Photo-Enhanced Deposition of Trace Gases at the Interface of Organic Surfaces

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Thanks to them!!
Thanks to them!!
Let us start with **Text Book Knowledge**

Must be true, isn’t it?
Tropospheric ozone...

\[ \text{O}_3 \xrightarrow{\text{hv}} \text{OH} \]
Tropospheric ozone…

\[ \text{O}_3 \xrightarrow{h\nu} \text{OH} \]

\[ \text{RH} \xrightarrow{} \text{RO}_2 \]

\[ \text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} \]

\[ \text{COV} \]

\[ \text{Noté: RH} \]
Tropospheric ozone…
Tropospheric ozone…

\[
\begin{align*}
\text{OH} & \quad \overset{\text{hv}}{\longrightarrow} \quad \text{O}_3 \\
\text{NO}_2 & \quad \overset{\text{hv}}{\longrightarrow} \quad \text{NO} \\
\text{HNO}_3 & \quad \overset{\text{hv}}{\longrightarrow} \quad \text{NO}_2 \\
\text{RO}_2 & \quad \overset{\text{hv}}{\longrightarrow} \quad \text{RO} \\
\text{ROOH} & \quad \overset{\text{hv}}{\longrightarrow} \quad \text{R'}\text{CHO} \\
\text{NO}_x (\text{NO} + \text{NO}_2) & \quad \text{NO}_x
\end{align*}
\]
photolysis of ozone: 
\[ \text{O}_3 + hv (+ \text{H}_2\text{O}) \]

photolysis of nitrous acid: 
\[ \text{HONO} + hv \]

photolysis of formaldehyde: 
\[ \text{HCHO} + hv (+ \text{NO}) \]

ozonolysis reactions: 
\[ \text{alkenes} + \text{O}_3 \]

N.B.: HONO only observed during night time…
HONO

= 

Early morning OH source
HONO is an important OH source, with still uncharacterised sources!!

HONO $\rightarrow$ OH + NO

Boundary layer

H2O

NO

NO2

HONO

O3

+ NO2

RH

Surface

Aerosol

NO2

H2O

Surface

?
But what’s outside?

Gas phase...
HONO = Early morning OH source

Santiago de Chile, 2005 (Kleffmann 2007)
HONO = Early morning OH source + daytime source

Santiago de Chile, 2005 (Kleffmann 2007)
missing additional source: 500 pptv/h
33 % contribution, >all other sources

Kleffmann et al., 2005
There is already some missing photochemistry!!

But what else is outside?
Condensed phase...
Where do we stay?
• $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}^{(1}\text{D})$ \hspace{1cm} $\lambda < 320$ nm

in competition with other processes…
Organics everywhere......

Zhang, Jimenez et al., GRL, 2007

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Humic like substances in aerosol particles

- High molecular weight (200 – 1400 AMU), multifunctional organic compounds in primary and secondary aerosol particles.
  - multifunctional, many phenolic, acidic and aromatic moieties.
    (“FULIS”?)
- Brown-yellowish material, contribute to absorption.

Model compounds

<table>
<thead>
<tr>
<th></th>
<th>Bulk</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromaticity</td>
<td>20%</td>
<td>12%</td>
<td>18%</td>
<td>23%</td>
<td>30%</td>
<td>32%</td>
</tr>
<tr>
<td>AMU</td>
<td>570</td>
<td>440</td>
<td>520</td>
<td>620</td>
<td>720</td>
<td>740</td>
</tr>
</tbody>
</table>

Atmospheric samples

500-600 AMU, ~20%

Y. Rudich
Humic Substances

<table>
<thead>
<tr>
<th>Humic substances (pigmented polymers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fulvic acid</td>
</tr>
<tr>
<td><strong>Light yellow</strong></td>
</tr>
<tr>
<td><strong>Yellow brown</strong></td>
</tr>
<tr>
<td>Humic acid</td>
</tr>
<tr>
<td><strong>Dark brown</strong></td>
</tr>
<tr>
<td><strong>Grey-black</strong></td>
</tr>
<tr>
<td>Humin</td>
</tr>
<tr>
<td><strong>Black</strong></td>
</tr>
</tbody>
</table>

- Increase in intensity of colour
- Increase in degree of polymerization
- Increase in molecular weight
- Increase in carbon content
- Decrease in oxygen content
- Decrease in exchange acidity
- Decrease in degree of solubility

Chemical properties of humic substances. (Stevenson 1982)
Model Structures of Humic Substances

Fulvic Acids from Suwannee River, Georgia
average formula $C_{33}H_{32}O_{19}$

Light absorbing aromatic ketones

[Averett et al. 1989]
Photolysis

Possible from excited states

No requirements of UV

Surface adsorption

Surface reaction (photocatalytic or not)

Desorption of products
Question... Can the HONO source be due to photoenhanced NO$_2$ uptake?
Heterogeneous processes

Surface adsorption

Desorption of products

Surface reaction (catalytic or not)

uptake coefficient $\gamma$:

efficiency of gas-particle interaction on per-collision basis

Depends on the surface…

For a trace gas (TG) reacting with a surface:

$$\frac{d[TG]}{dt} = \frac{\gamma \cdot \bar{c} \cdot a}{4V} \cdot [TG]$$
molecules cm$^{-3}$ s$^{-1}$
Flowtube study...

Thermostated coated flowtube

NO$_2$/N$_2$ (+H$_2$O)

Moveable injector

Reactive surface (solid or liquid if vertically mounted)
Organics deposited on the inner wall

Denuder (remove acids)

NOx analyser

NO$_2$ concentration

Adsorption with surface saturation

With a (fast) chemical reaction

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Determination of the uptake coefficient...

\[ \text{Length} \]

\[ \text{Concentration} \]

\[ \text{Ln}(C_{out}/C_{in}) \]

\[ k \text{ prop. to } \gamma \]

Time
Irradation intensities vs. Solar irradiance

Irradiance / Photons cm\(^{-2}\) s\(^{-1}\)

Solar irradiance

UV-PSI

Vis-PSI

UV-LYS

Vis-LYS

Absorbance / a.u.

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Irradation vs. Humic absorption

Photochemistry is in principle possible
Take caution to this…
We will be going through the entire UV-vis spectrum
Organic coating consisting of a reactive triplet forming light absorber and an electron-donor produces a photo-reductant. It reduces NO$_2$ to HONO.

George et al, Faraday Disc., 2005
NO$_2^+$ humics

reaction on different HAs in with similar efficiency

![Diagram showing reaction time vs. deltaNO$_2$ [ppb] for different conditions and HA samples.](image)
NO$_2$ + humics/soil

Real Soil (dust 20 mg) + NO$_2$ (20 ppb) + light (300-420 nm)

![Graph showing the change in HONO and deltaNO$_2$ over time with lamps on and off.](image-url)
Proposed Mechanism:

\[ \text{NO}_2 + \text{organics} + h\nu \rightarrow e^-, H^+ \]

Reduction oxidation photosensitizer

\[ \text{OH} \rightarrow \text{NO} \]

• Lab: photoinduced source 10-100 × faster than dark reaction!
  • compare atmosphere: factor 20-60 estimated
  • Both, NO$_2$ and the hydrocarbons studied are ubiquitous present in the atmosphere
• Mechanism can explain daytime formation of HONO in the atmosphere, at least for ppb levels of NO$_2$

• Photochemistry on humic acid surfaces is possible
• Photochemistry on soot surfaces is also possible
Investigate the role of photochemical transformations of organic aerosols and films

Ozone uptake…
Ozone on Aldrich HA films

In the dark

No uptake
With light

Photoenhanced uptake
Even after more than 6 hours exposure to ozone, The photochemistry can be activated again!!
Visible-PSI
Solar irradiation (fall)
Langmuir-Hinshelwood type mechanism?

![Graph showing the relationship between ozone concentration (ppbv) and uptake coefficient ($\gamma$). The graph has a logarithmic y-axis ranging from $10^{-5}$ to $6 \times 10^{-5}$. The x-axis represents ozone concentration in ppbv, ranging from 0 to 200. There are two curves on the graph, one with a label of $4.4 \times 10^{16}$ and another with $9 \times 10^{15}$. The graph suggests a decrease in uptake coefficient as ozone concentration increases. There is an indicator pointing to the right saying "More UV."
Langmuir-Hinshelwood type mechanism?
Dependence on relative humidity

Humidity / RH %
0 1 0 2 0 3 0 4 0 5 0 6 0 7

Uptake coefficient dark / γ
10^{-6} 2 \times 10^{-6} 3 \times 10^{-6} 4 \times 10^{-6}

Uptake coefficient UV-A / γ
10^{-5} 2 \times 10^{-5} 3 \times 10^{-5} 4 \times 10^{-5}

dark
The surface morphology of HA changes strongly with humidity.

Increasing rh = increasing surface (more adsorption sites?)
Dependence on relative humidity

Is water a quenching gas at the surface?
Dependence on pH

The graph illustrates the dependence of the steady-state uptake coefficient (γ) on pH. The data points are shown for different light conditions: UV, visible, and dark. The pH values range from 3 to 9, and the steady-state uptake coefficient values are plotted on a logarithmic scale ranging from $10^{-6}$ to $12 \times 10^{-6}$. The data points for Aldrich HA are marked with different symbols for each condition.
The structure of fulvic acid films changes with pH

Myneni et al., Science, 1999
Photochemistry on humic acid surfaces is possible for ozone also.

The uptake kinetics are photoenhanced.
Suggested surface chemistry...

Substrat: benzophénone

• Formation of surface reactive surface oxidant and radicals.
Substrat: benzophénone + phénol (1/1)

Electron transfer or H abstraction: phénoxy / ketyl radical formation

\[ \text{Ph}_2\text{CO}^* + \text{PhOH} \rightarrow [\text{Ph}_2\text{CO}^- \cdots \text{PhOH}^{+\cdot}] \rightarrow \text{Ph}_2\text{C}^* - \text{O}^- + \text{PhOH}^{+\cdot} \]

Suggested surface chemistry...

Radical formation → Oligomerisation
General Conclusion

- Photochemistry is important for many aspects of atmospheric heterogeneous chemistry
  - Photochemistry in the visible
  - Stop thinking (at least partially) only in terms of UV

- Greatly affect SOA ageing
  - Surfaces are getting hydrophobic
  - Uptake kinetics are enhanced
  - SOA mass increases
  - Becomes more oxygenated

- (We do need more money ...)

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