Laboratory studies of photochemical reactions in artificial snow

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Field experiment in Antarctica: Photochemical Experiment at Neumayer (PEAN’99)
Production of NO and NO$_2$ in a snow block: photolysis of nitrate

Jones et al., 2000
Absorption spectra of reactive trace compounds in the aqueous phase

Graedel and Weschler, 1981
Laboratory experiments with artificial snow
Set-up of the photolysis experiments

1000 W Hg-Xe arc lamp

Water filter

Teflon cell filled with snow

210 to > 1000 nm

210 – 900 nm

T = - 20 ± 2 °C
Decomposition of H$_2$O$_2$ in artificial snow in a 1 cm cell

\[ j_{\text{exp}}(\text{H}_2\text{O}_2) = (0.48 \pm 0.03) \text{ h}^{-1} \]

\[ j_{\text{exp}}(\text{H}_2\text{O}_2) = (0.48 \pm 0.09) \text{ h}^{-1} \]
Decomposition of HCHO in artificial snow in a 1 cm cell

\[
\ln \left( \frac{[\text{HCHO}]}{[\text{HCHO}]_0} \right) = -j_{\text{exp}}(\text{HCHO}) \times t
\]

- 0.0
- 0.2
- 0.4
- 0.6
- 0.8
- 1.0

\[
[\text{HCHO}]_0 = 5.9 \times 10^{-3} \text{ M}
\]

\[
j_{\text{exp}}(\text{HCHO}) = (0.103 \pm 0.08) \text{ h}^{-1}
\]
Or rather production of HCHO in artificial snow in a 1 cm cell?

100 to 200 ppbC needed to explain HCHO production
Decomposition of nitrate in artificial snow in a 1 cm cell

\[ j_{\text{exp}}(\text{NO}_3^-) = (0.50 \pm 0.03) \text{ h}^{-1} \]
Nitrite in artificial snow during the photolysis of nitrate
Photochemical production and destruction of nitrite during the nitrate photolysis in snow

\[ [\text{NO}_2^-] = [\text{NO}_2^-]_0 \cdot \exp(-j(\text{NO}_2^-) \cdot t) \]

\[ + \frac{j(\text{NO}_3^-) \cdot [\text{NO}_3^-]_0}{j(\text{NO}_2^-) - j(\text{NO}_3^-)} \left[ \exp(-j(\text{NO}_3^-) \cdot t) - \exp(-j(\text{NO}_2^-) \cdot t) \right] \]
Photochemical production and destruction of nitrite

\[ j_{\text{exp}}(\text{NO}_2^-) = 8.6 \text{ h}^{-1} \]
Reaction pathways during the photolysis of nitrate in snow

\[ \frac{\phi(\text{NO}_2)}{\phi(\text{NO}_2^-)} = 16 \]

\[ k_{\text{Hyd}} = 1.4 \cdot 10^7 \text{M}^{-1}\text{s}^{-1} \]

\[ \frac{n_{\text{NO}_2(\text{gas})}}{n_{\text{NO}_2(\text{SL})}} = 5.3 \cdot 10^5 \]
Nitrite in artificial snow during the photolysis of nitrate

Full mechanism:

\[ j_{\text{exp}}(\text{NO}_2^-) = 8.6 \, \text{h}^{-1} \]

\[ j_{\text{exp}}(\text{NO}_2^-) = 7.2 \, \text{h}^{-1} \]
Decomposition of nitrate in artificial snow in a 1 cm cell

Full mechanism:
\[ j_{\text{exp}}(\text{NO}_3^-) = 0.75 \text{ h}^{-1} \]
\[ j_{\text{exp}}(\text{NO}_3^-) = (0.50 \pm 0.03) \text{ h}^{-1} \]
Comparison of HO$_x$ production by different trace compounds in natural snow

<table>
<thead>
<tr>
<th></th>
<th>Number of HO$_x$ radicals produced</th>
<th>Rel. exp. photolysis rate</th>
<th>Range of surface snow concentrations (10$^{-6}$ M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$</td>
<td>1...2</td>
<td>1</td>
<td>1.5 – 3 (Greenland) 0.2 – 2 (Antarctica)</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>2</td>
<td>0.6</td>
<td>1 – 12 (Greenland) 0.3 – 5 (Antarctica)</td>
</tr>
<tr>
<td>HCHO</td>
<td>1...2</td>
<td>0.14</td>
<td>0.1 – 0.2 (Greenland) 0.1 – 0.5 (Antarctica)</td>
</tr>
</tbody>
</table>
Determination of nitrogen isotopes in nitrate using a microbiological method

*Pseudomonas Chlororaphis*

overnight incubation

\[ \text{NO}_3^- , \text{NO}_2^- \rightarrow \text{N}_2\text{O} \]

Not sensitive to organic nitrogen!

stripped with He

analysis by GC/MS

Sigman et al., 2001
Isotope fractionation for the photolysis of nitrate in artificial snow

Fractionation factor for photolysis of nitrate is \(-11.0 \pm 2.1\%\)
Isotope fractionation for nitrate measured in natural surface snow (Dome C, 14 cm)

Photolysis is possibly not the main nitrate sink in surface snow?

Fractionation factor for photolysis of nitrate is $-53.9 \pm 9.7 \%$
Conclusions

- Apart from NO$_3^-$ other compounds (NO$_2^-$, H$_2$O$_2$, HCHO) can also be photolysed in snow.

- The H$_2$O$_2$ photolysis is possibly an OH source comparable to the NO$_3^-$ photolysis.

- Isotope fractionation measurements indicate that in addition to the photolysis other post-depositional processes can be important for NO$_3^-$ in surface snow.