Photolysis and radiolysis of chlorophenols in ice

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ICE - most abundant, most fascinating crystalline solid material

- lake and river ice
- sea ice
- ice in the atmosphere
- snow
- glacier and polar ice
- frozen ground
- 10% of the landmass
- 5% of the ocean surface
- planetary ice
- interstellar ice

- ice $I_h$ (hexagonal) + 13 crystalline phases
- hydrogen bonding ~20 kJ mol$^{-1}$
- tetrahedral bond geometry: 109.5°
- defects / channels
Ice structure

Air temperature = -22°C
Surface temperature = -12°C

Air temperature = -15°C
Surface temperature = -8°C

Air temperature = -12°C
Surface temperature = -5°C

Air temperature = -15°C
Surface temperature = -8°C
Ice and impurities

Defects / channels:
- point defects (electrical conduction)
- crystal dislocations (line defects)
- grain boundaries (surface defects)

Substances soluble in water: usually not soluble in ice; incorporated as inclusions or clusters. Solutes tend to be segregated from the ice phase at the grain boundaries or interstitial pores. ... Reaction cavity

Exceptions (doped ice): HF, HCl, NH₃.
Some persistent organic compounds found in the snow samples collected in the polar regions (c < 1 ng l⁻¹):

- hexachlorocyclohexanes (HCH)
- polychlorinated biphenyls (PCBs),
- endosulphan
- chlorophenols
- hexachlorobenzene (HCB)
- chlordanes
- dieldrin
Photolysis of pure ice

Not completely transparent from 200 to 700 nm: photoproducts (high energy radiation) OH\(^-\), O\(^-\), e\(^-\), H\(_2\)O\(_2\), O\(_2\)
The snowpack at the atmospheric boundary layer

$\text{NO}_x$, HCHO, Br$_2$ emissions by snow

$$\begin{align*}
\text{NO}_3^- & \rightarrow h\nu \rightarrow \text{NO}_2^- + \cdot \text{O} \\
\text{NO}_3^- + H^+ & \rightarrow h\nu \rightarrow \text{NO}_2 + \text{OH}
\end{align*}$$

Honrath R. E., Domine F., Shepson P., Simpson B., and others
Ice photochemistry: Our questions before 2000

1. Does photosolvolysis occur in the frozen matrix?

2. How hydrophobic compounds in ice: aggregate; change the ice structure; and absorb the solar radiation.

3. How the mechanisms of the phototransformations in the ice matrix differ from those in aqueous solution?

4. Are common organic pollutants degradable in polar ice?

5. What are the photoproducts (toxicity; absorption properties; reactivity)?

6. Are the known ice-core data reliable?
Ice photochemistry in the laboratory

Norrish Type II reaction of valerophenone - conformational restrictions

Ice photochemistry in the laboratory

Chlorobenzene
- unique transformation pathways in ice matrix

\[
\text{Cl} \quad \xrightarrow{h\nu\text{ice}} \quad \begin{array}{c}
\text{Cl}_x \\
\text{Cl}_y \\
\text{Cl}_z
\end{array} \quad + \quad \begin{array}{c}
\text{Cl}_x \\
\text{Cl}_y \\
\text{Cl}_z
\end{array} \quad + \quad \text{phenol}
\]

(phenol is the major photoproduct from aqueous solution photolysis)

Ice photochemistry in the laboratory

Major products from photolysis of 2-dichlorobenzene

PCB 4
PCB 6
PCB 10
PCB 12
PCB 16
PCB 33

Major products from photolysis of 4-dichlorobenzene

PCB 9
PCB 13
PCB 31
PCB 37
Ice photochemistry in the laboratory

2-chlorophenol ($\Phi = 0.03$)

**major products**

- OH
- Cl
- OH
- HO
- Cl

**minor products**

- OH
- Cl
- other chlorobiphenyldiols
- other biphenyldiols
- chloroterphenyltriols

no photosolvolysis:
Ice photochemistry in the laboratory

**4-chlorophenol** ($\Phi = 0.04$)

**major product**

![Chemical structure of 4-chlorophenol]

**minor products**

- other chlorobiphenyldiols
- chloroterphenyltriols

**no photosolvolysis:**

Kláňová J., Nosek J.
Ice photochemistry in the laboratory

Proposed mechanisms

\[
\text{C-Cl scission} \quad \rightarrow \quad \text{radical coupling} \quad \rightarrow \quad \text{electron transfer} \quad \rightarrow \quad \text{C-Cl scission}
\]
Ice photochemistry in the laboratory

Temperature dependent irradiation of 2-chlorophenol: chemistry in a quasi-liquid layer

![Graph showing temperature dependence and relative amounts of reaction products.](image)
Ice photochemistry in the laboratory

Temperature dependent irradiation of 4-chlorophenol: chemistry in a quasi-liquid layer
Luciferase as a reporter protein induced after AhR-activation by dioxin-like compounds

(principle of the assay with transgenic rat hepatoma cells H4IIE.luc)

Adapted from Blankenship (1994)
Toxicity of the photoproducts formed in water

A

Toxicity (luminescence, % of control)

2-CP (% of initial conc.)

2-CP - irradiation (min)

B

Toxicity (luminescence, % of control)

4-CP (% of initial conc.)

4-CP - irradiation (min)
Toxicity of the photoproducts formed in ice

**Graph 1:**
- **x-axis:** 2-CP irradiation (h)
- **y-axis:** Toxicity (% of control / % of TCDD max)
- **Legend:**
  - Bacterial toxicity
  - CP concentration
  - Dioxin-like toxicity
  - Biphenyldiol

**Graph 2:**
- **x-axis:** 4-CP irradiation (h)
- **y-axis:** Toxicity (% of control / % of TCDD max)
- **Legend:**
  - Bacterial toxicity
  - CP concentration
  - Dioxin-like toxicity
  - Biphenyldiol
Induction of dioxin-like toxicity by photoproducts of \( p \)-chlorophenol in water ice

*(comparison with the toxic potency of 2,3,7,8-TCDD)*
Ice photochemistry in the laboratory

Hydrogen peroxide (+UV) vs. high-energy irradiation

Low temperature irradiation (-78 °C): suppression of the coupling reactions with OH radicals

Klánová J., Heger D., Dolinová J.
Ice photochemistry in the laboratory

$\text{H}_2\text{O}_2 / \text{UV}$

1. $\text{Cl}$

\[ \begin{align*}
\text{OH} & \quad \text{OH} \\
\text{Cl} & \quad \text{Cl} \\
\text{H}_2\text{O}_2 & \quad \text{UV}
\end{align*} \]
Ice photochemistry in the laboratory

**gamma irradiation**

\[ 1 + e^- \rightarrow \text{Compton} \]

\[ 1 \xrightarrow{\gamma\text{-radiation}} \text{- e}^- \]

\[ 1 \xrightarrow{^R} \text{- H}_2\text{O} \]
Absorption characteristics

Absorption characteristics of o- and p-chlorophenol vs. solar actinic flux
Absorption characteristics in ice

Ice matrix: absorption band shifts of Reichardt’s dye

red (bathochromic) shift
Temperature-dependent absorption characteristics in ice

![Graph showing absorption characteristics at 20 °C and -70 °C with various curves labeled a80 to a87.](image)

20 °C

-70 °C
Absorption characteristics in ice

Ice matrix: absorption band shifts

Michlers Keton

blue (hypsochromic) shift
Environmental ice photochemistry: The Svalbard Project

Ny-Ålesund

Brno
Environmental ice photochemistry: The Svalbard Project

Before ...

after ...
<table>
<thead>
<tr>
<th>compound</th>
<th>concentration ([\times 10^{-4} \text{ mol l}^{-1}])</th>
<th>A (300 nm)</th>
<th>consumption [%]</th>
<th>half-life</th>
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</thead>
<tbody>
<tr>
<td>valerophenone</td>
<td>5.8</td>
<td>0.22</td>
<td>100</td>
<td>50 min</td>
</tr>
<tr>
<td>2-nitrobenzaldehyde</td>
<td>4.4</td>
<td>1.35</td>
<td>100</td>
<td>8 min</td>
</tr>
<tr>
<td>dibenzyl ketone</td>
<td>6.0</td>
<td>0.17</td>
<td>100</td>
<td>40 min</td>
</tr>
<tr>
<td>1,2-dichlorobenzene</td>
<td>5.2</td>
<td>0.00</td>
<td>15</td>
<td>10 days</td>
</tr>
<tr>
<td>1,3,5-trichlorobenzene</td>
<td>3.1</td>
<td>0.02</td>
<td>&lt;1</td>
<td>n.a.</td>
</tr>
<tr>
<td>2-chlorophenol</td>
<td>5.1</td>
<td>0.02</td>
<td>14</td>
<td>10 days</td>
</tr>
<tr>
<td>4-chlorophenol</td>
<td>5.1</td>
<td>0.02</td>
<td>15</td>
<td>10 days</td>
</tr>
<tr>
<td>sodium 2-chlorophenate</td>
<td>5.0</td>
<td>0.22</td>
<td>86</td>
<td>2 days</td>
</tr>
<tr>
<td>sodium 4-chlorophenate</td>
<td>5.0</td>
<td>0.18</td>
<td>85</td>
<td>2 days</td>
</tr>
<tr>
<td>2,4,5-trichlorophenol</td>
<td>4.4</td>
<td>0.75</td>
<td>12</td>
<td>25 days</td>
</tr>
<tr>
<td>2,4,6-trichlorophenol</td>
<td>5.1</td>
<td>0.49</td>
<td>6</td>
<td>50 days</td>
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<tr>
<td>pentachlorophenol</td>
<td>0.4</td>
<td>0.10</td>
<td>58</td>
<td>3 days</td>
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<tr>
<td>2-nitrophenol</td>
<td>4.0</td>
<td>1.35</td>
<td>4</td>
<td>75 days</td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>3.4</td>
<td>2.67</td>
<td>23</td>
<td>13 days</td>
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<tr>
<td>2-chlorobiphenyl</td>
<td>0.3</td>
<td>0.01</td>
<td>&lt;1</td>
<td>n.a.</td>
</tr>
<tr>
<td>3-chlorobiphenyl</td>
<td>0.3</td>
<td>0.01</td>
<td>&lt;1</td>
<td>n.a.</td>
</tr>
<tr>
<td>4-chlorobiphenyl</td>
<td>0.3</td>
<td>0.01</td>
<td>&lt;1</td>
<td>n.a.</td>
</tr>
<tr>
<td>2,4-dichlorobiphenyl</td>
<td>0.1</td>
<td>0.01</td>
<td>&lt;1</td>
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</tr>
<tr>
<td>DDT</td>
<td>0.03</td>
<td>&lt;0.01</td>
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<tr>
<td>2,4'-DDE</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>&lt;1</td>
<td>n.a.</td>
</tr>
<tr>
<td>4,4'-DDE</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>&lt;1</td>
<td>n.a.</td>
</tr>
</tbody>
</table>
Environmental ice photochemistry: The Svalbard Project

\[ \text{Cl}_2 \text{OH} \xrightarrow{h\nu, \text{ice}} \text{Cl}_2 \text{O} \text{Cl}_2 \]

\[ \text{Cl}_2 \text{OH} \xrightarrow{h\nu, \text{ice}} \text{Cl}_2 \text{OH} + \text{Cl}_2 \text{OH} \]
Environmental ice photochemistry: The Svalbard Project
Environmental implications

GLOBAL TRANSPORT

DEPOSITION ACCUMULATION (PHOTO)CHEMISTRY

RELEASE TO THE ENVIRONMENT

products of ice (photo)chemistry

ice or snow

cloud

PBTs

Ice photochemistry - some conclusions

1. Unique transformation pathways
2. New (secondary) pollutants
3. Potentially high environmental risk when the ice sheets melt
4. Possible photochemical transformations should be considered in the ice-core record studies
Current and near-future research

1. Mechanistic studies (LFP, DR LFP)
2. Toxicity of the photoproducts
3. Secondary reactions within the ice matrix (photolysis in the presence of \( \text{H}_2\text{O}_2, \text{NO}_3^- \) etc.)
4. The study of sensitization and quenching reactions within the frozen matrix
5. Absorption properties of compounds in the ice matrix
6. Working with natural POPs concentrations
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