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 FTIR, GC and DMA
Base optical path 6 meter, total optical path 484.7 m
White System for FT-IR

White System for DOAS

Mixing Fan

Ports for Reactant Inlet and Sampling

Clean Air Inlet

LIF Mounting Position

Actinometers for $O_1^D$ and $J(NO_2)$

EUPHORE chamber at CEAM, Valencia, Spain

Outdoor Photoreactor, Valencia, Spain

EUPHORE chamber at CEAM, Valencia, Spain
Various mechanisms to form ring-retaining and ring-cleavage products

Recent review of the kinetics of aromatic-OH-adducts with $O_2$ and $NO_2$ in:
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

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>Yield (% molar)</th>
<th>Yield (lit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
<td>1,2-dihydroxybenzene</td>
<td>78.1 ± 4.4</td>
<td>6.7 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>1,4-benzoquinone</td>
<td>4.6 ± 2.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-nitrophenol</td>
<td>5.2 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>o-cresol</td>
<td>1,2-dihydroxy-3-methylbenzene</td>
<td>60.8 ± 6.2</td>
<td>5.1 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>methyl-1,4-benzoquinone</td>
<td>10.5 ± 1.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6-methyl-2-nitrophenol</td>
<td>5.5 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>m-cresol</td>
<td>1,2-dihydroxy-3-methylbenzene</td>
<td>70.0 ± 5.2</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>methyl-1,4-benzoquinone</td>
<td>17.2 ± 2.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3-methyl-2-nitrophenol</td>
<td>-</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>5-methyl-2-nitrophenol</td>
<td>4.2 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>p-cresol</td>
<td>1,2-dihydroxy-4-methylbenzene</td>
<td>64.1 ± 8.7</td>
<td>10 ± 4</td>
</tr>
<tr>
<td></td>
<td>4-methyl-2-nitrophenol</td>
<td>7.6 ± 2.1</td>
<td></td>
</tr>
</tbody>
</table>

Major products are 1,2-dihydroxybenzenes and benzoquinones

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

Simplified mechanism for the reaction of phenol/cresols with OH

\[
\text{Phenol/cresol} + \text{OH} \rightarrow \text{M}
\]

\[
\text{M} \rightarrow \text{1,2-dihydroxybenzenes}
\]

\[
\text{M} \rightarrow \text{ring opening-products}
\]

\[
\text{M} \rightarrow \text{benzoquinones}
\]

\[
\text{M} \rightarrow \text{nitrophenols}
\]

\[
\text{M} \rightarrow \text{NO}_2
\]

\[
\text{M} \rightarrow \text{HO}_2
\]
OH oxidation of benzene / toluene – Ring-retaining products

- Benzene: OH oxidation yields products with 50-60% yield, up to 80% of which are ring-retaining.
- Toluene: OH oxidation yields products with 16-18% yield, with + isomers and up to 80% yield.

*(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)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(k) (\times 10^{-11}) cm(^3) s(^{-1})</th>
<th>(\tau_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dihydroxybenzene</td>
<td>10.4 ± 2.1</td>
<td>100 min</td>
</tr>
<tr>
<td>1,2-dihydroxy-3-methylbenzene</td>
<td>20.5 ± 4.3</td>
<td>51 min</td>
</tr>
<tr>
<td>1,2-dihydroxy-4-methylbenzene</td>
<td>15.6 ± 3.3</td>
<td>67 min</td>
</tr>
</tbody>
</table>

Rate coefficients at 298 K for the reactions of O$_3$ with Dihydroxybenzenes
(relative kinetic technique at 298 K)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k$ (10$^{-17}$ cm$^3$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dihydroxybenzene</td>
<td>0.96 $\pm$ 0.0</td>
</tr>
<tr>
<td>1,2-dihydroxy-3-methylbenzene</td>
<td>2.80 $\pm$ 0.13</td>
</tr>
<tr>
<td>1,2-dihydroxy-4-methylbenzene</td>
<td>2.63 $\pm$ 0.34</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>1080 l reactor k (10⁻¹¹ cm³ s⁻¹)</th>
<th>EUPHORE k (10⁻¹¹ cm³ s⁻¹)</th>
<th>k(average) (10⁻¹¹ cm³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dihydroxybenzene</td>
<td>9.03 ± 3.7</td>
<td>10.6 ± 4.3</td>
<td>9.8 ± 5.0</td>
</tr>
<tr>
<td>1,2-dihydroxy-3-methylbenzene</td>
<td>17.3 ± 5.6</td>
<td>17.1 ± 4.8</td>
<td>17.2 ± 5.6</td>
</tr>
<tr>
<td>1,2-dihydroxy-4-methylbenzene</td>
<td>16.0 ± 5.2</td>
<td>13.4 ± 5.0</td>
<td>14.7 ± 6.5</td>
</tr>
</tbody>
</table>

Lifetimes of aromatic compounds

Atmospheric lifetimes calculated using:

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

\[
[\text{O}_3] \text{ a 24-h average of } 7 \times 10^{11} \text{ molecule cm}^{-3}
\]

\[
[\text{NO}_3] \text{ a 12-h nighttime average of } 5 \times 10^8 \text{ molecule cm}^{-3}
\]
For the isomers an average of the rate coefficients has been used. For benzene an upper limit of \( k_{\text{NO}_3} = 3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1} \) has been used.
Rate coefficients for the reaction of Cl with catechols (relative kinetic technique at 298 K)

<table>
<thead>
<tr>
<th>compound</th>
<th>reference</th>
<th>$k_1/k_2$</th>
<th>$k_1$ (10^{-10} cm^3 s^{-1})</th>
<th>$k_1$ (average) (10^{-10} cm^3 s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dihydroxybenzene</td>
<td>ethene</td>
<td>3.8±0.1</td>
<td>6.8±0.1</td>
<td>(6.6 ± 0.1)</td>
</tr>
<tr>
<td></td>
<td>isoprene</td>
<td>1.8±0.1</td>
<td>6.3±0.1</td>
<td></td>
</tr>
<tr>
<td>3-methyl-1,2-dihydroxybenzene</td>
<td>ethene</td>
<td>3.7±0.2</td>
<td>6.7±0.3</td>
<td>(6.7 ± 0.8)</td>
</tr>
<tr>
<td></td>
<td>isoprene</td>
<td>2.1±0.3</td>
<td>7.0±0.7</td>
<td></td>
</tr>
<tr>
<td>4-methyl-1,2-dihydroxybenzene</td>
<td>ethene</td>
<td>3.1±0.5</td>
<td>6.2±0.8</td>
<td>(6.2 ± 0.8)</td>
</tr>
</tbody>
</table>
Dihydroxybenzene (catechol) OH oxidation products (analysis with long path FTIR)

Evidence for formation*

- o-benzoquinone
- maleic anhydride
- CO observed
- not formed

An intermediate „ketene“ absorption is observed

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

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

An intermediate infrared absorption due to a **ketene** group (-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)

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
work on Cl + catechols has shown H-atom abstraction from an OH group is a major channel to ketene and benzoquinone formation.
Generation of phenoxy radicals

\[
\text{main product}
\]
Observation of intermediate ketene absorptions

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

- **Ring opening**: 2,3-dihydroxybenzophenone $\xrightarrow{O_2} 2$-butene-1,4-diketene
- **Ring size reduction**: 1,4-cyclopentadienyl-5-ketene
Dihydroxybenzene (catechol) - NO₃ 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) - NO₃ reaction
Mechanism?
(work 2006)
Oxidation of aromatics to nitrophenols

Nitrophenol formation
Gas phas 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_{\text{OH}}$</th>
<th>k (literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(10^{-12} \text{ cm}^3 \text{ s}^{-1})$</td>
<td>$(10^{-12} \text{ cm}^3 \text{ s}^{-1})$</td>
</tr>
<tr>
<td>NP</td>
<td>~ 1</td>
<td>0.9$^a$</td>
</tr>
<tr>
<td>3M2NP</td>
<td>$(3.69 \pm 0.16)$</td>
<td>11.2$^b$</td>
</tr>
<tr>
<td>4M2NP</td>
<td>$(3.46 \pm 0.18)$</td>
<td>5.38$^b$</td>
</tr>
<tr>
<td>5M2NP</td>
<td>$(7.34 \pm 0.52)$</td>
<td>11.2$^b$</td>
</tr>
<tr>
<td>6M2NP</td>
<td>$(2.70 \pm 0.17)$</td>
<td>-</td>
</tr>
</tbody>
</table>

a) Zetzsch and coworkers using FP-RF;
UV spectra of 2-nitrophenols

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)
UV spectra of 3-methyl-2-nitroresol
Proposed nitrophenol atmospheric photolysis pathways

- **Pathway 1**: 
  \[ \text{OH} + \text{NO}_2 \rightarrow \text{NO} + \text{H} \]  
  (minimum energy 389 KJ mol\(^{-1}\) = threshold of 307 nm)

- **Pathway 2**: 
  \[ \text{OH} + \text{NO}_2 \rightarrow \text{O}^3P + \text{NO}_2 \]  
  (minimum energy 297 KJ mol\(^{-1}\) = 403 nm)

- **Pathway 3**: 
  \[ \text{OH} + \text{NO}_2 \rightarrow \text{H} + \text{NO}_2 \]  
  (minimum energy 362 KJ mol\(^{-1}\) = 330 nm)
H-bonding in 2-nitrophenols

\[
\text{OH} \quad \text{NO}_2
\]

\[ + \text{hv} \quad \Rightarrow \]

\[
\text{photolytic assisted}
\]

\[
\text{H-atom transfer}
\]

\[
\text{radical product + nitrous acid}
\]

\[
\text{I} \quad \text{II} \quad \text{III}
\]
Flow system used for study of nitrophenol photolysis

- LOPAP (HONO)
- NOx monitor (NO and NO₂)
- Optical cell
- FTIR (nitrocresols)
- Excess
- Photoreactor
- Heating system with temperature controlled
- Flow contr.
- Syn. air, N₂, O₂, Ar, He
- Alternative to FTIR
- FTIR (nitrocresols)
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


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

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

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

<table>
<thead>
<tr>
<th>compound</th>
<th>2-nitrophenol</th>
<th>3-methyl-2-nitrophenol</th>
<th>4-methyl-2-nitrophenol</th>
<th>5-methyl-2-nitrophenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{hv}^{(a)}$ (min)</td>
<td>~ 25 min</td>
<td>~ 23 min</td>
<td>~ 44 min</td>
<td>~ 37 min</td>
</tr>
<tr>
<td>$\tau_{OH}^{(b)}$</td>
<td>7.2 d</td>
<td>~ 47 h</td>
<td>~ 50 h</td>
<td>~ 24 h</td>
</tr>
</tbody>
</table>

(a) Calculated for atmospheric conditions against J(NO$_2$)
(b) Daily average OH = 1.6 x 10$^6$ cm$^{-3}$ (Prinn et al., 1995).
Assuming 1 ppb total 2-nitrophenols in the atmosphere

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

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 very 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  
<table>
<thead>
<tr>
<th></th>
<th>(cm³ molecule⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-nitrophenol</td>
<td>(0.69 ± 0.02)</td>
</tr>
<tr>
<td>3-methyl-2-nitrophenol</td>
<td>(14.97 ± 0.38)</td>
</tr>
<tr>
<td>4-methyl-2-nitrophenol</td>
<td>(4.92 ± 0.03)</td>
</tr>
<tr>
<td>5-methyl-2-nitrophenol</td>
<td>(2.13 ± 0.03)</td>
</tr>
<tr>
<td>6-methyl-2-nitrophenol</td>
<td>(3.04 ± 0.07)</td>
</tr>
<tr>
<td>2-chlorophenol</td>
<td>(0.63 ± 0.05)</td>
</tr>
</tbody>
</table>
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/NOx system**
Laboratory photolysis rates and steady-state OH radical concentrations observed for 2-nitrophenols in a photoreactor.

<table>
<thead>
<tr>
<th>Compound</th>
<th>2-nitrophenol</th>
<th>3-methyl-2-nitrophenol</th>
<th>4-methyl-2-nitrophenol</th>
<th>5-methyl-2-nitrophenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis$^a$ (s$^{-1}$)</td>
<td>(1.5 ± 0.5) × 10$^{-4}$</td>
<td>(1.67 ± 0.11) × 10$^{-4}$</td>
<td>(8.86 ± 1.07) × 10$^{-5}$</td>
<td>(1.07 ± 0.14) × 10$^{-4}$</td>
</tr>
<tr>
<td>OH concentration (cm$^{-3}$)</td>
<td>~ 3 × 10$^5$</td>
<td>~ 3 × 10$^5$</td>
<td>~ 2 × 10$^5$</td>
<td>~ 3 × 10$^5$</td>
</tr>
</tbody>
</table>

(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$^{-1}$)


Identification of the aci-nitro form of 2-nitrophenol


Matrix-isolation infrared spectroscopy in combination with density Function (DFT) calculations
<table>
<thead>
<tr>
<th></th>
<th>k(OH)</th>
<th>k(O$_3$)</th>
<th>k(NO$_3$)</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CH$_3$OH</strong></td>
<td>$1.22 \times 10^{-12}$</td>
<td>$&lt; 1 \times 10^{-20}$</td>
<td>$\leq 3 \times 10^{-17}$</td>
<td>cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td><strong>CH$_3$C$\equiv$H</strong></td>
<td>$2.7 \times 10^{-11}$</td>
<td>not known</td>
<td>$3.8 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td><strong>CH$_3$COH</strong></td>
<td>$10.4 \times 10^{-11}$</td>
<td>$1 \times 10^{-17}$</td>
<td>$9.8 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td><strong>CH$_3$C$\equiv$OH</strong></td>
<td>$5.6 \times 10^{-12}$</td>
<td>$&lt; 1 \times 10^{-20}$</td>
<td>$7 \times 10^{-17}$</td>
<td>cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td><strong>CH$_3$C$\equiv$OH</strong></td>
<td>$4.1 \times 10^{-11}$</td>
<td>$3 \times 10^{-19}$</td>
<td>$1.4 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td><strong>CH$_3$C$\equiv$OH</strong></td>
<td>$20.5 \times 10^{-11}$</td>
<td>$2.8 \times 10^{-17}$</td>
<td>$17 \times 10^{-11}$</td>
<td></td>
</tr>
</tbody>
</table>
Recent quantification of dienedials by IFG and EUPHORE
(Berndt and Böge, PCCP 2006, 8, 1205-1214)
Nitrophenol, 2Cl-phenol, HCl

Dark, with chlorine

Dark initial, without chlorine

VIS lamps (320 – 480 nm )

Dark
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)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Mass catechol reacted (mg m³)</th>
<th>Mass aerosol (mg m³)</th>
<th>Aerosol yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-DHB (cyclohexane) + O₃</td>
<td>279</td>
<td>44.3</td>
<td>19.9</td>
</tr>
<tr>
<td>1,2-DHB (cyclohexane) + O₃</td>
<td>229</td>
<td>44.7</td>
<td>24.8</td>
</tr>
<tr>
<td>1,2-DHB + O₃</td>
<td>1308</td>
<td>299.6</td>
<td>27.6</td>
</tr>
<tr>
<td>1,2-DHB + O₃</td>
<td>422</td>
<td>85.3</td>
<td>23.7</td>
</tr>
<tr>
<td>1,2-DHB + O₃</td>
<td>158</td>
<td>54.5</td>
<td>33.6</td>
</tr>
<tr>
<td>3M-1,2-DHB (cyclohexane) + O₃</td>
<td>613</td>
<td>117</td>
<td>21.8</td>
</tr>
<tr>
<td>3M-1,2-DHB + O₃</td>
<td>891</td>
<td>197</td>
<td>26.1</td>
</tr>
<tr>
<td>4M-1,2-DHB (cyclohexane) + O₃</td>
<td>1024</td>
<td>1727</td>
<td>18.1</td>
</tr>
<tr>
<td>3M-1,2-DHB + O₃</td>
<td>1490</td>
<td>282</td>
<td>21.0</td>
</tr>
</tbody>
</table>