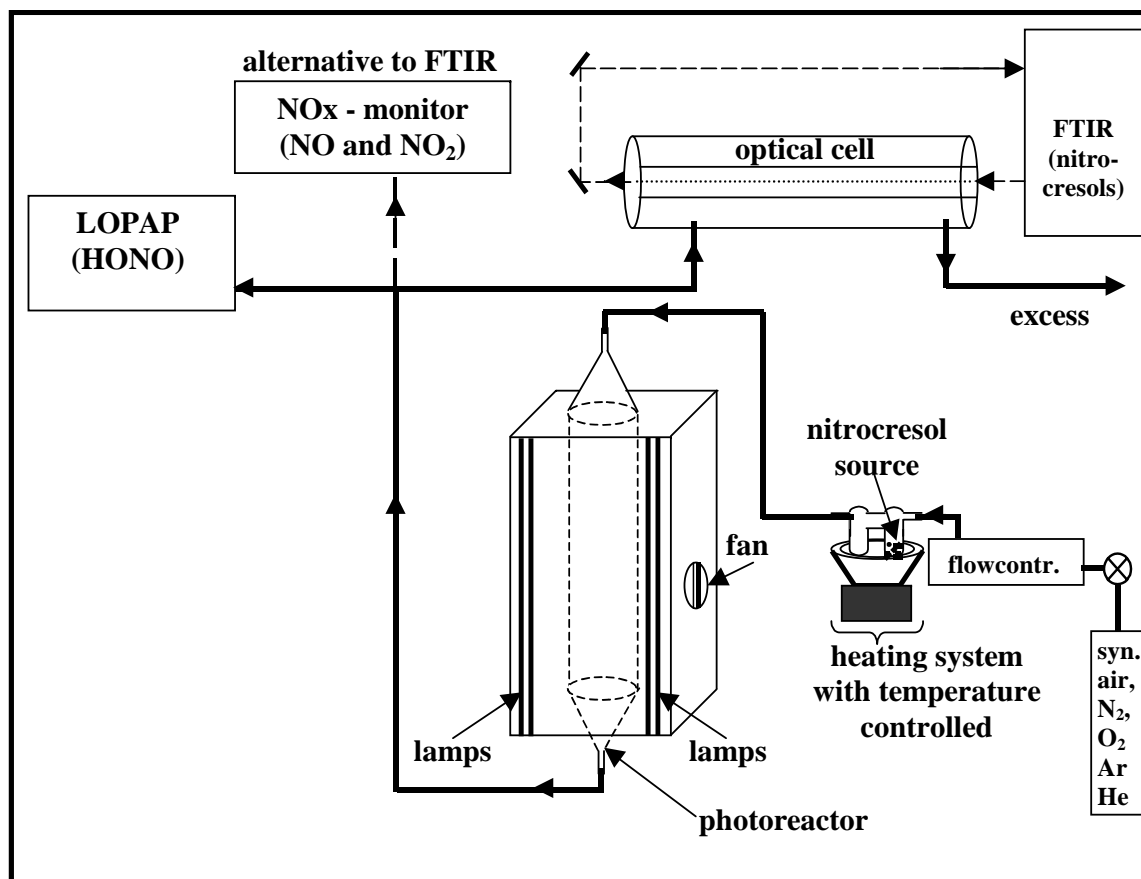
Proposed nitrophenol atmospheric photolysis pathways



H-bonding in 2-nitrophenols



Flow system used for study of nitrophenol photolysis



For Harvey (and others)

LOPAP (HONO) instrument costs around 50.000 EURO.

More information can be found at: info@quma.com.

Experiments on the photolysis of 2-nitrophenols

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

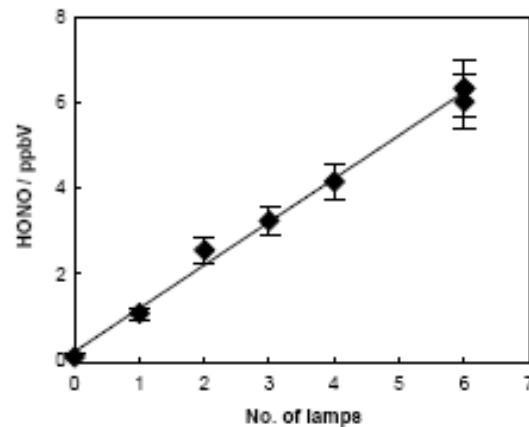
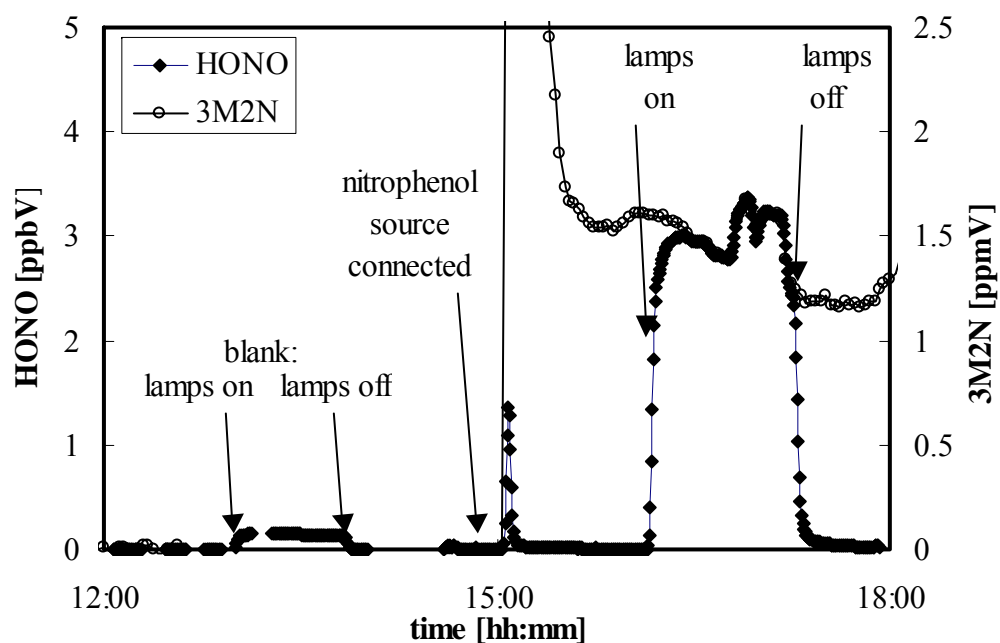


Fig. 4 HONO formation during the photolysis of 3M2NP in the large photoreactor as a function of the number of operating lamps ($t_{\text{res. (large)}} = 26.7$ s).

Photolysis of 2-nitrophenols

Extensive tests performed to test mechanism of HONO formation

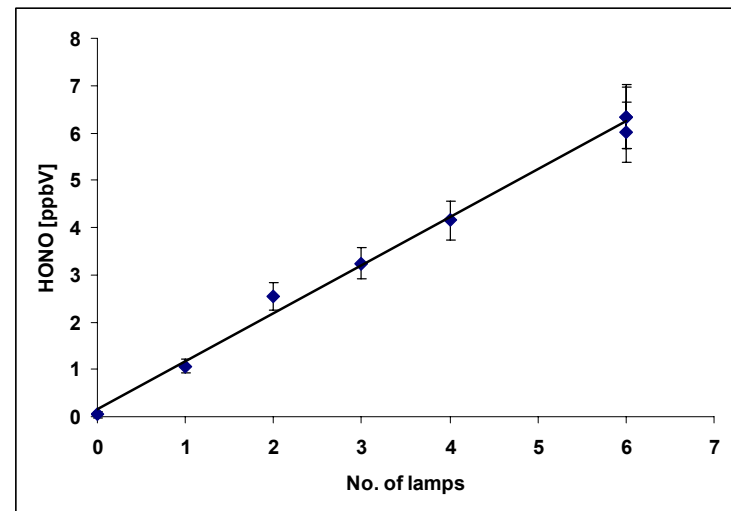
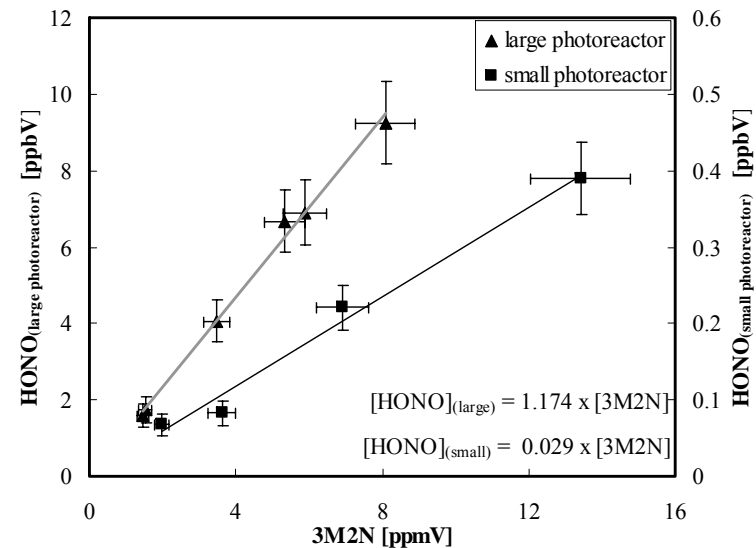
Tested effects of:

Number of photolysis lamps

Concentration of the nitrophenols

Change in surface to volume ratio

Bath gas (Ar, N₂, O₂, syn air)



Photolysis of 2-nitrophenols

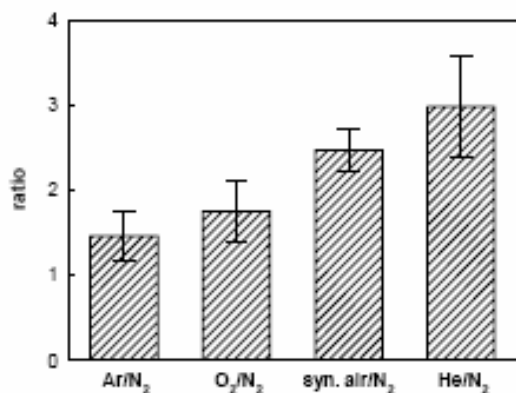
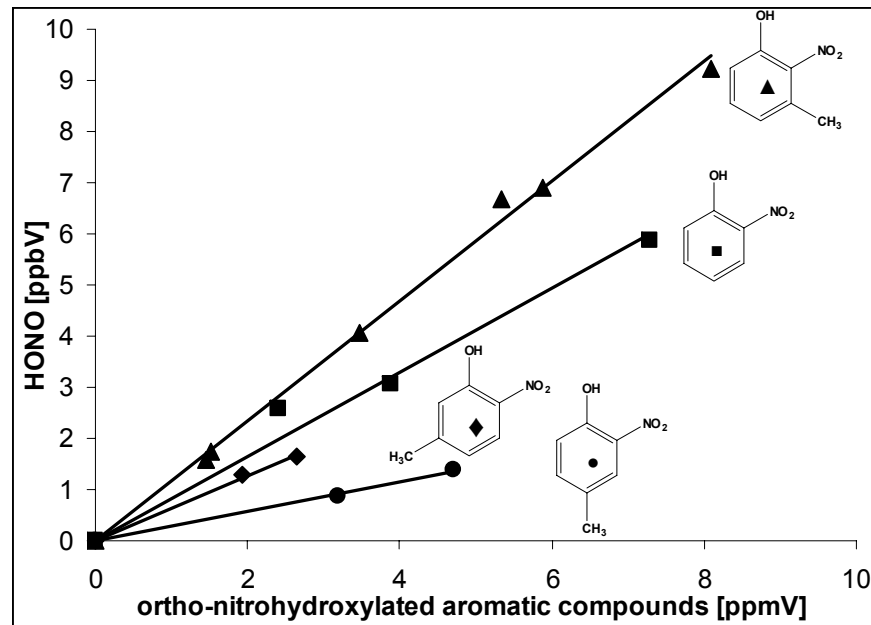


Fig. 6 Ratio of the HONO formation during the irradiation of 3M2NP in a certain buffer gas to the formation in pure nitrogen normalized to the same concentration of 3M2NP.

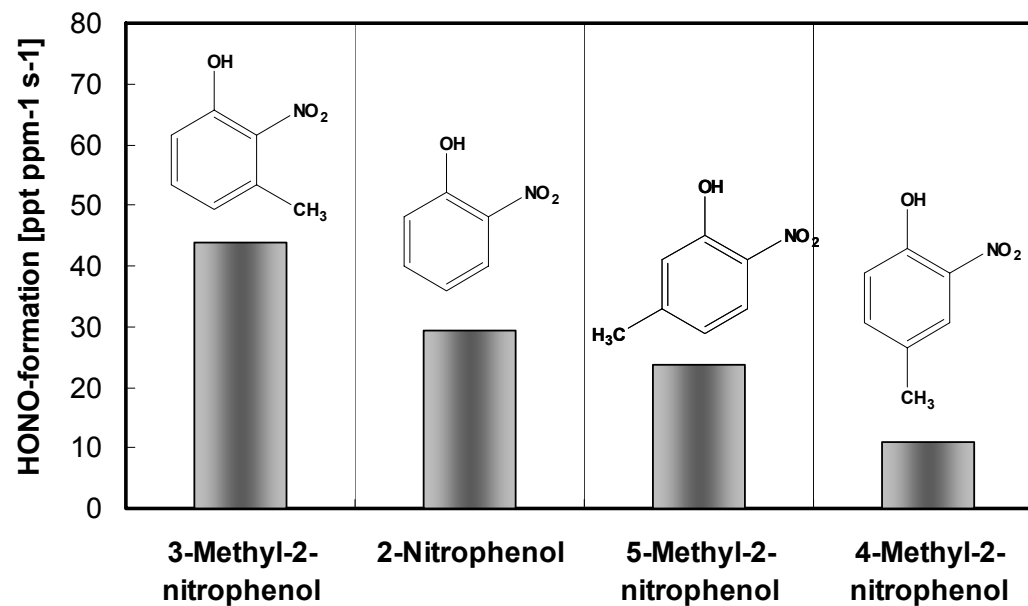
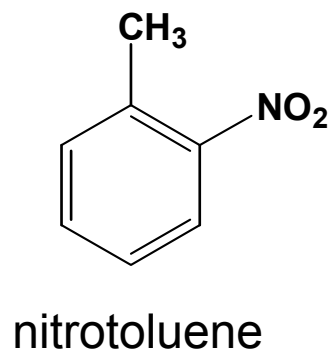


All observations are in line with a purely photolytic production of HONO

No formation of NO₂ observed

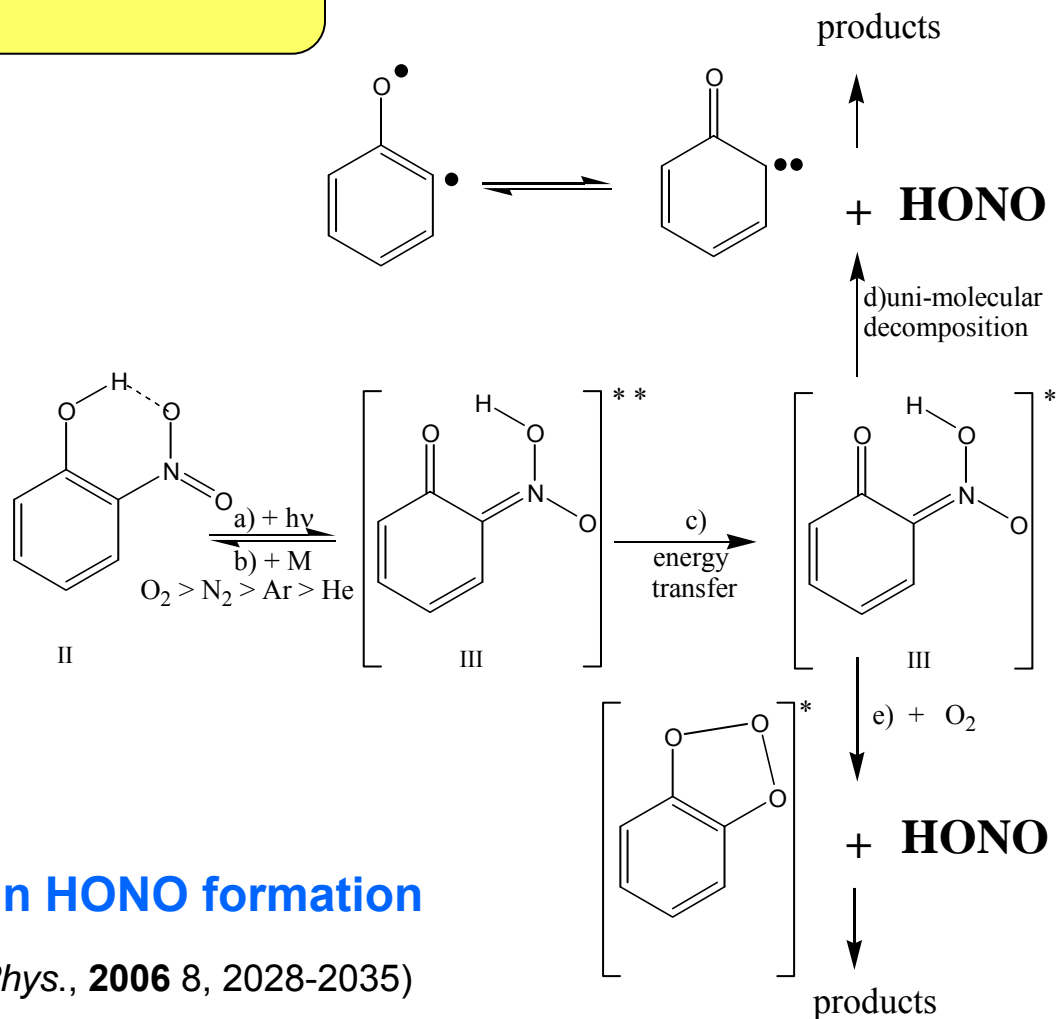
O₂ is not only a quench gas but appears to be active in the mechanism

Photolysis of 2-nitrophenols



HONO formation rate (ppt ppm⁻¹ s⁻¹) from the different ortho-nitrohydroxylated monoaromatic compounds observed in the flow system.

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
$\tau_{hv}^{(a)}$ (min)	~ 25 min	~ 23 min	~ 44 min	~ 37 min
$\tau_{OH}^{(b)}$	7.2 d	~ 47 h	~ 50 h	~ 24 h

(a) Calculated for atmospheric conditions against $J(NO_2)$

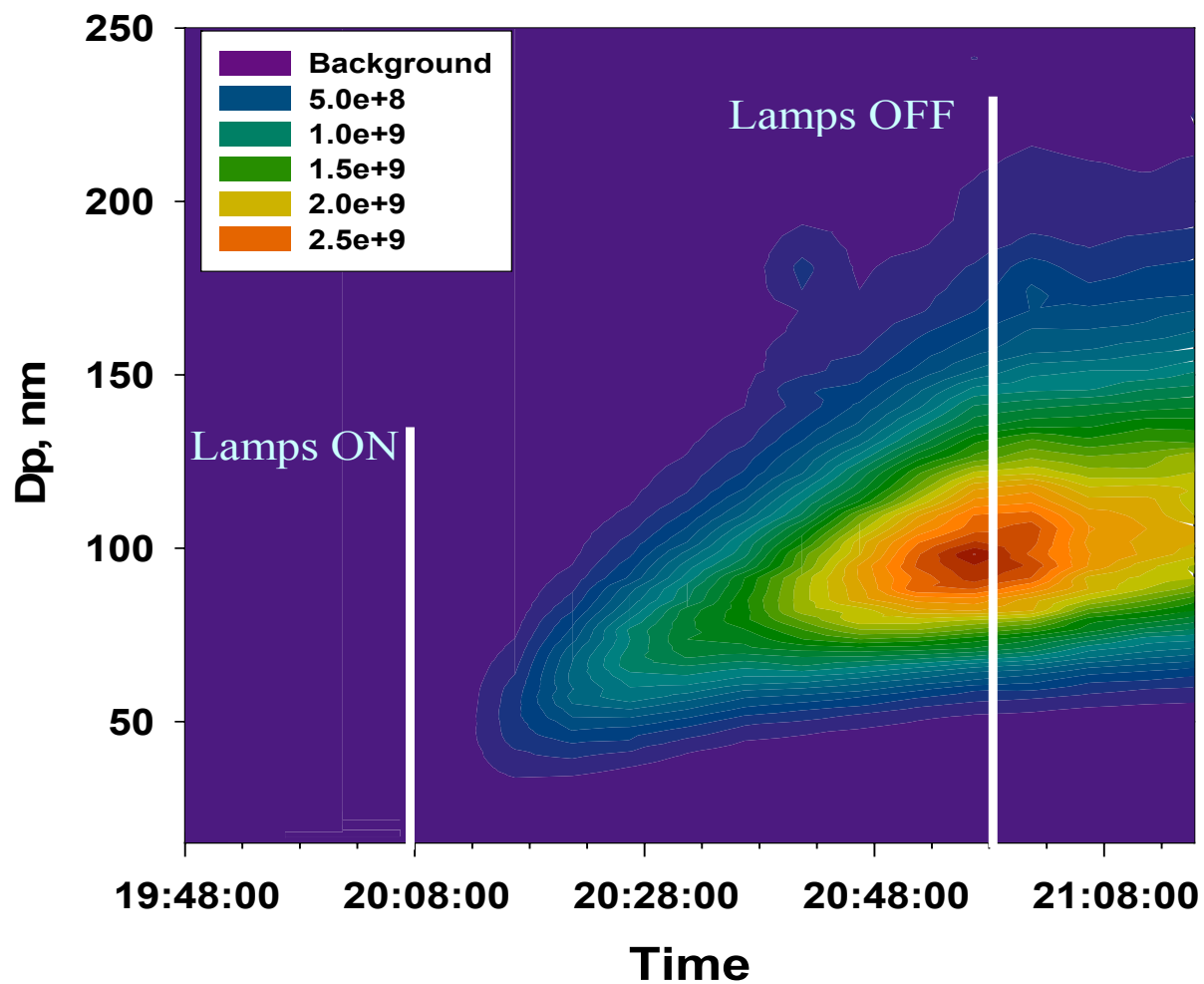
(b) Daily average OH = 1.6×10^6 cm⁻³ (Prinn *et al.*, 1995).

Assuming 1 ppb total 2-nitrophenols in the atmosphere

and a $J(\text{NO}_2)$ of 10^{-2} s^{-1}

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

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



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

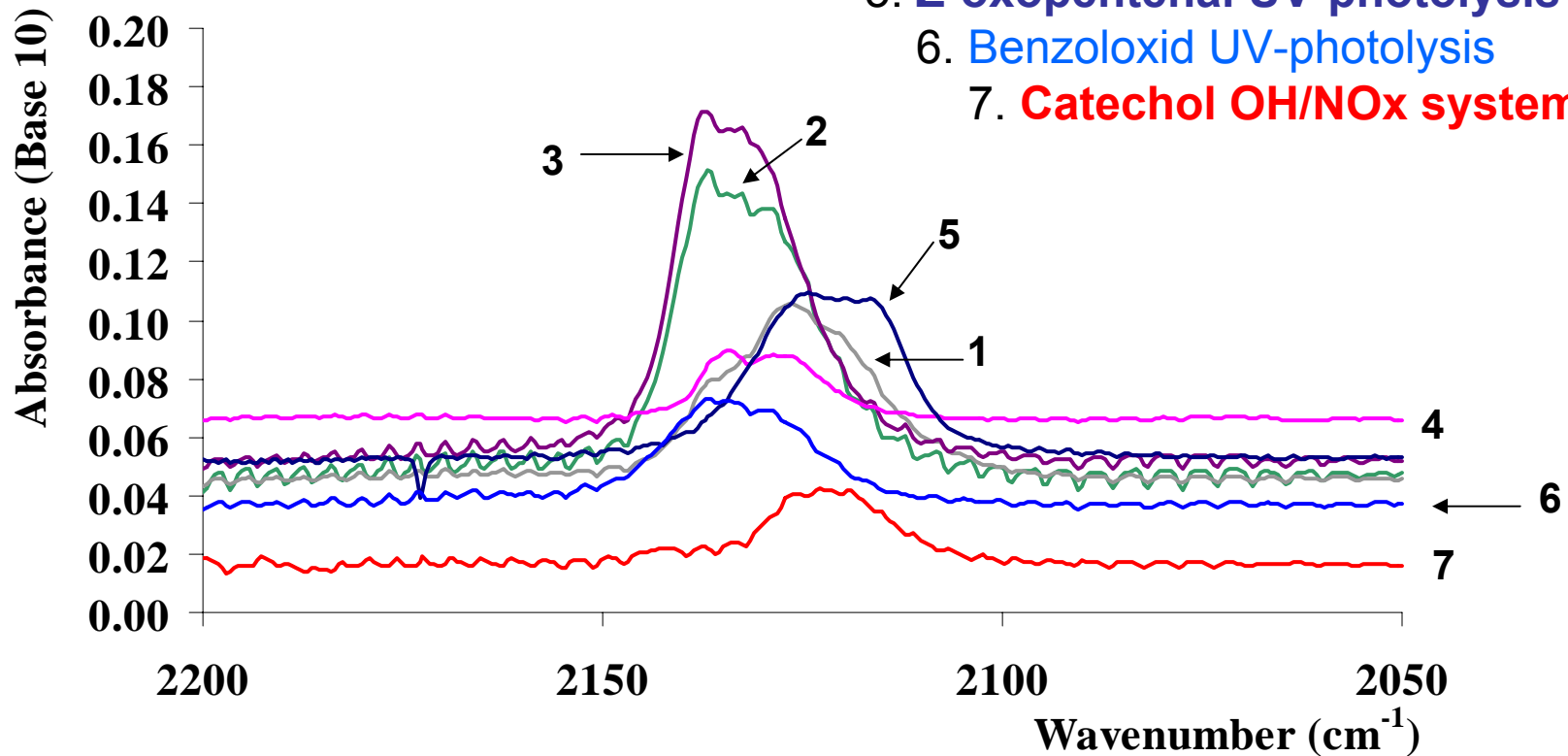
**Rate coefficients for the reactions of Cl atoms with
2-nitrophenol, methyl-2-nitrophenols
and 2-chlorophenol at 298 K**

Compound	k (cm³ molecule⁻¹ s⁻¹)
2-nitrophenol	(0.69 ± 0.02)
3-methyl-2-nitrophenol	(14.97 ± 0.38)
4-methyl-2-nitrophenol	(4.92 ± 0.03)
5-methyl-2-nitrophenol	(2.13 ± 0.03)
6-methyl-2-nitrophenol	(3.04 ± 0.07)
2-chlorophenol	(0.63 ± 0.05)

THANKS FOR LISTENING

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/NO_x system**



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)	$\sim 3 \times 10^5$	$\sim 3 \times 10^5$	$\sim 2 \times 10^5$	$\sim 3 \times 10^5$

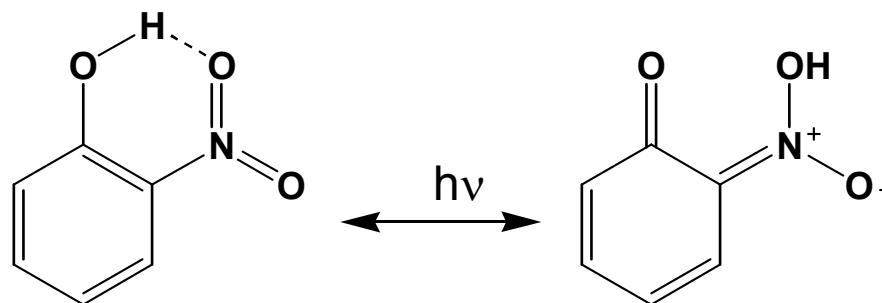
(a) Values for the photolysis rate obtained in the 1080 L quartz glass reactor.

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

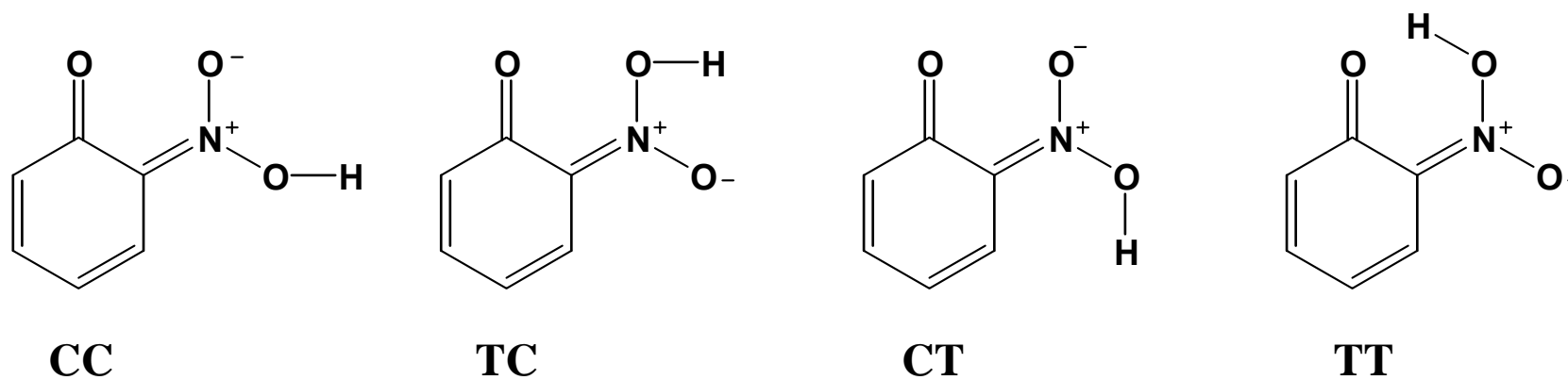
Value for 2-nitrotoulene $7.3 \times 10^{-5} \text{ s}^{-1}$)

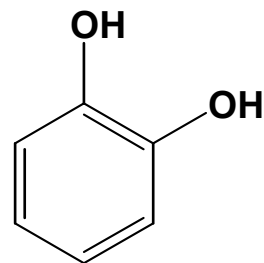
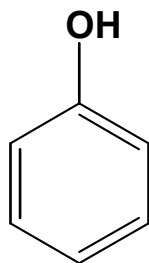
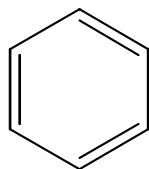
Identification of the aci-nitro form of 2-nitrophenol

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

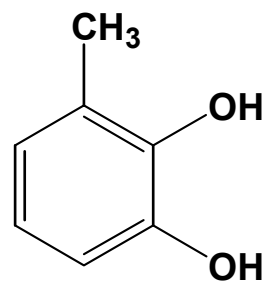
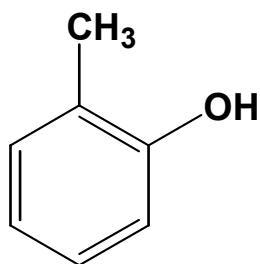
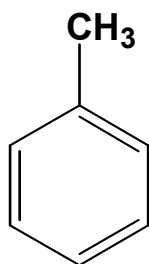


Matrix-isolation infrared spectroscopy in combination with density Function (DFT) calculations



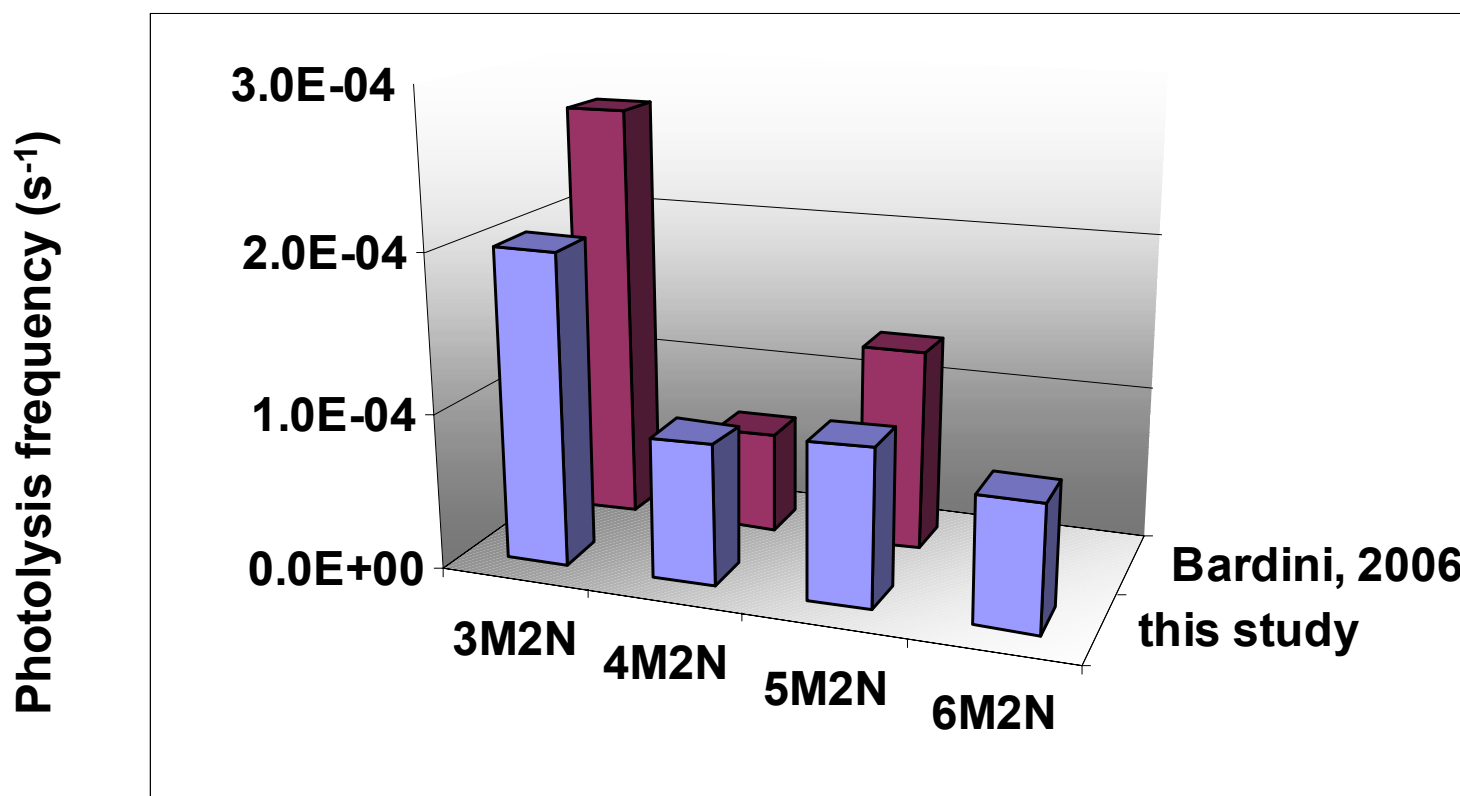


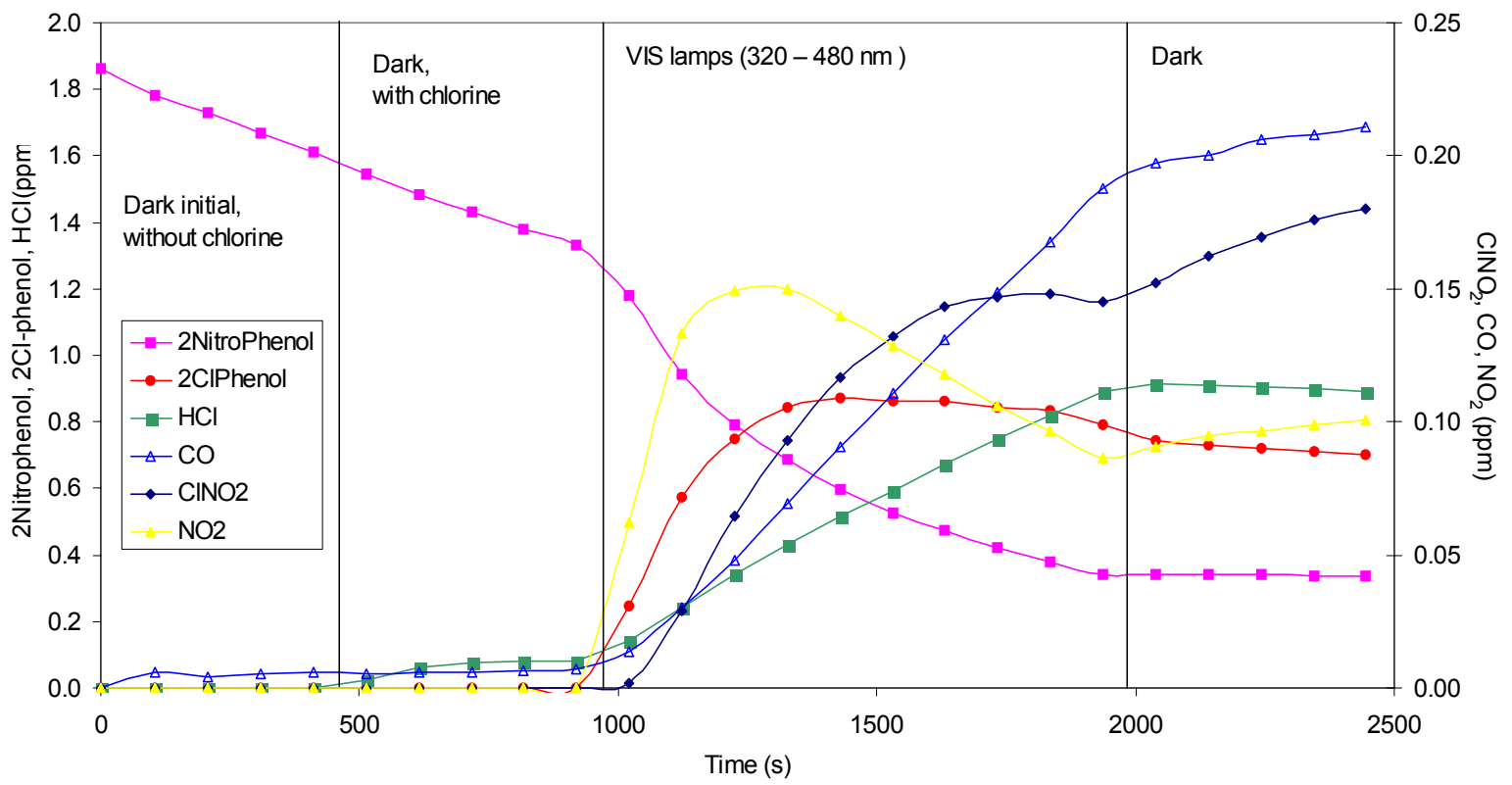
k(OH)	1.22×10^{-12}	2.7×10^{-11}	10.4×10^{-11}	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
k(O₃)	$< 1 \times 10^{-20}$	not known	1×10^{-17}	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
k(NO₃)	$< 3 \times 10^{-17}$	3.8×10^{-12}	9.8×10^{-11}	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

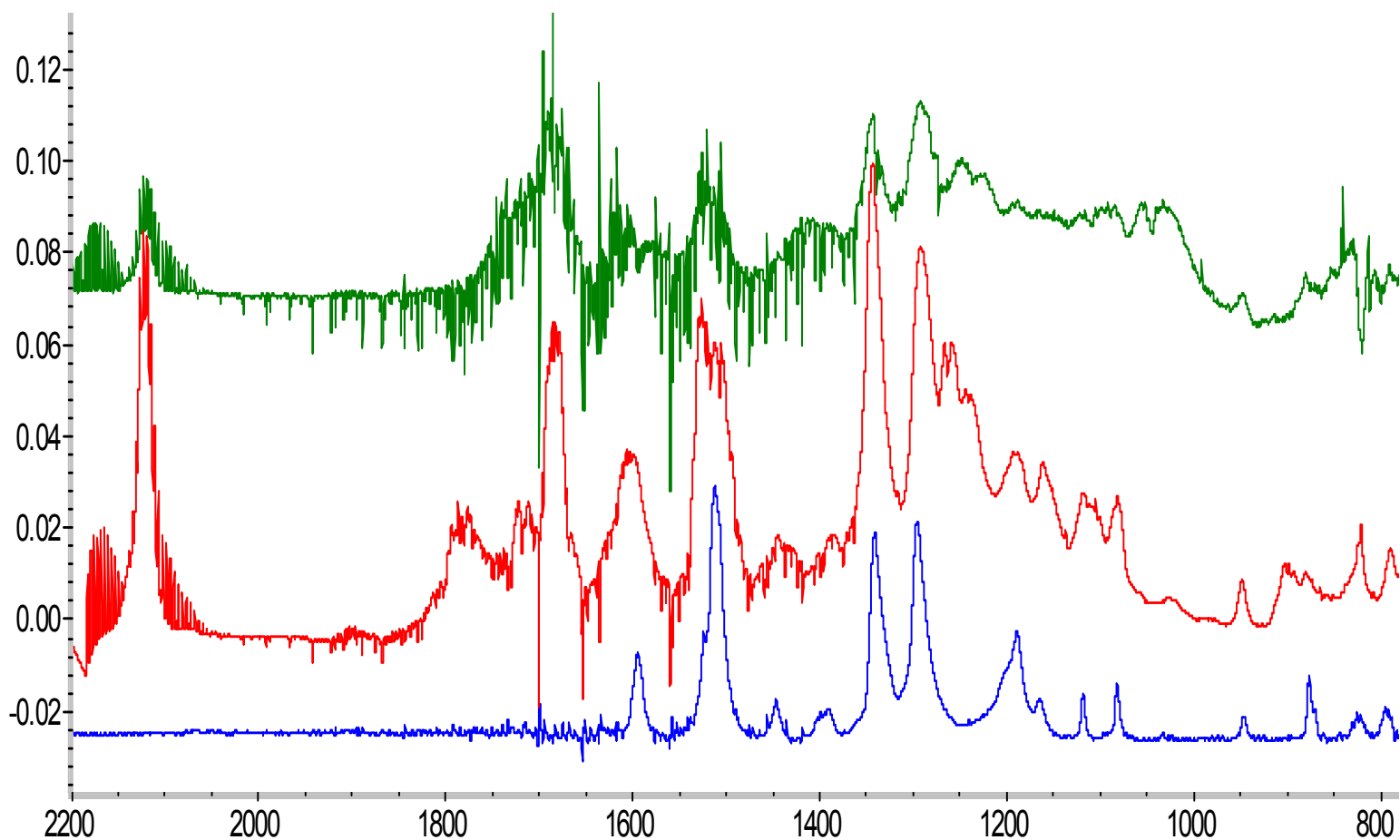


k(OH)	5.6×10^{-12}	4.1×10^{-11}	20.5×10^{-11}	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
k(O₃)	$< 1 \times 10^{-20}$	3×10^{-19}	2.8×10^{-17}	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
k(NO₃)	7×10^{-17}	1.4×10^{-11}	17×10^{-11}	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

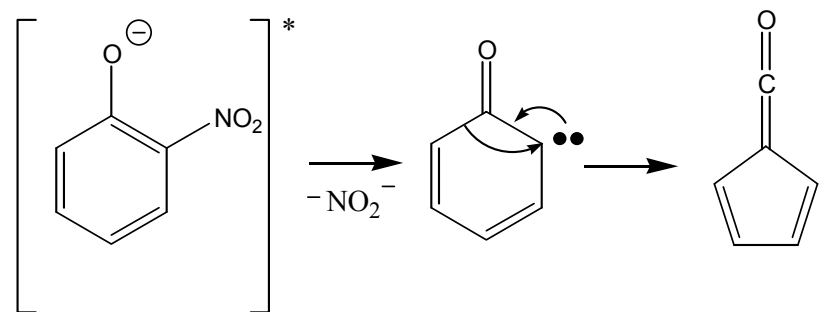
Comparison of estimated atmospheric J-values for 2-nitrocresols with those measured by Bardini (2006) in the EUPHORE chamber, Valencia, Spain.







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

