

## BIMOLECULAR PHOTOCHEMICAL REACTIONS IN ICE

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### Introduction

The laboratory research results have provided evidence that many organic compounds can undergo light-induced chemical transformations in the ice matrix. This may have large consequences for the environment since many secondary photoprocesses may occur in natural ice or snow with photoproducts completely different from those obtained in liquid solutions or gas phase.

Here we present the results from the study of photochemical bimolecular processes among persistent organic pollutants and trace components, such as inorganic nitrates and nitrites or hydrogen peroxide, in ice and snow. Hydrogen peroxide as well as nitrates serve as the sources of hydroxyl radicals in the photolyzed medium, causing efficient hydroxylation reactions.

Hydrogen peroxide is an important oxidation agent in the atmosphere<sup>1</sup> but it is also a common trace constituent of natural snow and ice<sup>2</sup>. Many field studies at different locations in polar and mid-latitude regions have demonstrated that H<sub>2</sub>O<sub>2</sub><sup>3,4</sup> as well as nitrates<sup>5-7</sup> are responsible for emitting the hydroxyl (HO•) or hydroperoxyl (HO<sub>2</sub>•) radicals (in addition to NO<sub>x</sub>• in case of nitrate) to the atmosphere. Concentrations of H<sub>2</sub>O<sub>2</sub> in surface snow were found to depend largely on its atmospheric concentration<sup>8</sup>. Photolysis of hydrogen peroxide is known to produce HO• with the quantum yield near unity in water<sup>9</sup> but it decreases with decreasing temperature<sup>10</sup>. Distribution of inorganic nitrate in Antarctic ice is relatively constant comparing to other ions; mean levels in ice cores and surface snow usually vary from 20 to 80 µg L<sup>-1</sup><sup>11</sup>, but its concentration may occasionally reach higher values in the surface snow<sup>6</sup>. Jacobi et al. have recently shown that the photolysis of H<sub>2</sub>O<sub>2</sub> and nitrate in snow occurs with a similar efficiency, thus both species are equally important in natural snow covers as the HO• sources. It was suggested that HO• could oxidize organic precursors to produce carbonyl compounds, such as formaldehyde, in the snowpack<sup>12-14</sup>.

### Materials and Methods

All aqueous solutions of phenol, with or without an excess of nitrite or nitrate, were bubbled with nitrogen or oxygen for 30 minutes prior to freezing. In addition, the frozen aqueous solutions of an organic compound (benzene, phenol, naphthalene, 2-naphthol, anthracene, cyclohexane, butane, 1-butanol, 2-butanol, butanal, or methane), containing hydrogen peroxide, were prepared. Samples in 13 × 100 mm quartz (transparent at >254 nm) or Pyrex (an additional Pyrex sleeve eliminated wavelengths below 300 nm) tubes, sealed with septa, were solidified in a cryostat box filled with ethanol as a cooling medium at -15 °C, and irradiated using a 125-W medium-pressure mercury lamp (Tselamp). After irradiation, thawed sample solutions were extracted with dichloromethane (for GC-MS) or analyzed directly on HPLC. Identification and quantification of the photoproducts was carried out by comparison their retention and/or MS spectra with those of the authentic compounds or the mass spectral library. The nitrite/nitrate concentrations were analyzed using an ion chromatography. The photochemical irradiation was also carried out on an optical bench consisting of a monochromator with grating set to 313±5 nm, and a 1-cm quartz cell in a Peltier sample holder (-25 °C).

### Results and Discussion

When aqueous solutions of inorganic or organic compounds are frozen, the solutes became spontaneously segregated at the grain boundaries of polycrystalline ice. They are not incorporated into the solid ice crystals but they accumulate in the layers surrounding their walls that eventually solidify as temperature decreases. It was, therefore, expected that local concentrations of aromatic compounds and sodium nitrite/nitrate will dramatically

increase during the freezing process. Photolysis of such a mixture of chromophores should result in a complex of different products. High chromophore concentrations, in addition, introduce an internal optical filter effect, which lowers the overall photoreaction efficiencies. In the absence of other reagents (water molecules are not available in common photoinitiated reactions as a nucleophile), excited organic compounds could undergo intra- or intermolecular transformations, dependent on their starting concentrations and restricted molecular diffusion.

In conclusion, it was found that freezing of aqueous solutions of organic compounds and inorganic nitrite/nitrate produces a concentrated mixture of all components, and its photolysis leads to nitrated and hydroxylated products. The production of nitro- and hydroxyproducts was found to occur primarily because of the  $\text{NO}_2^-/\text{NO}_3^-$  excitation and the process efficiencies apparently decreased when a competing photolysis of aromatic compounds produced quenchers. The presence of the OH group on the aromatic system was found to be essential for efficient nitration and hydroxylation processes but the exact mechanism remains unclear. The production of a large number of various trace products accompanied all photolyses at wavelengths at which the organic precursors absorb even at low conversions.

Similarly, oxidation of aromatic and saturated aliphatic hydrocarbons in frozen aqueous solutions by the hydroxyl radicals, photochemically produced from hydrogen peroxide, was investigated in the temperature range of  $-20$  to  $-196$  °C. While aromatic molecules (benzene, naphthalene, or anthracene) underwent primarily addition-elimination reactions to form hydroxy compounds, saturated hydrocarbons (cyclohexane, butane, methane) were oxidized to the corresponding alcohols via hydrogen abstraction reactions.

### Environmental implications

Hydroxybenzenes are known to be formed as intermediates in the photooxidation of aromatic compounds in nature. Trace levels of phenols, methoxyphenols, and nitrophenols have even been detected in snow samples from the polar regions or high mountains. Various hypotheses suggest that the occurrence of these compounds in remote environments might reflect local atmospheric or snow (photo)chemistry. Many recent reports indicate that nitrate, commonly found in the polar regions, is photochemically active in the snowpack and it has been hypothesized about its account to post-depositional processes. The flux of formaldehyde and acetaldehyde from sunlit snow containing a snow-phase organic matter was shown to be enhanced with the addition of nitrate, being a precursor to  $\text{HO}^\bullet$ . Our experiments clearly signify this observation; hydroxylation was one of the important processes observed, however, there might be significant restrictions which confine the extent and character of a corresponding chemical process. In this work, nitration process was observed to be an alternative sink for the organic matter present in ice or snow for the first time. Using very simple organic molecules did not ease our experimental work and only higher, environmentally not very relevant, starting concentrations allowed us to identify photoproducts. Larger reaction conversions produced a very complex mixture of photoproducts and we believe that an extensive irradiation would eventually lead to very simple, perhaps gaseous, compounds and, at the same time, to persistent organic oligomers/polymers depending on the concentration of the reactive species. In case that the starting (natural) concentration of impurities in snow is low, the latter process will be largely diminished.

The results suggest that these reactions are qualitatively similar to those known to take place in liquid aqueous solutions or gas phase, and support the hypotheses according to which oxidation of organic impurities in the snowpack can produce volatile hydroxy and carbonyl compounds, which are consequently released to the atmosphere. Furthermore, possible photochemically induced formation of highly mutagenic or carcinogenic nitro- or nitrosoaromatic compounds in the polar regions is considered.

Understanding the fundamental chemical processes in ice is unquestionably very important in related environmental or cosmochemical investigations.

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## DECOMPOSITION OF POLYCHLORINATED BIPHENYLS WITH ACTIVATED CARBON-SUPPORTED IRON

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### Introduction

Commercial PCBs had been first produced in the United States since 1929<sup>1</sup>, and have been used as dielectric fluids for transformers and capacitors because of their excellent stability and thermal properties<sup>2</sup>. Between the start of production in 1954 and end in 1974, approximately 59,000 tons of PCB were manufactured in Japan<sup>3</sup>.

Owing to PCBs' persistence and propensity to bio-accumulate in the fatty tissues of animals, the manufacture of PCBs in Japan ceased in 1974. Whereas a part of the PCBs went into the environment by illegal dumping or accidental spill, remediation of PCB-contaminated soils, groundwater, and sediments has become a major environmental management problem.

Presently, chemical decomposition methods were used to destroy most of the PCBs waste with high amount; however, the processes generate exhaust gas with low concentration of PCBs in large quantities. The use of activated carbon (AC) to adsorb the residual PCBs has been developed at present. And then AC can be disposed of by incineration. However, this involves many problems, such as the high construction and maintenance costs of high temperature equipment, the generation of dioxins with facility, and the risk of PCB exposure during the conveyance and pulverization process of AC before incineration. Therefore, it is important to find an inexpensive, safe method to dispose of the low concentration of PCB waste derived from processing high amount. AC is not only a strong adsorbent; it can also be used as a catalyst support in many reactions<sup>4</sup>. On the other hand, transition metals are reported to dechlorinate PCDD and PCDF derivatives and other chlorinated compounds<sup>5</sup>. In this study, we tried to utilize the synergism between AC and iron, so AC-supported iron was made to decompose low concentrations of PCBs.

### Materials and Methods

Two methods for producing AC-supported iron were proposed. LaFe-C was produced by impregnating AC (20–48 mesh, Shirasagi C2C20/48; Takeda Pharmaceutical, Osaka, Japan) with iron ion solution. A novel method prepared AC with highly dispersed Fe by the carbonization of ion-exchange resins (Mitsubishi Chemical, WK-11). AC prepared by this method was called IRFe-C. Inductively coupled plasma-atomic emission spectrometry (IRIS-Intrepid ICAP, Thermo Electron) was used to measure the iron concentration in AC-supported iron after decomposed

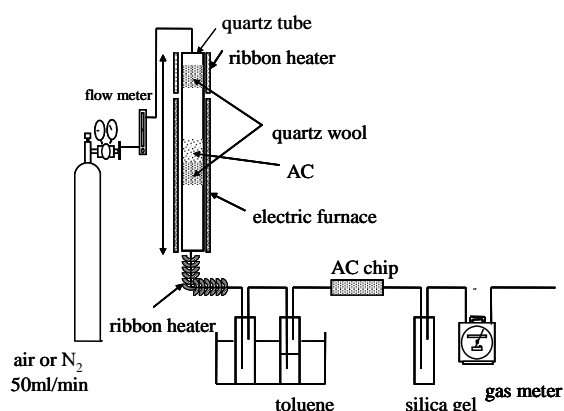


Fig.1 Schematic illustration of the system used to analyze decomposition of polychlorinated biphenyl-153 catalyzed by activated carbon-supported iron.