The Reactions of Flame Soot with Nitrogen Oxides (NO₂, NO₃, N₂O₅, HONO, HNO₃): a brief Overview

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SOOT

• Definition: Soot is a product of incomplete flame combustion of hydrocarbon fuels at a given value of fuel/oxygen ratio $\lambda$ (stoichiometric c. at $\lambda = 1.0$)

Stoichiometric Combustion: $C_nH_{2n+2} + (1.5n + 0.5) O_2 \rightarrow nCO_2 + (n + 1)H_2O$

• Soot = EC (=BC) + Organic Phase (OC)

• Ubiquitous occurrence (on a global level)

• 10-50% of all tropospheric particulate matter is carbonaceous

• Worldwide anthropogenic emissions: 12-24 Tg/yr (Penner, 1998): N.B. Uncertainty!

• Long range transport observed (Arctic Haze)
Chemical Model of Soot Structure
(Sergides et al., 1987)

ether linkage  acid anhydride  quinone
aldehyde, ketone
lactone
ketene
PAH
hydrogen bonding

Fig. 24. A proposed model of the three-dimensional n-hexane soot.
SOOT (cont.)

- The only atmospheric aerosol with a sizable optical absorption in the UV/VIS range
- Remarkable influence on climate (positive radiative forcing), public health (inhalation of nanoparticles) and tropospheric chemistry (reducing properties)
  - **Decrease** in albedo (SSA) owing to absorption of radiation (short- and longwave radiation)
  - **Increase** in cloud albedo owing to activation of CCN and decrease in precipitation (Twomey)

JJA Surface Temperatures (Hansen, 2002)

SSA = 0.85

No GH Gases!
Custom-designed Co-Flow Device for reproducible generation of decane \((C_{10}H_{22})\) soot: **Diffusion Flame**

<table>
<thead>
<tr>
<th>Flame type</th>
<th>Flame height [mm]</th>
<th>Flame colour</th>
<th>Soot deposition [mg min(^{-1})]</th>
<th>Air flow [l min(^{-1})]</th>
<th>Fuel duct (pore (\Phi))[(\mu m)]</th>
<th>Soot type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>rich</em></td>
<td>(~ 60)</td>
<td>orange–red</td>
<td>(2.0\pm0.5)</td>
<td>1.2–1.4</td>
<td>17–40</td>
<td>”grey”</td>
</tr>
<tr>
<td><em>lean</em></td>
<td>(~ 55)</td>
<td>yellow–white</td>
<td>(0.8\pm0.4)</td>
<td>1.3–1.5</td>
<td>11–16</td>
<td>”black”</td>
</tr>
</tbody>
</table>
Control of Soot Production is mandatory in view of its Effects on Kinetics

Figure 6.1.1: Uptake of NO₂ on decane soot as a function of the NO₂ concentration. Soot samples were produced using a simple oil lamp; 4 mm diameter escape orifice, 1 over 100 seconds, mean sample weight was 17.5 mg.

Figure 6.1.2: Uptake of NO₂ on decane soot as a function of the NO₂ steady state concentration. Soot samples were produced using the new co-flow device; 4 mm diameter escape orifice, integrated over 100 seconds, mean sample weight was 16.4 mg.

Unstable flickering flame

Stabilized (controlled) flame

CAST or Co-Flow Device
Elemental analysis for several types of soot

Anticorrelation of H- and O-content of soot depending on $\lambda$ - ratio

<table>
<thead>
<tr>
<th>Author</th>
<th>Soot ($\lambda$)</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salgado,</td>
<td>hexane ($\lambda$=0.82)</td>
<td>94.73 ± 0.15</td>
</tr>
<tr>
<td>2002</td>
<td>hexane ($\lambda$=0.16)</td>
<td>93.01 ± 0.31</td>
</tr>
<tr>
<td>CAST Burner</td>
<td>hexane ($\lambda$=0.09)</td>
<td>92.03 ± 0.34</td>
</tr>
<tr>
<td>Matter</td>
<td>gray decane soot (rich flame)</td>
<td>97.27 ± 0.05</td>
</tr>
<tr>
<td>Engineering</td>
<td>black decane soot (lean flame)</td>
<td>96.39 ± 0.22</td>
</tr>
<tr>
<td>Stadler,</td>
<td>n-hexane</td>
<td>87-92.5</td>
</tr>
<tr>
<td>2000</td>
<td></td>
<td>1.2-1.6</td>
</tr>
<tr>
<td>Akhter,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1985</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\lambda = \text{fuel}/\text{O}_2$ on a per C basis
Knudsen Flow Reactor: Kinetics, Branching Ratios and Reaction Products using MBMS

- Gas Phase is monitored: Molecular Beam-modulated MS
- Multispecies capabilities: MS and laser-based *in situ* detection techniques
- Relative Rate Technique put on an absolute Basis using measured $k_{esc}$ (rate constants for effusion)
- Measurement of gas “uptake” in terms of uptake probabilities ($\gamma$)
NO₂ Reaction Mechanism for Amorphous Carbon
DEGUSSA Materials (Tabor 1994)

• Net reaction: NO₂ + {C} \rightarrow NO + {C•O}
• \( \gamma = 5 \times 10^{-2} \)
• Evolution of CO, CO₂ upon heat treatment of soot (incandescent lamp).

\[
\begin{align*}
\text{NO}_2 + \{\text{SS}\} & \leftrightarrow \{\text{SS} \cdot \text{NO}_2\}_p \\
\text{Reversible adsorption} \\
\text{NO}_2 + \{\text{SS}\} & \leftrightarrow \{\text{L}\} \\
\text{Reversible adsorption to a non-reactive species} \\
\{\text{SS} \cdot \text{NO}_2\}_p & \rightarrow \{\text{NO}_2 \cdot \text{I}\} + \{\text{SS}\} \\
\text{Conversion into an intermediate I (deeper layer)} \\
\{\text{NO}_2 \cdot \text{I}\} & \rightarrow \{\text{NO}_2 \cdot \text{R}\} \\
\text{Transfer to reservoir R} \\
\{\text{NO}_2 \cdot \text{I}\} & \rightarrow \text{NO} + \{\text{C•O}\} \\
\text{Decomposition to NO and a surface oxygen complex \{C•O\}.}
\end{align*}
\]
Correlation between NO$_2$ and HONO for reaction of NO$_2$ on gray (rich flame) decane soot (Stadler 2000)

Figure 6.2.1: Uptake experiment of NO$_2$ on ‘grey’ decane soot; sample mass = 16.3 mg, 4 mm diameter escape orifice, NO$_2$ concentration = 8.3x10$^{12}$ molecule cm$^{-3}$.
Suggested Reaction Mechanism for HONO Formation on rich Flame Soot

• \(\text{NO} + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_3 + \text{M}\)  
  gas phase reaction
• \(\text{N}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{HONO}\)  
  heterogeneous reaction
• \(2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3\)  
  Too slow
• \(\text{NO}_2 + \{\text{C-H}\}_\text{red} \rightarrow \text{HONO} + \{\text{C-}\}_\text{ox}\)
• \(\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{OH}\)

\[\Delta H_r^0 = 40 \text{ kcal/mol (est.)}\]

Yields of HONO and NO are position dependent and complementary (anticorrelated) in ethylene flame

<table>
<thead>
<tr>
<th>Gerecke GRL 1998</th>
<th>Mass/mg</th>
<th>(\Phi(\text{HONO}))</th>
<th>(\Phi(\text{NO}))</th>
<th>(\gamma_0 \times 100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue Flame</td>
<td>3</td>
<td>93±1</td>
<td>4±1</td>
<td>4±0.1</td>
</tr>
<tr>
<td>Standard spot</td>
<td>8</td>
<td>71±4</td>
<td>5±1</td>
<td>9.5±0.6</td>
</tr>
<tr>
<td>Flame top</td>
<td>6</td>
<td>68±5</td>
<td>31±2</td>
<td>3.2±0.3</td>
</tr>
<tr>
<td>Above flame</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>0.6±0.2</td>
</tr>
</tbody>
</table>

\(a\) The relative yields \(\Phi\) in % (per NO\(_2\) taken up) are integrated over 50s.
CONCLUSIONS: NO$_2$ - Soot

- Reaction products depend on type of soot unlike kinetics ($\gamma$).
- Reaction occurs with reducing surface functional groups on substrate, NOT CATALYTIC decomposition.
- X-tremes: 100% NO on amorphous carbon FW2 (channel black)  
  100% HONO on hexane, decane soot from rich flame
- Both carbon-matrix as well as semivolatile organic fraction of soot partake in heterogeneous chemical reaction.
- HONO decomposes on (black) soot from lean combustion to yield NO as a final product: $2\text{HONO} \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O}$.
- Complex surface reaction mechanism: inhibition and competition.
NO$_3$ / gray (rich flame) decane soot

N$_2$O$_5$ $\rightarrow$ NO$_3$ + NO$_2$

Kinetics and Reaction Products have been investigated in Knudsen flow reactor under molecular flow conditions using in situ REMPI detection of NO, NO$_2$.

(a) m/e 30, (b) m/e 46, (c) raw REMPI signal for NO$_2$ detection at $\lambda = 511$ nm scaled to a MS signal at m/e 46, (d) m/e 62, (e) m/e 47, (f) m/e 63
(cont.)

(a) m/e 62, (b) m/e 47 (HONO), (c) NO

(a) m/e 62, (b) \( \text{N}_2\text{O}_5 \) (m/e 46), (c) m/e 63
Reaction Mechanism for NO$_3$ + decane soot

Source (N$_2$O$_5$ thermal dec.) → NO$_3$ (25%) + NO$_2$ (75%)

NO$_3$ + {C} → NO + {C•O$_2$} (12-17%)

Most of the lost NO$_3$ remains adsorbed on soot

NO$_2$ + {NO$_3$} → N$_2$O$_5$ (20-24%) (+ H$_2$O → 2HNO$_3$)

Rich (gray) Flame Soot:

NO$_2$ + {C-H}$\text{red} \rightarrow$ HONO + {C}$\text{ox}$ (≈ 100%)

Lean (black) Flame Soot:

{2HONO} → {H$_2$O} + NO + NO$_2$ (5%) (A lot of NO$_2$ remains adsorbed!)

RED: genuine NO$_3$ reaction

BLUE: complication as a consequence of the presence of NO$_2$. 
Steady State Uptake Coefficient for NO₃ on decane soot: extrapolation to ambient concentrations enabled by known rate law

Uptake coefficient $\gamma_{ss}$ of NO₃ as a function of [NO₃] (orifice diameter = 8 mm): NO₃ on black (full triangles) and gray soot (open circles).
CONCLUSIONS: NO$_3$ - Soot

- Most of lost NO$_3$ remains adsorbed on soot
- Yield of NO is 12 (gray) -17 % (black) soot
- Adsorbed NO$_3$ leads to N$_2$O$_5$ formation in the gas phase with excess NO$_2$
- Small yield of HNO$_3$
- Large $\gamma$ @ [NO$_3$] $\Rightarrow$ 0 (ambient conditions: hundred ppt at night)
- Renoxification mechanism: NO$_y$ $\Rightarrow$ NO$_x$
- Soot substrate is partaking in the reaction
Reaction Mechanism: $\text{N}_2\text{O}_5 + \text{Decane Soot}$

- $\text{N}_2\text{O}_5 + \{\text{C}\} \rightarrow \text{NO} + \text{NO}_2 + \{\text{C}\cdot\text{O}_2\}$  Redox reaction
- $\text{N}_2\text{O}_5 + \{\text{H}_2\text{O}\} \rightarrow 2\ \text{HNO}_3$ heterogeneous Hydrolysis reaction – surprisingly SLOW!

Mechanism:

\[
\text{N}_2\text{O}_5(\text{ads}) + \{\text{C}\} \rightarrow \text{N}_2\text{O}_3(\text{ads}) + \{\text{C}\cdot\text{O}_2\}
\]

\[
\text{N}_2\text{O}_3(\text{ads}) + \rightarrow \text{NO} + \text{NO}_2
\]

equimolar amounts of NO and NO$_2$

approaching 100% at low concentration.
Steady State Uptake Coefficient for $\text{N}_2\text{O}_5$ on Decane Soot: Importance of Rate Law !!!

Uptake coefficient $\gamma_{ss}$ of $\text{N}_2\text{O}_5$ as a function of $[\text{N}_2\text{O}_5]$: $\text{N}_2\text{O}_5$ on black (circles) and gray soot (open squares). For all measurements we used the 8 mm orifice diameter except for the point marked by the arrow where a 4 mm orifice diameter has been used.
CONCLUSIONS: $\text{N}_2\text{O}_5$ - Soot

- Hydrolysis ($\text{HNO}_3$) and Redox (NO) reaction are concurrent and depend on the type of soot. Redox reaction occurs until exhaustion of redox reactive sites.
- Reaction products are equimolar NO + NO$_2$. Relative yields depend on type of carbon substrate. No NO$_3$ observed in the gas phase.
- Renoxification Mechanism, soot substrate is reacting
- Large $\gamma$ value (roughly 10 times lower than for NO$_3$)
Reaction Mechanism for HNO₃ + Soot

- \(2\text{HNO}_3 \rightarrow \{\text{N}_2\text{O}_5\}\)  
  Hypothesis
- \(\{\text{N}_2\text{O}_5\} \rightarrow \{\text{NO}_2\} + \{\text{NO}_3\}\)  
  Surface decomposition
- \(\text{HNO}_3 \rightarrow \{\text{C-H}\}_\text{red} \rightarrow \{\text{HONO}\} + \{\text{C}\cdot\text{O}_2\}_\text{ox}\)  
  Reduction of HNO₃ on rich flame (gray) soot (NO₂!!)
- \(\{\text{HONO}\} \rightarrow \text{HONO}\)  
  gray soot (rich combustion)
- \(2\{\text{HONO}\} \rightarrow \{\text{H}_2\text{O}\} + \{\text{N}_2\text{O}_3\} \rightarrow \text{NO} + \{\text{NO}_2\}\)  
  black soot (lean combustion)

In addition:
- \(\text{NO} + \{\text{HNO}_3\} \rightarrow \text{HONO} + \{\text{NO}_2\}\)  
  gray soot (rich or stoichiometric flame): Supports adsorbed HNO₃
- \(\text{HNO}_3 + \{\text{HONO}\} \rightarrow 2\{\text{NO}_2\} + \{\text{H}_2\text{O}\}\)  
  High surface coverage: Supports adsorbed HONO
- \(\{\text{NO}_2\} + \{\text{C-H}\}_\text{red} \rightarrow \text{NO} + \{\text{C}\}_\text{ox}\)  
  secondary reaction of NO₂
CONCLUSIONS: HNO$_3$ - Soot

• Reaction products depend on type of soot

• X-tremes: amorphous carbon FW2 (channel black), lean flame soot (decane): NO, small amounts of NO$_2$. hexane, decane soot from rich flame: HONO exclusively.

• Evidence for adsorbed HNO$_3$, HONO. N$_2$O$_5$??

• Renoxification – atmospheric significance: ratio [NO$_y$] / [NO$_x$] or [HNO$_3$] / [NO$_x$] is overpredicted by photochemical transport (CRT) models. Models “need” more NO$_x$. 