Polycyclic Aromatic Hydrocarbons (PAHs): Sources of Ambient Quinones: (Contract No. 03-314)

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Potential Health Impacts of Ambient Quinones

- Quinones may covalently bind to proteins and/or DNA.
- Quinones may undergo redox cycling with their semiquinones, leading to formation of reactive oxygen species (ROS).

Atmospheric Formation of Nitro-PAHs & PAH-quinones

**Gas-phase PAHs**
- OH Radical - Daytime
- NO₃ Radical - Nighttime

**Particle-associated PAHs**
- Photolysis (& OH Radical?)
- Ozone – 24 hrs.
- NO₂/HNO₃

**Nitro-PAHs**
- \( hν \)

**Quinones**
- OH Radical - Daytime
- NO₃ Radical - Nighttime
- Photolysis (& OH Radical?)
- Ozone – 24 hrs.
- NO₂/HNO₃
Sources of Ambient PAH-quinones

- Direct emissions, e.g. from diesel exhaust.

- Atmospheric formation from radical-initiated gas-phase reactions of PAHs.

- Photolysis of nitro-PAHs.

- Heterogeneous reactions of PAHs on particles, e.g. with ozone.
Jan. 2003, Los Angeles

Gas-phase

Naphthalene
0.08 Torr
1600 ng/m³

Phenanthrene
1.2 x 10⁻⁴ Torr
17 ng/m³

2-MN 730 ng/m³
Σ MNs 1000 ng/m³

Σ DMNs + ENs 155 ng/m³

More abundant

Particle-associated

Benzo[a]pyrene
0.8 ng/m³
*Fine et al.

Benzo[ghi]perylene
1.9 ng/m³

Fluoranthene
9.2 x 10⁻⁶ Torr
6.0 ng/m³

Pyrene
4.5 x 10⁻⁶ Torr
6.9 ng/m³

Less abundant


*Fine et al.
PROJECT OBJECTIVES

Evaluate the potential for atmospheric reactions to contribute to the atmospheric PAH-quinone burden by:

• Assessing formation of PAH-quinones from atmospheric reactions (OH, NO₃, O₃) of naphthalene, alkynaphthalenes and phenanthrene.

• Identifying the dimethylnitronaphthalenes (DMNNs) formed from atmospheric reactions of selected dimethylnaphthalenes (DMNs) and studying their photolysis products, which were expected to include quinones.
Atmospheric Pressure Ionization-Mass Spectrometry for Product Identification

In-situ API-MS/MS: selective sensitivity, (excellent for screening for polar products). Protonated [M+H]^+ ions (separation of isomers may be possible by MS/MS, but requires standards to be available).

In-situ screening for quinones.
Gas Chromatography/Mass Spectrometry (GC/MS)

- Quadrupole and ion trap instruments [low mass resolution]
- Electron impact (EI) – [characteristic fragmentations]
- Chemical ionization - positive mode (PCI) [molecular ions]
- Chemical ionization - negative mode (NCI) [very sensitive for nitro-PAHs]

Proton NMR

- Identified by 400 MHz $^1$H NMR: 39 DMNNs/ENNs, two side-chain nitrated DMNs, and 3-methylphthalide.
Sampling of Naphthalene, Alkynaphthalenes and Phenanthrene

- Sampling onto Tenax cartridges for thermal desorption/GC with flame ionization detection (GC-FID). Used to measure amounts reacted during chamber reactions (calibrate, but gives predictable detector response for organic compounds).

Sampling Products for GC/MS Analysis

- Solid Phase Micro-Extraction (SPME) – different fibers for various volatility products and for on-fiber derivatization of carbonyls. Sample chamber contents post-reaction and inject directly into GC/MS. Needs to be calibrated.
Sampling Products for GC/MS Analysis

- Polyurethane foam plugs (PUFs) and filter/PUF combinations – used to sample entire chamber volume for semi-volatile and non-volatile products. Extract with solvent, fractionate by HPLC (if necessary), analyze by GC/MS. (Found some particles “go-through” PUF.)

“Operational” gas/particle distribution because:

- gases may be adsorbed onto the filter or onto particles on the filter.

- particle-adsorbed species may “blow-off” the filter (and be collected on the PUFs).

In ambient operation: PUFs collect 3- and 4-ring PAHs and 2-ring nitro-PAHs.
Phenanthrene (Most abundant 3-ring PAH)

<table>
<thead>
<tr>
<th>Phenanthrene gas-phase reaction with</th>
<th>OH radical(^a)</th>
<th>NO(_3) radical(^b)</th>
<th>Ozone(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lifetimes ((\tau))</td>
<td>4.3 hr</td>
<td>4.6 hr</td>
<td>41 days</td>
</tr>
</tbody>
</table>

\(^a\)12-hr daytime average OH radical concentration of 2.0 \(\times\) \(10^6\) molecules \(\text{cm}^{-3}\).

\(^b\)12-hr nighttime average NO\(_3\) radical concentration of 5 \(\times\) \(10^8\) molecules \(\text{cm}^{-3}\).

\(^c\)24-hr average O\(_3\) concentration of 7 \(\times\) \(10^{11}\) molecules \(\text{cm}^{-3}\).

Note: atmospheric formation of nitro-phenanthrenes expected to be negligible.
9,10-Phenanthrenequinone (9,10-PQ)

- 9,10-PQ has a favorable reduction potential to undergo redox cycling in biological systems; in aerobic yeast systems, 9,10-PQ exerts toxicity through ROS.\(^1\)
- 9,10-PQ was found in diesel and ambient particles and at elevated concentrations at “downwind sites”.\(^2\) 9,10-PQ has been postulated to play a role in the pulmonary toxicity of diesel exhaust particles.\(^3\)
- 9,10-PQ has been observed in ambient air at up to 1 ng m\(^{-3}\) and is responsible for the majority of ROS generation in extracts from ambient Fresno, CA particles.\(^4\)

\(^1\)Rodriguez et al., Toxicology, 201, 185-196 (2004).  
\(^3\)Hiyoshi et al., J. Applied Toxicol. 25, 47-51 (2005).  
Phenanthrene: abundant, gas-phase, 3-ring PAH in ambient air.

9,10-PQ: relative yields measured with SPME sampling [Wang et al., Atmos. Environ. 41, 2025-2035 (2007)].

\[
\text{Phenanthrene} + \text{OH} \rightarrow \text{2,2'-diformylbiphenyl} + 9,10\text{-PQ + other products [0.10]}
\]

\[
\text{Phenanthrene} + \text{O}_3 \rightarrow \text{secondary ozonide from API-MS} + 9,10\text{-PQ + other products [0.06]}
\]

\[
\text{Phenanthrene} + \text{NO}_3 \rightarrow \text{9,10-phenanthrenequinone + other products}
\]

PUF/filter samples, extract, HPLC→GC/MS. Calibrate with standard. 33% yield = [1.0]
Ambient Formation of 9,10-Phenanthrenequinone

Assuming:  
[\text{phenanthrene}] = 10 \text{ ng m}^{-3} \\
[\text{OH}] = 2.0 \times 10^6 \text{ radicals cm}^{-3} \\
[\text{NO}_3] = 5 \times 10^8 \text{ radicals cm}^{-3} \\
[\text{O}_3] = 7 \times 10^8 \text{ molecules cm}^{-3} \\

9,10\text{-PQ} = k_{\text{OH}} [\text{OH}] \times t \times \text{Yield} \times [\text{phen}] = 80 \text{ pg m}^{-3} \text{ hr}^{-1} \\
9,10\text{-PQ} = k_{\text{NO}_3} [\text{NO}_3] \times t \times \text{Yield} \times [\text{phen}] = 800 \text{ pg m}^{-3} \text{ hr}^{-1} \\
9,10\text{-PQ} = k_{\text{O}_3} [\text{O}_3] \times t \times \text{Yield} \times [\text{phen}] = 0.2 \text{ pg m}^{-3} \text{ hr}^{-1} \\

Lifetime of phenanthrene in an organic film exposed to 50 ppbv of O_3 was calculated to be 44 days [Kahan et al., Atmos. Environ., 40, 3448-3459 (2006)].
Recommendations for Future Research

• Ambient measurements should be made of 9,10-phenanthrene quinone to assess the importance of NO$_3$ radical-initiated formation pathways. Since certain nitro-PAHs, or nitro-PAH ratios, are indicators of NO$_3$ chemistry, nitro-PAHs should simultaneously be measured.

• Health effects studies designed to specifically address the importance of nighttime NO$_3$ chemistry should be initiated. An optimum study would have measurements of the NO$_3$ radical, nitro-PAHs, 9,10-phenanthrene quinone (and other PAH quinones), and an appropriate bioassay and/or biological exposure.
### Calculated Tropospheric Lifetimes

<table>
<thead>
<tr>
<th>PAH</th>
<th>( \text{OH}^a )</th>
<th>Extreme ( \text{NO}_3^b )</th>
<th>( \text{O}_3^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>5.7 hr</td>
<td>5.3 day</td>
<td>&gt;80 day</td>
</tr>
<tr>
<td>1-Methylnaphthalene</td>
<td>3.4 hr</td>
<td>2.7 day</td>
<td>&gt;125 day</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>2.8 hr</td>
<td>1.9 day</td>
<td>&gt;40 day</td>
</tr>
<tr>
<td>Dimethylnaphthalenes</td>
<td>1.8-2.4 hr</td>
<td>1-18 hr</td>
<td>&gt;40 day</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>4.3 hr</td>
<td>28 min</td>
<td>41 day</td>
</tr>
</tbody>
</table>

^a Assumes 12-hr daytime average \([\text{OH}] = 2 \times 10^6\) radicals \(\text{cm}^{-3}\).

^b Assumes 12-hr nighttime average \([\text{NO}_3] = 5 \times 10^9\) radicals \(\text{cm}^{-3}\) (100 ppbv \(\text{NO}_2\)).

^c Assumes 24-hr average \([\text{O}_3] = 7 \times 10^{11}\) molecules \(\text{cm}^{-3}\) (30 ppbv).
Chamber hydroxyl (OH) radical-initiated reactions of:
Naphthalene, 1- and 2-MN, 10 DMNs, 1- and 2-EN.
In a series of chamber reactions, API-MS analyses of OH + naphthalene, 1- and 2-methylnaphthalene (MN), the 10 dimethylnaphthalenes (DMNs) and the ethynaphthalenes (ENs) showed quinone products were minor.

API-MS analyses showed major products were:

1. Ring-opened dicarbonyls (32 mass units above parent MW).
2. Ring-opened dicarbonyls of lower MW resulting from loss of two β-carbons (and associated alkyl groups). 
   Shown to be at least partly primary in naphthalene system.
3. Ring-containing products that may be epoxides.

SPME GC/MS analyses (in addition to above, showed): 

4. Anhydride secondary products. [Potential source of phthalic acids suggested as markers of secondary organic aerosol (SOA).] Shown to be secondary in naphthalene system.
Reaction time (sec)

Counts

MW 160

MW 134

dashed line 2\textsuperscript{nd} generation

solid line 1\textsuperscript{st} generation

MW 148

2\textsuperscript{nd} generation from 1\textsuperscript{st} generation phthalaldialdehyde

Atmospheric chemistry studied

Atmospheric chemistry studied

\begin{align*}
\text{MW} & 160 \\
\text{MW} & 134 \\
\text{MW} & 148
\end{align*}
naphthalene: $R_1, R_2 = H$
2-MN: $R_1 = CH_3; \ R_2 = H$
2-EN: $R_1 = CH_3CH_2; \ R_2 = H$
2,3-DMN: $R_1, R_2 = CH_3$

Phthalic acid suggested marker for SOA.

Consistent products from naphthalene-$d_8$, 1-MN-$d_{10}$ and 2-MN-$d_{10}$
MW 148 species, resulting from the loss of two β-carbons from the MNs and two β-carbons and an associated alkyl group from the DMNs.

2-Acetylbenzaldehyde confirmed with standard

Relative amounts of MW 148 products based on GC/MS CI peak areas. OH preferentially attacks the substituted ring.
Dicarbonyl products are generally consistent with the OH radical adding preferentially to the position \textit{ortho} to alkyl-substitution. However, products of 1,2-DMN are consistent with ring-opening between C$_1$ and C$_2$, implying \textit{ipso} addition of OH to ring.

\[ \begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
+ & \quad \text{OH} \\
\rightarrow & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{OH} \quad \text{CH}_3
\end{align*} \]

Sole MW 188 product. Identification based on MS fragmentation.
Recommendations for Future Research

• We have identified a suite of oxygenated products from the OH radical-initiated reactions of the alkynaphthalenes and the presence of these products in ambient air should be examined, as well as their potential toxicity. These products include reactive unsaturated dicarbonyls and epoxides. Additionally, glyoxal, methylglyoxal and biacetyl are the expected co-products when the alkynaphthalene-OH adducts decompose by loss of adjacent β-carbons.
Chamber nitrate (NO₃) radical-initiated reactions of: Naphthalene, 1- and 2-MN, ten DMNs, 1- and 2-EN. Assess formation of quinones and of nitro-products, some of which may photolyze to form quinones.

Isomers shown in their elution order on a 5% phenylmethyl-siloxane capillary column.
## Genotoxicity and Carcinogenicity of Nitro-PAHs

**Identified in Diesel Exhaust Particles**

- ++ + 1-nitropyrene
- ++ + 2-nitrofluorene
- ++ + 1,6- and 1,8-dinitropyrene
- ++ + 6-nitrochrysene
- + + 3-nitrobenzanthrone

**Identified as Products of Atmospheric Reactions of PAHs**

- ++ 2-nitrofluoranthene
- ++ + 2-nitropyrene
- + + nitronaphthalenes
- + methylnitronaphthalenes
- ++ 2-nitrodibenzopyranone
- + + nitropyrene lactones

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“Nitro-PAHs are probably human carcinogens”*

Gas-phase PAHs

- OH Radical - Daytime
- NO₃ Radical - Nighttime

Particle-associated PAHs

- Photolysis (also OH Radical?)
- Ozone – 24 hrs.
- NO₂/HNO₃ – 2ndary

Nitro-PAHs

- Fluoranthene (g) + OH → 2-Nitrofluoranthene (3% yield)
- Fluoranthene (g) + NO₃ → 2-Nitrofluoranthene (24% yield)
- Fluoranthene (s) + HNO₃/NO₂ → 3-Nitrofluoranthene
- Pyrene (g) + OH → 2-Nitropyrene (0.5% yield)
- Pyrene (s) + HNO₃/NO₂ → 1-Nitropyrene

Oxy-PAHs
Nitro-PAHs in ambient particles are dominated by isomers formed in the atmosphere from gas-phase reactions.

Gas-phase radical-initiated reactions leading to less volatile particle-associated products.

**OH Radical Chemistry**
Daytime
Torrance, CA

**NO₃ Radical Chemistry**
Nighttime
Claremont, CA

Diesel Particles
The ratio 2-nitrofluoranthene/2-nitropyrene (2NF/2NP) < 10 indicates OH chemistry dominates.

The ratio 2NF/2NP large, suggests NO₃ radical formation of 2-nitrofluoranthene.

In So.Cal. NO₃ is Important.

Mexico City
Apr. 27-30, 2003
Methylnitronaphthalenes (MNNs) result from OH or NO$_3$ radical reactions of 1- and 2-methylnaphthalene. At Azusa, OH chemistry dominates (markers: 1M5NN, 1M4NN). Downwind markers of NO$_3$ radical reactions increase.

Nighttime samples shown. If only OH chemistry, daytime and nighttime samples will be very similar – as at Azusa and Mexico City.

At Banning increased 2M1NN, 2M4NN & 1M3NN indicate NO$_3$ reactions.
Task 4: Conduct synthesis of dimethylnitronaphthalenes.

- Reactions of dimethylnaphthalenes with N$_2$O$_5$ in CCl$_4$ solution expected to give isomers similar to those formed by NO$_3$ in the gas phase.

- Synthesis will allow identification of dimethylnitronaphthalenes formed in OH and NO$_3$ radical reactions of 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN.

- Synthesis will produce sufficient dimethylnitronaphthalenes for photolysis studies.
Conducted nitrations with \( \text{N}_2\text{O}_5 \) in \( \text{CCl}_4 \) for all ten DMNs and both ENs. We were able to report the EI mass spectra and retention indices (on a 5% phenylmethyl-siloxane capillary column) of all 42 DMNNs (with NMR characterization of 32 of these) and of 11 of the 14 ENNs (with NMR characterization of 7 of these). Three assignments were tentative.

For each DMN there are either 3 or 6 DMNN isomers and for each EN there are 7 ENN isomers.

The 42 DMNNs isomers can be divided into 6 groups with characteristic EI mass spectral fragmentation, GC retention behavior and characteristic chemical shifts of the protons influenced by the \( \text{NO}_2 \) group.
1. DMNN isomers with NO₂ substitution on an α-carbon and no steric interaction with the methyl substituents. 

![Image](1)

Shift of protons ortho or peri to NO₂ is 0.6-0.9 ppm

2. DMNN isomers with NO₂ and CH₃ substituents in peri positions.

![Image](2)

3. DMNN isomers with NO₂ substitution on an α-carbon and with an ortho CH₃ group.

![Image](3)

4. DMNN isomers with NO₂ substitution on a β-carbon and no steric interaction with the methyl substituents.

![Image](4)

5. DMNN isomers with NO₂ substitution on a β-carbon and an ortho CH₃ group also on a β-carbon.

![Image](5)

6. DMNN isomers with NO₂ substitution on a β-carbon and an ortho CH₃ group on an α-carbon.
Retention Indices (RI)

1-NN (m/z 173) (RI = 200)

9-NPhen (m/z 223) (RI = 300)

DMNNs (m/z 201) (RIs between 200 & 300)
2. DMNN isomers with NO$_2$ and CH$_3$ substituents in \textit{peri} positions.

Characteristic fragmentation: [$\text{M-OH}^+$] is the base peak in the EI spectra.

The NO$_2$ group is anisotropic (electron density around C-NO$_2$ bond is not symmetric). Crowding of \textit{peri} CH$_3$ and NO$_2$ groups twists the NO$_2$ and causes the proton ortho to NO$_2$ to have only a very slight downfield shift from its position in the parent DMN.

These peri-substituted isomers elute early. For example, 1,2-DM-8NN elutes 1$^{st}$ of the six 1,2-DMNN isomers.
3. DMNN isomers with NO$_2$ substitution on an $\alpha$-carbon and with an ortho CH$_3$ group.

Characteristic fragmentation: [M-OH]$^+$ at m/z = 184 is present in the EI spectra.

The chemical shift of the proton peri to the NO$_2$ is upfield from its position in the parent DMN.

Interaction (hydrogen bonding) of the CH$_3$ and NO$_2$ group reduces the polarity of the molecule and these elute early. For example, 2,7-DM-1NN elutes 1$^{st}$ of the three 2,7-DMNN isomers.
4. DMNN isomers with NO₂ substitution on a β-carbon and no steric interaction with the methyl substituents.

Note that the molecular ion, [M]+ at m/z =201 is the base peak in all these spectra.

The “uncrowded” NO₂ group is in the plane of the naphthalene ring and causes large downfield shifts for the protons ortho to the NO₂ group.

Consistent with 2-NN eluting after 1-NN, each of these isomers elutes last of the isomers from a given DMN parent. For example, 1,6-DM-3NN elutes last of the six 1,6-DMNN isomers.
Amounts of Dimethylnitronaphthalene crystals produced (purities).

<table>
<thead>
<tr>
<th></th>
<th>&gt; 200 mg</th>
<th>40-100 mg</th>
<th>10-20 mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6-DM-1NN</td>
<td>(&gt;99%) 2,6-DM-1NN (&gt;99%)</td>
<td>1,2-DM-4NN (&gt;98%)</td>
<td>1,6-DM-4NN (&gt;99%)</td>
</tr>
<tr>
<td>1,3-DM-4NN</td>
<td>(&gt;99%) 1,3-DM-4NN (&gt;99%)</td>
<td>1,7-DM-4NN (&gt;98%)</td>
<td></td>
</tr>
<tr>
<td>1,5-DM-4NN</td>
<td>(&gt;99%) 1,5-DM-4NN (&gt;99%)</td>
<td>1,8-DM-2NN (~87%)</td>
<td></td>
</tr>
<tr>
<td>1,6-DM-5NN</td>
<td>(&gt;99%) 1,6-DM-5NN (&gt;99%)</td>
<td>2,3-DM-5NN (&gt;99%)</td>
<td></td>
</tr>
<tr>
<td>1,7-DM-8NN</td>
<td>(&gt;99%) 1,7-DM-8NN (&gt;99%)</td>
<td>2,6-DM-4NN (&gt;98%)</td>
<td></td>
</tr>
<tr>
<td>1,8-DM-4NN</td>
<td>(&gt;99%) 1,8-DM-4NN (&gt;99%)</td>
<td>2,7-DM-1NN (&gt;99%)</td>
<td></td>
</tr>
<tr>
<td>2,3-DM-1NN</td>
<td>(&gt;99%) 2,3-DM-1NN (&gt;99%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Retention indices and mass spectra sufficient to identify the DMNNs/ENNs produced in NO₃ and OH radical-initiated reactions. For ambient analyses, many “co-elutions” are a problem.
Photolysis of 2,6-DM-1NN gave 2,6-DM-1,4-naphthoquinone.

\[
\begin{align*}
\text{CH}_3\text{CH}_3 & \quad \text{NO}_2 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\hline
\text{hv} & \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{O} & \\
\text{O} & \\
\end{align*}
\]

Photolysis of 2-M-1NN gave 2-M-1,4-naphthoquinone as previously reported, but a very low yield was measured in the absence of NO\textsubscript{x}.

\[
\begin{align*}
\text{CH}_3 & \quad \text{NO}_2 \\
\text{CH}_3 & \\
\hline
\text{hv} & \\
\text{CH}_3 & \\
\text{O} & \\
\text{O} & \\
\end{align*}
\]
Formation of 2-methyl-1,4-naphthoquinone (2-M-1,4-NQ) from photolysis of 2-M-1NN under varied starting NO\textsubscript{x} concentrations. The lines are for illustrative purposes only.

NO\textsubscript{x} dependence surprising, possibly a chamber artifact???

MTC gave lower yields of DMNN from DMN + NO\textsubscript{3} at low NO\textsubscript{x} than the ITC. Also, heterogeneous product formation (side-chain nitro discussed below) very high in MTC.

Recommend additional experiments.
Task 3: Identification of dimethylnitronaphthalenes from the OH and NO$_3$ radical-initiated reactions of 1,6-, 1,7-, 2,6- and 2,7-dimethylnaphthalenes (the most abundant isomers observed in ambient air samples).

- OH Radical-initiated reactions of 1,6-, 1,7-, 2,6- and 2,7-DMN gave low yields of DMNNs. Yields not quantified, but DMNN/ENN profile produced from reaction of ambient surrogate DMN/EN mixture. Profile of DMNNs/ENNs from NO$_3$ radical-initiated reaction of ambient DMN/EN mixture also produced.

- DMNN and ENN profiles determined and yields measured individually for all 10 DMNs and 1- and 2-EN reacting with the NO$_3$ radical (yields determined by GC-FID). The yields of quinones formed were also determined. Examining the effect of the NO$_2$ concentration is an on-going investigation.
NO₃ Radical-Initiated Reaction of DMNs/ENs (Σ300 ppbv)

2-EN 1,6-DMN 1,2-DMN
2,6-DMN 1,7-DMN 2,3-DMN
2,7-DMN 1,3-DMN 1-EN 1,4-DMN 1,5-DMN
1: 0.7: 0.5: 0.3: 0.2

*additional isomer(s)
DMNNs/ENNs from chamber reaction of NO$_3$ with DMNs/ENs

DMNNs/ENNs in HPLC fraction of nighttime PUF sample from Redlands, CA

GC/MS-NCI
m/z 201

Retention Time

32 40 min

Highest in chamber OH reaction
DMNNs/ENNS
GC/MS-NCI
m/z 201

In the previously published reaction of "diesel DMNs/ENs" + OH, the early-eluting peaks were artifacts.

Some NO₃ chemistry in Mexico City?? or electrophilic nitration??

Chamber reaction of OH with DMNs/ENs

Mexico City Morning PUF sample HPLC fraction

Retention Time

32 40 min

1,7-DM-5NN + 1,6-DM-2NN

2-E8NN

1,4-DM-6NN

1,3-DM-7NN

1,2-DM-7NN
Yields of DMNNs/ENNs from OH radical reactions are small.

Products: ring-opened dialdehydes > dialdehydes with loss of 2-beta carbons (co-products, glyoxal, methylglyoxal and biacetyl) > dimethylnitronaphthalenes.

RA will discuss NO$_2$ dependence!
DMNNs/ENNs & quinones formed from NO$_3$ radical reactions.

Currently studying reactions as a f(NO$_2$).
Yields shown are for 1ppm NO$_2$. 

CH$_3$CH$_3$ + NO$_3$ → reaction products (15%, 4%, 5%) 

+ HNO$_3$
In NO$_3$ radical-initiated reactions, compounds with alkyl group(s) on $\beta$-carbon(s) form more quinones.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quinone</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-MN</td>
<td>1-M-5,8-NQ</td>
<td>0.7</td>
</tr>
<tr>
<td>2-MN</td>
<td>2-M-5,8-NQ</td>
<td>0.6</td>
</tr>
<tr>
<td>1-EN</td>
<td>1-E-5,8-NQ</td>
<td>0.3</td>
</tr>
<tr>
<td>2-EN</td>
<td>2-E-5,8-NQ</td>
<td>0.4</td>
</tr>
<tr>
<td>1,6-DMN</td>
<td>1,6-DM-5,8-NQ</td>
<td>1.8</td>
</tr>
<tr>
<td>1,7-DMN</td>
<td>1,7-DM-5,8-NQ</td>
<td>0.8</td>
</tr>
<tr>
<td>2,3-DMN</td>
<td>2,3-DM-1,4-NQ</td>
<td>4.1</td>
</tr>
<tr>
<td>2,6-DMN</td>
<td>2,6-DM-1,4-NQ</td>
<td>2.2</td>
</tr>
<tr>
<td>2,7-DMN</td>
<td>2,7-DM-1,4-NQ</td>
<td>3.9</td>
</tr>
</tbody>
</table>
Nitration of the alkyl group was seen for 1,2-DMN, 1,4-DMN, 1,8-DMN and 1,3-DMN.

<table>
<thead>
<tr>
<th></th>
<th>side-chain</th>
<th>1,2-DM-3NN</th>
<th>1,2-DM-4NN</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTC</td>
<td>0.3</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>ITC</td>
<td>0.01</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

The relative yield of the side-chain nitro-product/1,2-DM-4NN varies by a factor of 30 between the two chambers used. This suggests that the side-chain nitration is heterogeneous and the MTC may have had “wall problems”.
Postulated mechanism of reaction of 1,2-DMN with the NO$_3$ radical showing ipso addition to give the major nitro-product, 1,2-DM-4NN.
Recommendations for Future Research

• Questions remain regarding mechanisms following the initial addition of the OH and NO$_3$ radicals to naphthalene and alkynaphthalenes. The *ipso* addition of OH and/or NO$_3$ radicals with alkyl-PAH should be further investigated.

• The apparent NO$_x$ dependence of the quinone yields from the photolysis of alkynitronaphthalenes must be assessed.

• Ambient measurements of quinones should be made at upwind and downwind sites and locations where NO$_3$ radical chemistry is likely and unlikely to occur in order to evaluate the importance of atmospheric formation and confirm laboratory chamber data with ambient observations.

• Potential artifactual formation of DMNNs/ENNs during ambient sampling should be evaluated.
Papers resulting from this contract:


