MASARYK UNIVERSITY

The Applicability of Artificial Snow for Environmental Studies

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Photochemistry of semi/nonvolatile organic compounds in/on snow and ice

Motivation

… **anthropogenic organic compounds** are present in high latitude and related ice and snow environments at noticeable concentrations

… some organic compounds can undergo primary **photochemical** or secondary (either dark or photochemically initiated) chemical processes on/in ice and snow

… to improve the current knowledge about the accumulation and photochemical transformations of organic compounds, such as POPs, in polar regions and atmospheric cloud particles

Information is needed

… physical interactions
… mechanisms of the phototransformations
… the pollutants' lifetimes in the polar areas
… environmental risk

Laboratory experiments

Field measurements: hardly reproducible (different loads of contaminants in every sample), photochemical reactions: none of the factors is constant enough…

Frozen ice samples: simulation of contaminant aggregation processes and the reactions within the frame of the clusters (bimolecular reactions)

Ice surface: difficult arrangement of matrix isolation-type experiments; may not be relevant to natural conditions

Can we make relevant snow (ice) samples?
Can we simulate natural „polar" photoprocesses in the lab?
Can we predict the scope of photoprocesses?

→ **contaminated natural snow samples**
→ **artificial snow samples**
… very low contaminant concentrations, no organic co-solvents, homogeneity

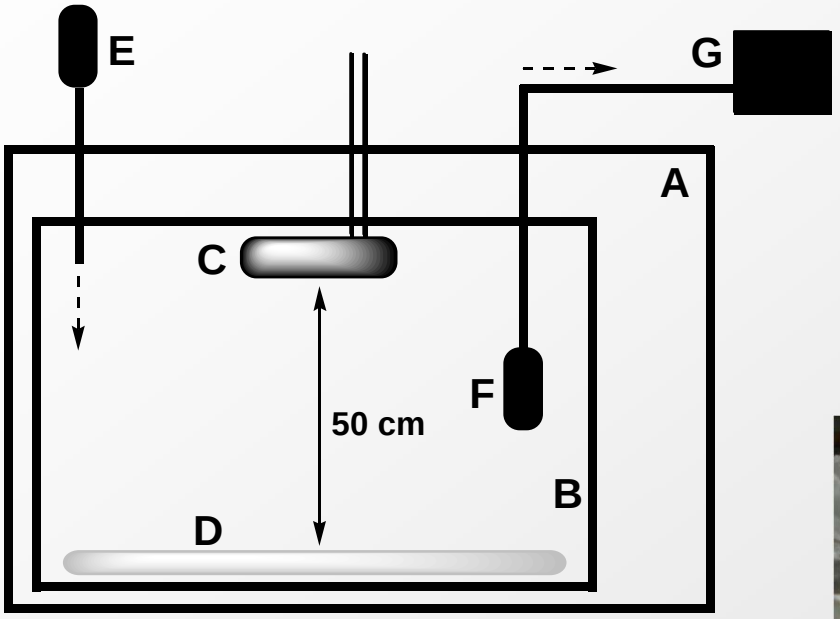
How to make artificial (contaminated) snow

… Fast/slow **freezing of a solution** being sprayed
… to liquid nitrogen or in a cold room.

… **Adsorption** of gaseous compounds on pure artificial (or even natural) snow (experimentally challenging)

(a known method: HW Jacobi (photochemistry), JPD Abbat (SSA), T Okada (ice chromarography), freeze-drying technology (biochemistry)…)

Artificial snow and cold chamber (reactor)



A photochemical cold chamber: A, freezer; B, steel box; C, UV lamp in a Pyrex/quartz-jacketed housing; D, snow sample; E, polyurethane foam filter (inlet); F, polyurethane foam filter; G, pump (outlet).

Artificial snow

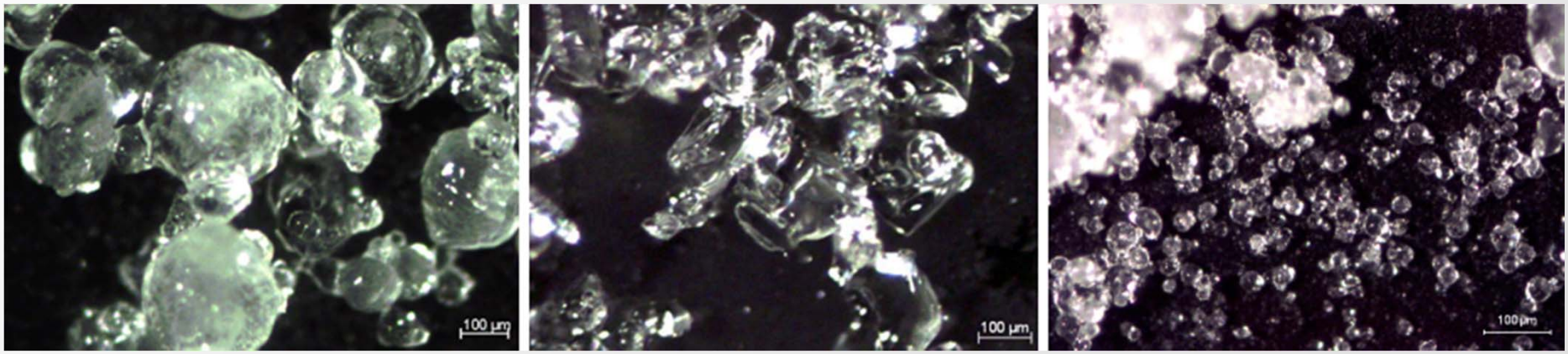
… fast vs. slower freezing of a solution

… original question: is most of the hydrophobic material expelled on ice surface?

… from (g): contaminats: adsorption/desorption, saturation, site availability; aging

… photochemistry, surface chemistry … with gases

snow gun: liquid N_2 snow gun: cold room nebulizer: liquid N_2



… grain size; specific surface area; surface coverage, contaminant associations

Specific surface area of artificial snow

Surface coverage … the **fraction of the adsorption sites occupied** by molecules

… Langmuir adsorption isotherm; or calculated from the known solid surface area and the area occupied by a single molecule

… different techniques (e.g., adsorption of Kr, CH_4)

… natural snow (10-10^3 cm^2 g^{-1}, F. Domine)

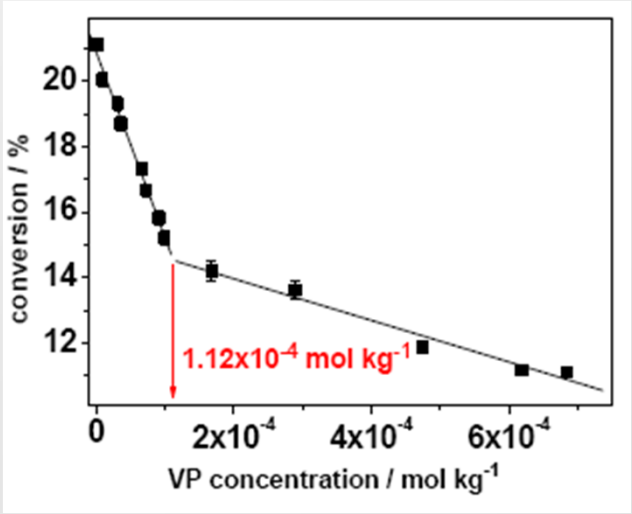
Valerophenone photochemistry

… different surface loads under the same irradiation conditions

… act as an internal optical filter

… a decrease in the reaction efficiency

Similar (ca. **400 cm^2 g^{-1}**) for all types of snow, incl. snow contaminated from vapors



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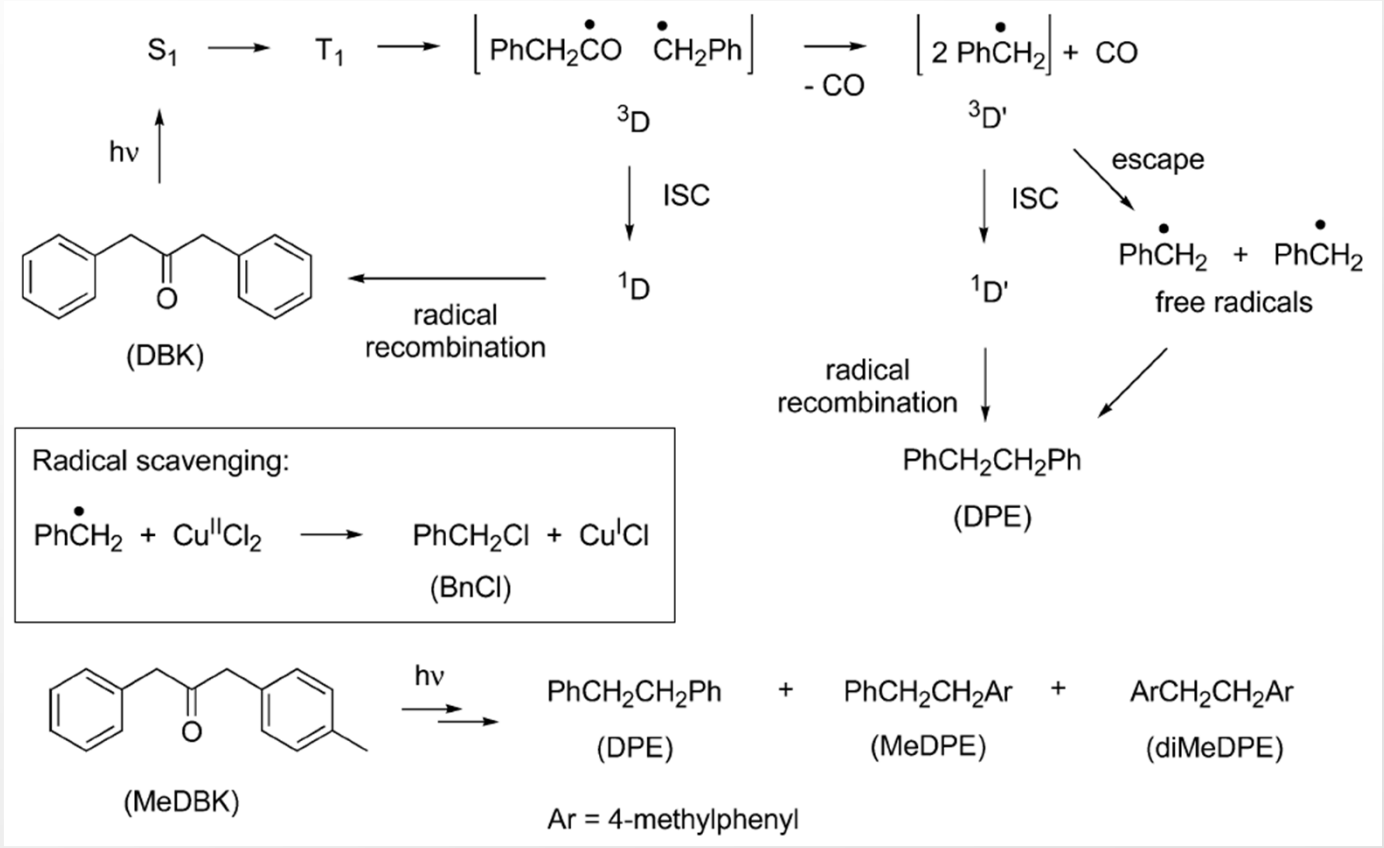
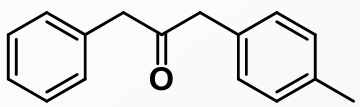
Cage effect

… the fraction of radical pairs that undergo reactions within a primary **reaction cage**

… diffusion, restrictions of the microenvironment, associations



Diffusion on the surface of snow grains/in frozen solutions



$h\nu$

(MeDBK)

Ar = 4-MePh

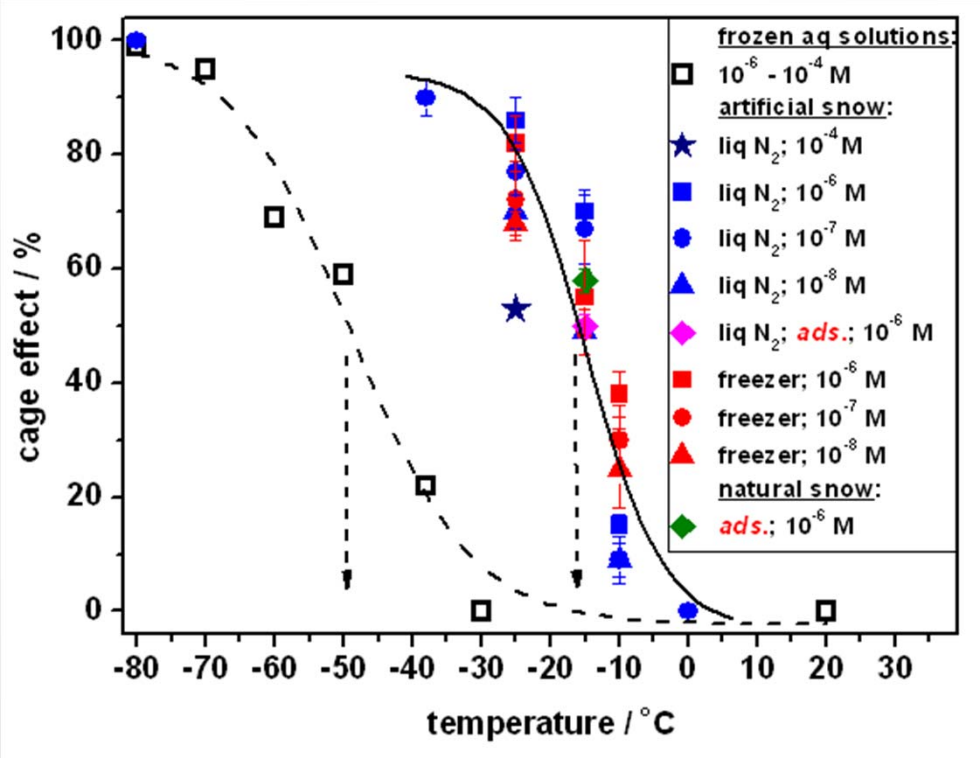
$PhCH_2CH_2Ph$ + $PhCH_2CH_2Ar$ + $ArCH_2CH_2Ar$

(DPE) (MeDPE) (diMeDPE)

$$CE = \frac{[MeDPE] - ([DPE] + [diMeDPE])}{[MeDPE] + [DPE] + [diMeDPE]} \times 100\ (\%)$$

Frozen solutions:
- inflection point = **–48 ºC**: $k_{diff} \sim k_{recomb}$
- concentration independent

Artificial snow samples:
- inflection point = **–17 ºC**
- concentration independent
- snow/deposition type independent



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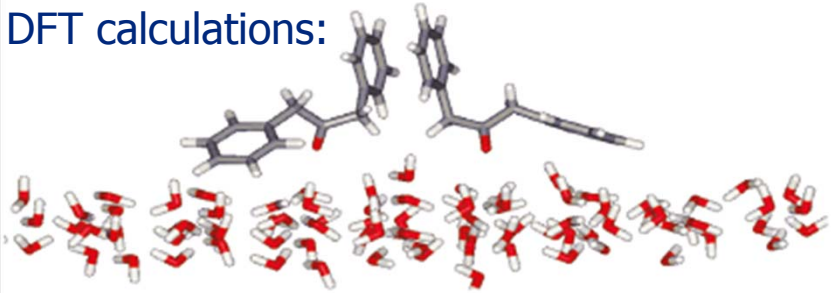
Diffusion on the surface of snow grains

CE magnitude: … the **mobility** (diffusion) **of radicals** in a constraining environment (as a temperature-dependent variable)
… a local concentration of MeDBK … freezing point depression

Frozen solutions: … aggregates in vains, micropockets
… frozen matrix … **3D cage**

Snow grains: … same CE for samples of different deposition (VP: monolayer below $c = 10^{-5}$ mol L^{-1})
… surface … **2D cage**
… independent on c
… **associations** (equilibrated)

DFT calculations:



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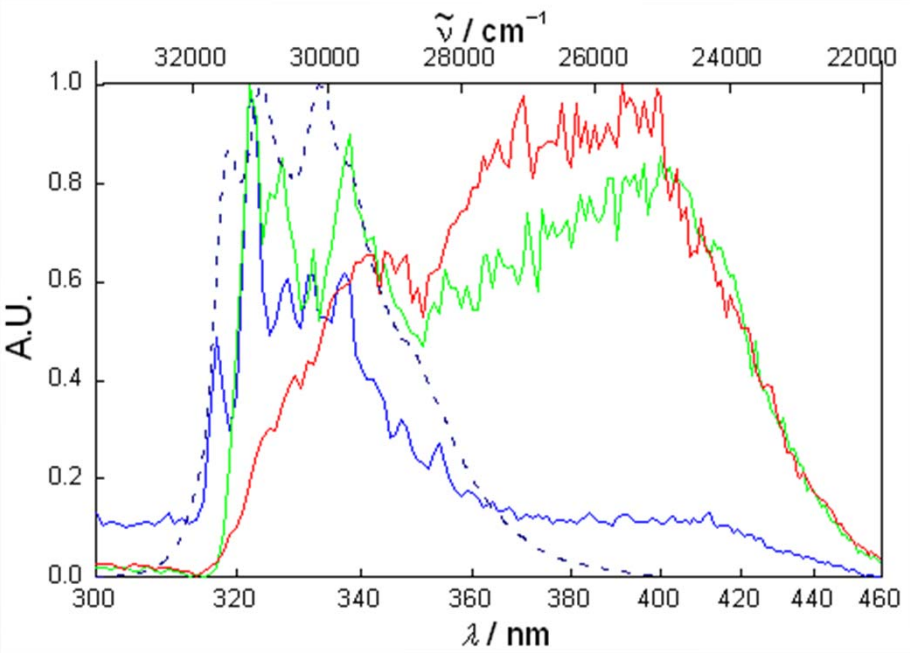
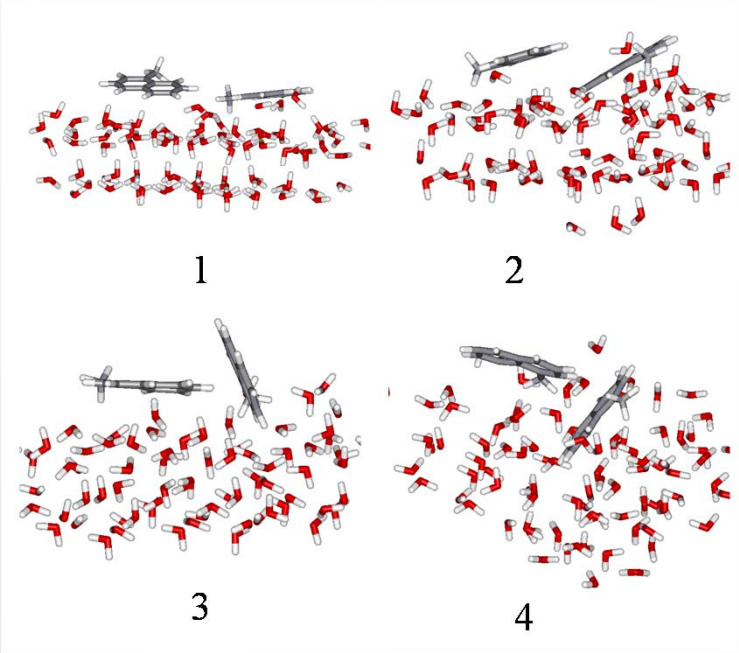
Snow grains … 1-methylnaphthalene spectroscopy

deposition from vapors

(monomer vs.) associations DFT calculations (QLL)

… GS dimer (weak, higher *T*), excimer (stronger)



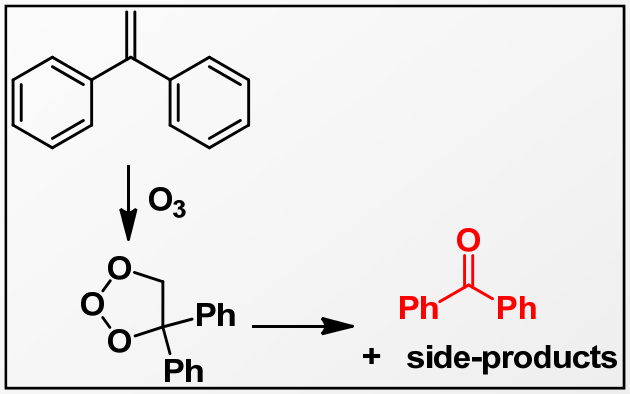


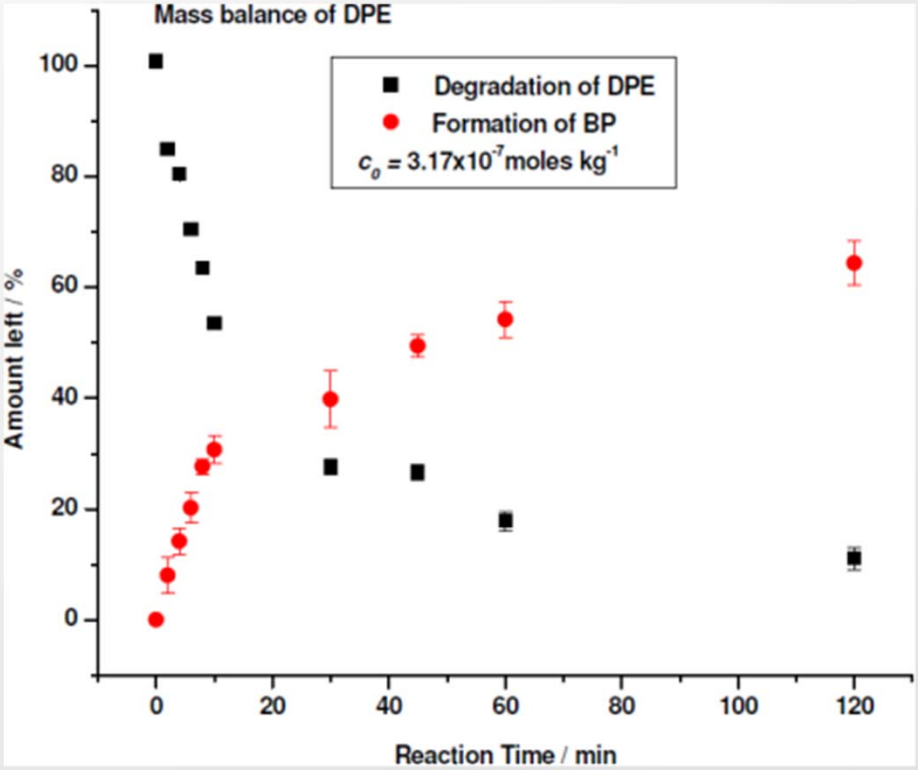
The emission spectra of **1MN** deposited on artificial snow grains (the surface loads: $c = 5.6 \times 10^{-6}$, blue line; $c = 7.0 \times 10^{-5}$, green line; and $c = 9.0 \times 10^{-5}$ mol kg^{-1}, red line). The samples were excited at $\lambda_{exc} = 282$ nm. The black line represents the emission spectrum of **1MN** of an aqueous solution ($c = 7.7 \times 10^{-5}$ M) for comparison.

D. Heger, F. Surman, D. Nachtigallova, P. Klan

Gas → snow surface reaction

… adsorption of DPE from (g); different *c*
… ozonolysis at *T* = –15 ºC
… benzophenone production
… negligible volatilization





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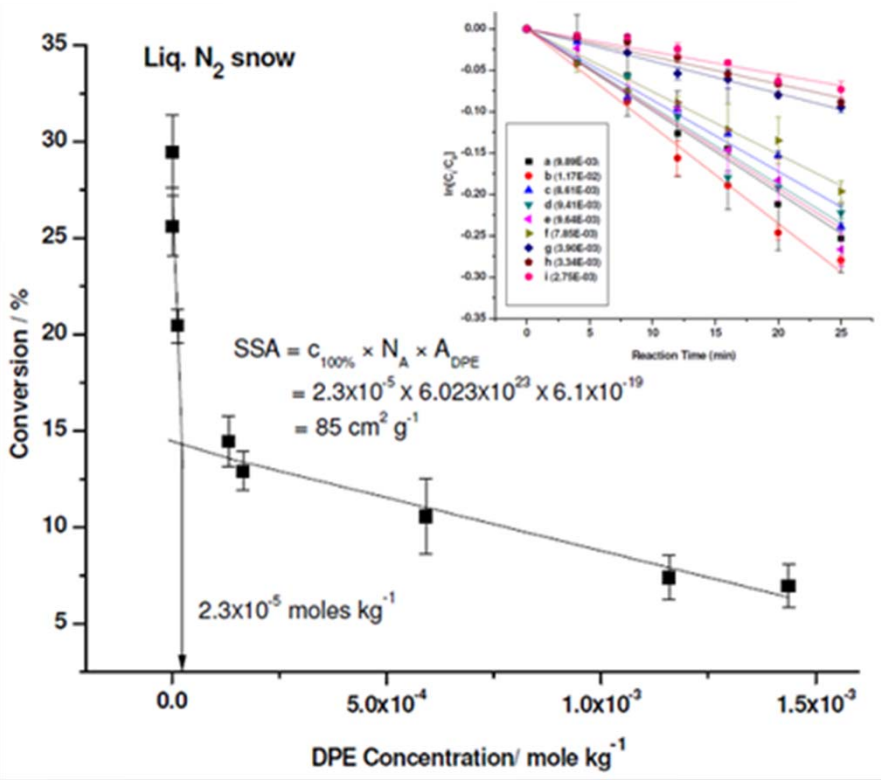
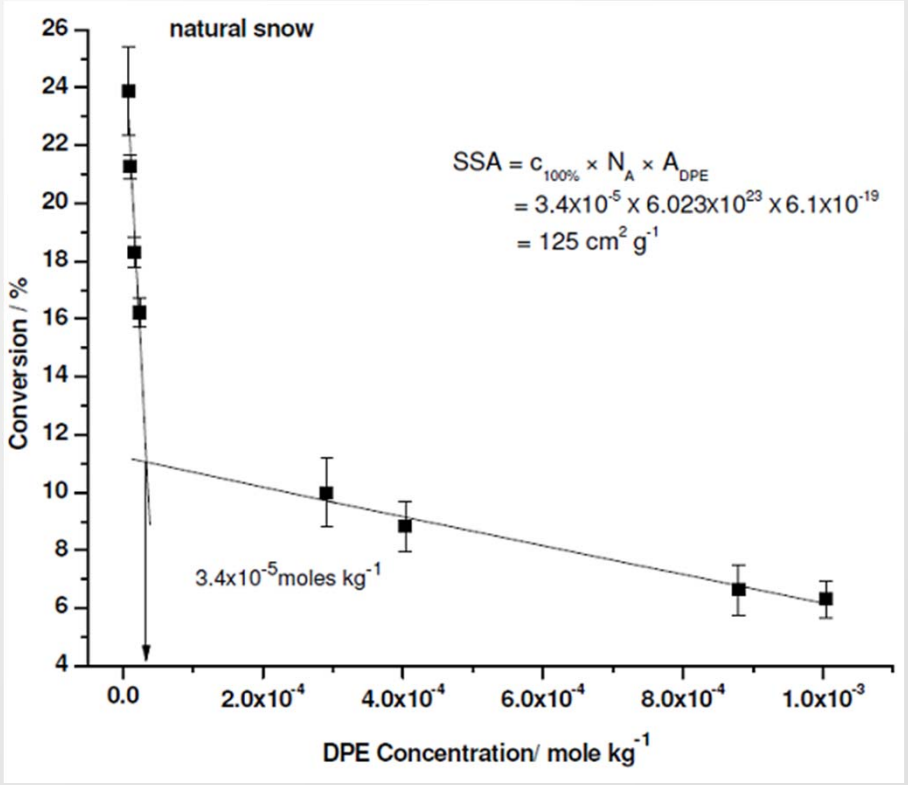
Gas → snow surface reaction

… **specific surface area** determination
SSA /cm^2 g^{-1} = c_{cont} x N_A x A_{DPE}
… sites available for surface-gas reaction





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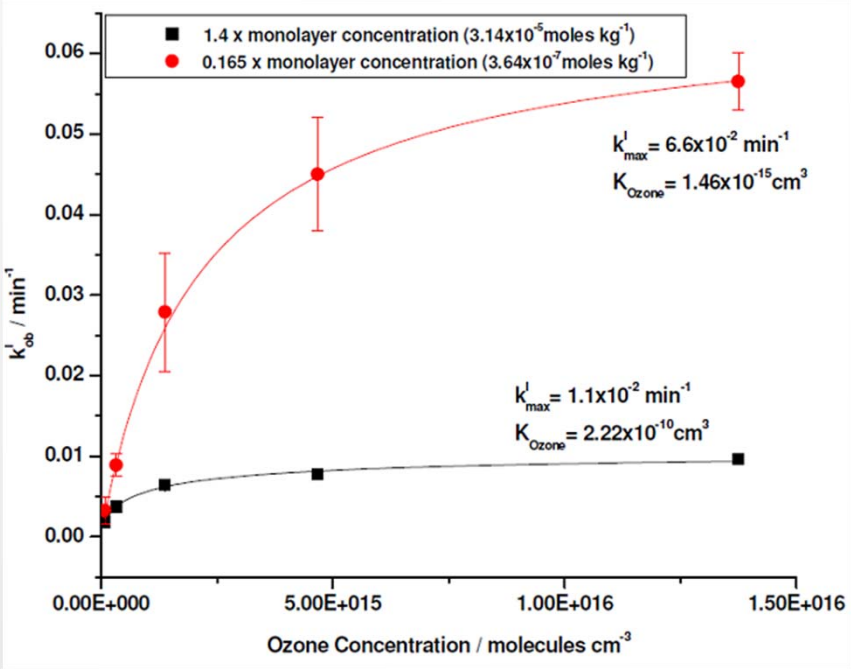
Gas → snow surface reaction

the **Langmuir-Hinshelwood** ozonization mechanism

… a bimolecular surface reaction between two molecules which are adsorbed on adjacent sites

… fit of the experimental data



(k^I_{max} is the maximum first order rate coefficient at saturated surface concentration of ozone, K_{O3} is the adsorption equilibrium constant of ozone and [O_3] is the gas phase ozone concentration)

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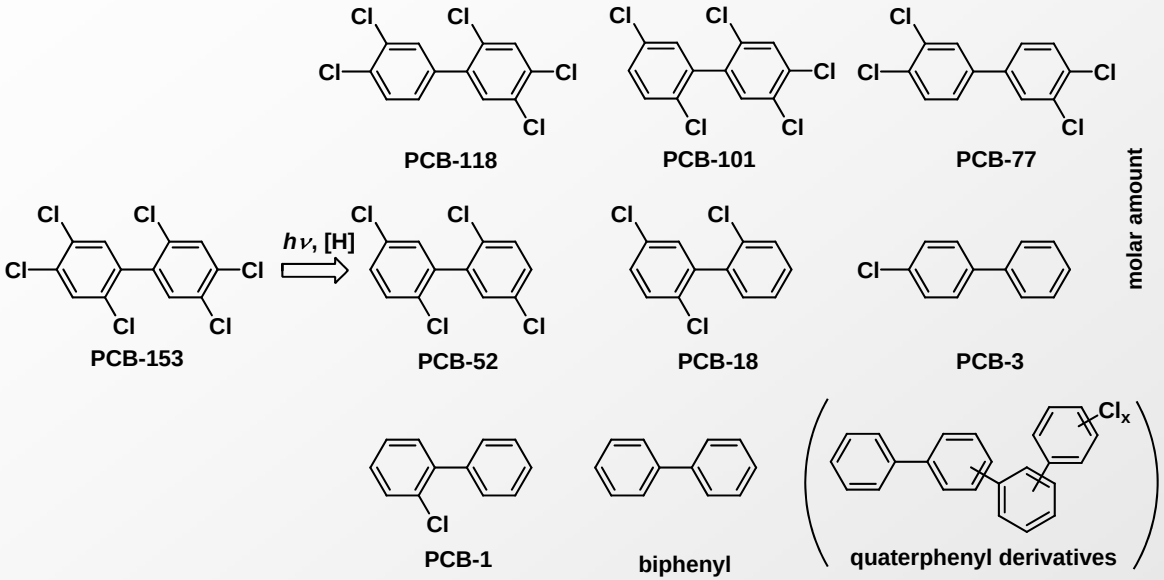
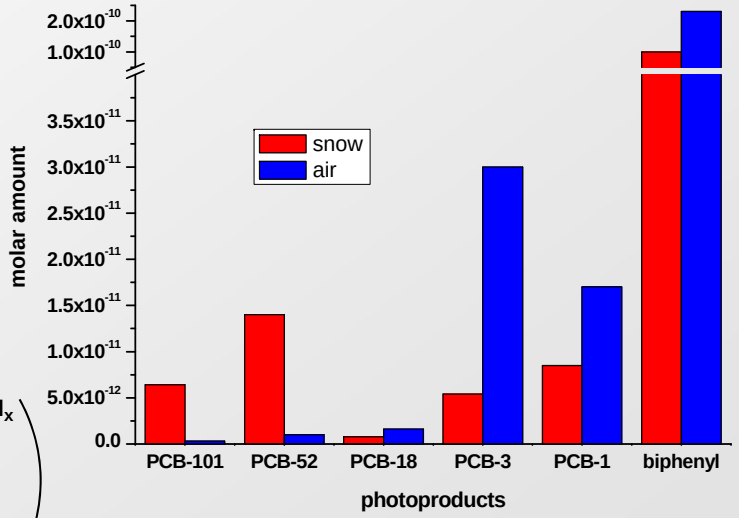
Photodegradation of pollutants - PCBs

… environmentally relevant concentrations (100 ng kg^{-1})





- **lifetimes 1 order of magnitude longer that those in surface waters**
- coupling reactions suppressed (as in water)
- minor oxidation by O_2
- volatile compounds' desorption

Matykiewiczova, N., Klanova J., Klan P., Environ. Sci. Technol. 2007, 41, 8308-8314.

Photochemistry of organic compounds in polar areas?

We can measure absorption properties of organic impurities, excited state and short-lived species lifetimes (LFP), and the reaction quantum yields.

We could **predict the pollutants' lifetimes**

… **for bimolecular processes**: if we evaluate

a) local concentration (uptake; aggregation, surface coverage, desorption)

b) mobility (diffusion) within the lifetime of a reactive species

c) aggregation due to hydrophobic and other non-covalent interactions

d) bimolecular quenching, filter effect

e) primary reactions and secondary dark reactions with (g); side reactions (O_2 vs. H-donors; OH; acids… but *c* is uknown)

… **for purely unimolecular processes**

similar points; but we do not need to consider external reactants

… let's be aware of side-bimolecular processes!

… **artificial snow as a laboratory study matrix**

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