Identification and Atmospheric Reactions of Polar Products of Selected Aromatic Hydrocarbons (contract no. 03-319)

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• Aromatic hydrocarbons, including PAHs, are present in gasoline and diesel fuels and are emitted in the exhaust from gasoline- and diesel-fueled vehicles.

• The most abundant aromatic compounds are benzene and alkylbenzenes (toluene, the xylenes, ethylbenzene, and 1,2,4-trimethylbenzene) and naphthalene and C\textsubscript{1}-C\textsubscript{2} alkynaphthalenes.
Transformation processes

In the troposphere, these monocyclic aromatics and PAHs react in the gas phase with:

- OH radicals during daytime.
- \( \text{NO}_3 \) radicals during evening and nighttime hours.
- The daytime OH radical reaction is calculated to dominate as their tropospheric loss process.
OH radical reaction

• Kinetic and product studies show that for both monocyclic aromatic hydrocarbons and PAHs, these reactions proceed mainly by initial OH radical addition to the aromatic ring(s) at room temperature and below.

• At elevated temperatures, the reactions proceed by H-atom abstraction.
OH + toluene

OH + aromatic (or OH-PAH) adduct

OH-aromatic (or OH-PAH) adduct
Reactions of OH-aromatic adducts

• For benzene, toluene and the xylenes, the OH-aromatic adducts react with \( \text{O}_2 \) and \( \text{NO}_2 \), with these reactions being of equal importance in air at 1.1 ppm \( \text{NO}_2 \) for benzene, 3.3 ppm \( \text{NO}_2 \) for toluene and 8-13 ppm \( \text{NO}_2 \) for the xylenes.

• Under ambient atmospheric conditions, the OH-monocyclic aromatic adducts react dominantly with \( \text{O}_2 \).

• However, the observation in ambient air of nitro-PAH formed from gas-phase OH radical-initiated reactions suggests that the OH-PAH adducts react to a significant extent with \( \text{NO}_2 \) under ambient atmospheric conditions.
Products, including ring-cleavage dicarbonyls

Products, including nitro-aromatics
Formation of 3-hexene-2,5-dione from OH + p-xylene as a function of [NO₂]

From Bethel et al., 2000
3-Nitrotoluene yields from OH + toluene (data from Atkinson et al., 1989)

\[ k_{\text{NO}_2} = 3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

\[ k_{\text{O}_2} = 5.7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]

92% OH addition to the aromatic ring

\[ \alpha = 7.6\% \text{ (fitted)} \]
Specific tasks carried out

1. Investigation of ring-cleavage dicarbonyls from the OH radical-initiated reactions of monocyclic aromatic hydrocarbons.

2. Develop a reliable and convenient *in situ* source of glyoxal for routine quantitative calibration of analysis methods.

3. Investigation of ring-cleavage dicarbonyls from the OH radical-initiated reactions of selected PAHs.

4. Investigation of nitro-aromatic and nitro-PAH formation yields from the OH radical-initiated reactions as a function of NO₂ concentration.
1. Carbonyl products from OH + monocyclic aromatic hydrocarbons

- Investigated the formation of 1,2- and unsaturated 1,4-dicarbonyls from the OH radical-initiated reactions of toluene, the xylenes and the trimethylbenzenes.

- OH radicals generated by:

\[
\begin{align*}
\text{CH}_3\text{ONO} + h\nu & \rightarrow \text{CH}_3\text{O}^\bullet + \text{NO} \\
\text{CH}_3\text{O}^\bullet + \text{O}_2 & \rightarrow \text{HCHO} + \text{HO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2
\end{align*}
\]
Experiments carried out in 7000 liter Teflon chamber.

Initial concentrations of aromatic, CH$_3$ONO and NO, $\sim$1 ppm each.

20-30% of initial aromatic consumed by reaction.

Final NO$_2$ concentration 0.4-0.9 ppm.
• Aromatic hydrocarbon concentrations measured by GC-FID. Samples collected onto Tenax solid adsorbent, with subsequent thermal desorption and GC-FID analysis.

• Carbonyl products measured by Solid Phase MicroExtraction fibers pre-coated with a derivatizing agent for on-fiber derivatization, with subsequent thermal desorption and analysis by GC-MS.
Solid-Phase MicroExtraction fibers

Pre-coated with O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) for on-fiber derivatization of carbonyl-containing compounds.

\[
\text{PFBHA} \quad + \quad \text{carbonyl-containing compounds} \quad \rightarrow \quad \text{oxime} \quad + \quad \text{H}_2\text{O}
\]
Fibers are retractable. After coating with PFBHA, the fibers are exposed to the chamber contents with the chamber mixing fan on for typically 5 min.

Fiber, \(\sim 20\) mm long
OH + ρ-Xylene

- 3H25DO
- CH₃C(O)CHO
- (CHO)₂
- CH₃C(O)CH=CHC(O)CH₃
- MW 100
- tolualdehyde
<table>
<thead>
<tr>
<th>ring-opened product</th>
<th>toluene</th>
<th>xylene</th>
<th>trimethylbenzene</th>
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<tbody>
<tr>
<td></td>
<td>o-</td>
<td>m-</td>
<td>p-</td>
</tr>
<tr>
<td>(CHO)$_2$</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>CH$_3$C(O)CHO</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>CH$_3$C(O)C(O)CH$_3$</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>HC(O)CH=CHCHO</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>CH$_3$C(O)CH=CHCHO</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>CH$_3$C(O)C(CH$_3$)=CHCHO</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>CH$_3$C(O)CH=CHC(O)CH$_3$</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>CH$_3$C(O)CH=C(CH$_3$)CHO</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Dicarbonyls from OH + monocyclic aromatics

- All possible 1,2-dicarbonyls (glyoxal, methylglyoxal and biacetyl) are observed. Biacetyl is only formed from o-xylene and 1,2,3- and 1,2,4-trimethylbenzene.
- A series of unsaturated 1,4-dicarbonyls are observed (but not all possible ones).
- 3-Hexene-2,5-dione ($\text{CH}_3\text{C(O)CH=CHC(O)CH}_3$) is only formed from $p$-xylene and 1,2,4-trimethylbenzene.
- These data are qualitative.
- 3-Hexene-2,5-dione can be analyzed by GC without prior derivatization. At low NO$_2$ concentrations the 3-hexene-2,5-dione formation yield from OH + $p$-xylene is identical to that of the potential co-product glyoxal (Bethel et al., 2000; Volkamer et al., 2001, 2005).
- Yields of 1,2-dicarbonyls and, if possible, unsaturated 1,4-dicarbonyls are needed as a function of [NO$_2$].
Proposed reaction scheme for OH-toluene adduct + O₂

-only important at high (ppm) NO levels

\[
\begin{align*}
\text{CH}_3\text{C(O)CHO} & \quad \text{HC(O)CH=CHCH=C(CH}_3\text{)CHO} \\
\text{HC(O)CH=CHCH=C(CH}_3\text{)CHO} & \quad \text{CH}_3\text{C(O)CHO} + \text{HC(O)CH=CHCHO}
\end{align*}
\]
2. Source of glyoxal for routine calibration

- Glyoxal, $(\text{CHO})_2$, is available as a hydrate and is difficult to prepare pure in the gas phase.
- Use a gas-phase reaction to generate known amounts of glyoxal.

- $\text{OH} + (\text{CH}_3)_2\text{C}=\text{CHCHO}$ (3-methyl-2-butenal) was chosen as a candidate.
OH + (CH₃)₂C=CHCHO

• Measured OH radical reaction rate constant of 3-methyl-2-butenal; k = 6.2 x 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ at 296 ± 2 K. 7000 liter Teflon chamber used, with GC-FID analyses.

• Investigated products using in situ FT-IR spectroscopy in 5870 liter evacuable chamber.

• Additionally, the formation of (CH₃)₂C(OH)CHO was observed using coated-SPME/GC-FID analyses, and a formation yield of 4.6 ± 0.7% measured.
5870 liter evacuable chamber interfaced to an FT-IR spectrometer
OH + 3-methyl-2-butenal: FT-IR spectra

Initial 3-methyl-2-butenal

Products, after reaction

After subtraction of glyoxal and acetone

Reference spectra
Formation yields from FT-IR analyses

- Acetone: 76 ± 6%
- Glyoxal: 40 ± 3%
- RONO₂: 8.5 ± 2.3%
OH + (CH₃)₂C=CHCHCHO

• Glyoxal is formed in 40 ± 3% yield.

• 3-Methyl-2-butenal is a factor of 5.6 more reactive towards OH radicals than is glyoxal; secondary reaction of glyoxal with OH radicals is hence minor during the reactions.

• OH + (CH₃)₂C=CHCHO is a good *in situ* source of glyoxal for routine calibration purposes.
3. Formation of glyoxal and selected dicarbonyls from OH + PAHs

- Glyoxal formation from OH + acenaphthene and acenaphthylene.
- Glyoxal and phthaldialdehyde from OH + naphthalene.
- Glyoxal and 2-acetylbenzaldehyde from OH + 1-methylnaphthalene.
- Glyoxal and 1,2-diacetylbenzene from OH + 1,4-dimethylnaphthalene.
Glyoxal yields measured. Are the aromatic dicarbonyl yields the same as those for glyoxal?
Experiments carried out in 7000 liter Teflon chamber.

OH radicals generated by photolysis of CH$_3$ONO or, at low NO$_x$ or in absence of NO$_x$, by the dark O$_3$ + 2-methyl-2-butene reaction.

PAH measured by GC-FID after collection onto Tenax solid adsorbent.

Glyoxal by coated SPME/GC-FID, with calibrations using the OH + (CH$_3$)$_2$C=CHCHO reaction to generate known amounts of glyoxal.

Aromatic dicarbonyl by SMPE/GC-FID.
Glyoxal from OH + naphthalene

Note:
Most data offset vertically for clarity.
Maximum glyoxal formed was 35 ppb.
Glyoxal yield $= 6 \pm 2\%$, independent of initial $\text{NO}_x$.

OH from photolysis of $\text{CH}_3\text{ONO}$

OH from dark $\text{O}_3 + 2$-methyl-$2$-butene reaction
OH + acenaphthene and acenaphthylene; initial NO\textsubscript{x} = 0.2-5 ppm

16 ± 5%

1.3 ± 0.4%
OH + naphthalene, initial NOₓ = 0.2-5 ppm

Glyoxal yield = 4.9%
Phthalialdehyde yield = 4.7%

Slope = 0.944
<table>
<thead>
<tr>
<th>PAH</th>
<th>glyoxal (%)</th>
<th>dicarbonyl coproduct (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acenaphthene</td>
<td>16 ± 5</td>
<td></td>
</tr>
<tr>
<td>acenaphthylene</td>
<td>1.3 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>naphthalene</td>
<td>6 ± 2</td>
<td>4.9 ± 1.5</td>
</tr>
<tr>
<td>1-methylnaphthalene</td>
<td>4.1 ± 1.5</td>
<td>6.8 ± 2*</td>
</tr>
<tr>
<td>1,4-dimethylnaphthalene</td>
<td>4.4 ± 1.5</td>
<td>6.1 ± 2*</td>
</tr>
</tbody>
</table>

*Likely upper limit due to losses during calibration in chamber*
Glyoxal and potential co-product formation

• Glyoxal is a product from OH + acenaphthene and (very minor) from acenaphthylene.
• Glyoxal is a relatively minor product from OH + naphthalene and selected alkylnaphthalenes. Within the experimental uncertainties, the corresponding aromatic dicarbonyl is formed with the same yield as glyoxal, indicating they are co-products.

• For the NO$_x$ concentrations used here, the dominant reactions of the OH-naphthalene and OH-alkylnaphthalene adducts are with NO$_2$.
• The major pathway of these reactions appears to be ring cleavage to form 2-formylcinnamaldehyde ($\geq$30-35%) from naphthalene and homologous dicarbonyls from other alkylnaphthalenes (CARB contract no.03-314).
4. Nitro-aromatic formation from OH radical-initiated reactions of selected aromatic hydrocarbons

- As noted, nitro-aromatic formation from monocyclic aromatics (benzene, toluene, xylenes) is a function of the NO\textsubscript{2} concentration and approaches zero at ambient NO\textsubscript{2} levels.

- However, the nitro-PAHs formed from OH radical-initiated reactions of PAHs conducted in the laboratory are observed in ambient air at concentrations consistent with yields measured in the laboratory at high (>1 ppm) NO\textsubscript{2} concentrations.
General mechanism

\[
\text{Nitroaromatic yield} = \alpha \frac{k_c[\text{NO}_2]}{(k_c[\text{NO}_2] + k_d[\text{O}_2])}
\]
Nitro-aromatic yields from OH + toluene, naphthalene and biphenyl as a function of NO₂

- Experiments carried out in a 7500 liter Teflon chamber. OH radicals formed by:
  \[ \text{NO}_2 \geq 0.1 \text{ ppm:} \]
  \[ \text{CH}_3\text{ONO} + \text{hv} \rightarrow \text{CH}_3\text{O}^\cdot + \text{NO} \]
  \[ \text{CH}_3\text{O}^\cdot + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \]
  \[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]
  \[ \text{NO}_2 \leq 0.2 \text{ ppm:} \]
  from \( \text{O}_3 \) + 2-methyl-2-butene reaction in the dark.

- Analyses by GC-FID and GC/MS.
Analysis methods

• Toluene and naphthalene analyzed by GC-FID after collection of gas samples onto Tenax-TA solid adsorbent.

• Naphthalene and biphenyl analyzed by GC-FID after exposure of PDMS SPME fiber to chamber contents.

• Nitroaromatics analyzed by GC/MS-NCI after exposure of PDMS/DVB SPME fiber to chamber contents.
3-Nitrotoluene formation from OH + toluene

Adduct reactions with O$_2$ and NO$_2$ equal at 3.3 ppm NO$_2$

Range in yields due to uncertainties in SPME/GC-MS response factor at very low 3-nitrotoluene levels
1- and 2-Nitronaphthalene formation from OH + naphthalene

Adduct + O₂ and NO₂ reactions equal at 60 ppb NO₂. α = 0.6%.

NO₃ radical formation likely, leading to enhanced nitronaphthalene formation.
3-Nitrobenzyl formation from OH + biphenyl

Adduct reactions with O₂ and NO₂ equal at 600 ppb NO₂. \( \alpha = 12\% \).

NO₃ radical formation likely
Aromatic and nitroaromatic concentrations were measured at Upland, CA (1000-1500 hr, October 2006)

\[
\begin{align*}
\text{OH + aromatic} & \rightarrow \text{nitroaromatic} \\
\text{nitroaromatic} & \rightarrow \text{loss by dilution} \\
\text{nitroaromatic + h}_\nu & \rightarrow \text{products}
\end{align*}
\]

\[
\frac{[\text{nitroaromatic}]}{[\text{aromatic}]} = \frac{\alpha k_{OH}[OH]}{k_d + k_{phot}}
\]

\[
\left(\frac{[\text{nitroaromatic}]}{[\text{aromatic}]}\right)\div\left(\frac{[3-\text{nitrotoluene}]}{[\text{toluene}]}\right) = \left(\frac{\alpha k_{OH}}{k_d + k_{phot}}\right)_{\text{aromatic}}\div\left(\frac{\alpha k_{OH}}{k_d + k_{phot}}\right)_{\text{toluene}}
\]

Get from our laboratory data for the ambient \(\text{NO}_2\) concentration

No photolysis of 3-nitrobiphenyl or 3-nitrotoluene assumed
1- and 2-Nitronaphthalene formation from OH + naphthalene

[Graph showing the relationship between NO₂ (ppm) and Nitronaphthalene yield (%).]

1-Nitronaphthalene?
3-Nitrobiphenyl formation from OH + biphenyl

- Yields from laboratory experiments
- Yields from ambient data
Nitroaromatic formation from OH reactions

• The dependence of the 3-nitrotoluene formation yields from OH + toluene on NO₂ is totally consistent with literature kinetic and mechanistic data. The OH-toluene adducts react with O₂ under atmospheric conditions.

• The OH-biphenyl adducts react dominantly with NO₂ down to ~600 ppb of NO₂, and the OH-naphthalene adducts react dominantly with NO₂ down to ~60 ppb of NO₂.

• Laboratory data are generally consistent with ambient measurements of aromatics and their nitro-products.
Acknowledgements:

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