PHOTOCHEMISTRY OF PBT COMPOUNDS IN ICE: A NEW POTENTIAL SOURCE OF ICE CONTAMINATION?

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Introduction

Organic substances that are persistent and bioaccumulative, and possess toxic characteristics likely to cause adverse human health or environmental effects, are called PBTs (Persistent, Bioaccumulative, and Toxic substances). In this context, the "substance" means a single chemical species, or a number of chemical species, which form a specific group by virtue of (a) having similar properties and being emitted together into the environment or (b) forming a mixture normally marketed as a single product. Depending on their mobility in the environment, PBTs could be of a local, regional or global concern[1].

Subclass of PBTs so called POPs (Persistent Organic Pollutants) is a group of compounds, which are prone to a long-range atmospheric transport and deposition[2]. The global extent of POP pollution became apparent with their detection in areas such as the Arctic[3,4], where they have never been used or produced at levels posing risks to both wildlife[5] and humans[6].

Hypothesis

PBTs have the propensity to enter the gas phase under environmental temperatures. Hence, they may volatilise from soils, vegetation, and water bodies into the atmosphere and – because of their resistance to breakdown reactions in air – travel long distances before being re-deposited[7]. Their concentration in environmental compartments is controlled by various chemical properties, including their own properties as well as properties of the environment. In general, persistent chemicals have higher levels in environmental compartments and they are eliminated more slowly. The discussion of the PBTs environmental fate is to focus on compartments such as air, soil or sediment. Net losses from the systems can occur due to degradation/burial/occlusion in the soil/water body and atmospheric reactions (i.e. photolysis, OH radical reaction), shifting the air-surface equilibrium status. A relative lack of attention, information, and knowledge is given to ice. Here we discuss the problem of a long-range transport of PBTs to the polar regions, their deposition there and the following accumulation. But what is the fate of these compounds in ice? This topic is practically unknown and open. Could the compounds be degraded or are they persistent and non-degradable in ice for long time? What can be the result of global warming process when ice melts? Is ice a potential source of primary deposited compounds only or a source of metabolites (products) of degradation in ice? Among other pathways of possible degradation processes, photodegradation by the sunlight seems to be the most readily available, especially now when the ozone layer is a less effective UV filter.

The photobehaviour of molecules in the constrained and organised media has been studied for many decades. Weiss and his co-workers provided a model for a characterisation of the *effective reaction cavity*[8]. Some solid materials possess free volume that is essentially stationary and constant. Thus, the photoreactivity of compounds inside such a reaction cavity may vary upon the character of the organised medium. Here, we wish to present results from the investigation of photoreactivity of some PBTs in ice.

A typical experimental procedure

Aqueous chlorobenzene solutions (1.4×10^{-3} – 4×10^{-5} M) were prepared by centrifugation of the saturated solution (~3×10^{-3} M) for 15 min. at 4 °C, following by dilution. Oxygen was removed from the samples either by bubbling the solutions with argon for 15 min or by sonication. For photolysis of the mixtures (~0.1 %, w/w), the sample was sonicated and immediately cooled in the liquid nitrogen bath. The sealed samples in quartz tubes, placed into the merry-go-round apparatus, were irradiated using a 125 W medium-pressure mercury lamp (Teslamp) in a cryostat box with ethanol as a cooling medium at -20 °C. Solutions were extracted with dichloromethane solution of hexadecane (2 ml) used as an internal standard.

Identification of photoproducts was carried out by GC/MS analysis on a HP 6890 gas chromatograph, equipped with the mass selective detector HP 5972 (Hewlett Packard, USA). A sample of 1-µl volume was introduced in a split mode (split ratio 20:1) into the capillary column DB5-MS (J&W Scientific, Folsom, USA) of 60-m length, 0.25-mm i.d., and 0.25-µm film thickness. The mass spectrometer was operated in the scan mode using EI ionisation; the mass spectra were collected in the mass range 50-550 m/z.

Results and discussion

Recently, we have undertaken an original investigation of valerophenone[9] and polychlorobenzenes photobehavior[10] in the solid matrix of ice and other solvents. Such medium presents surroundings, which prevents drastic conformational, translational, and rotational changes along the reaction co-ordinate. We found that photolysis of chlorobenzenes with quartz filtered UV light was entirely different than that observed in liquid water where phenol derivatives – products of the radical nucleophilic substitution reaction with the solvent - were almost exclusively isolated. Thus, only mono- and polychlorinated biphenyls (PCBs) and many other coupling photoproducts were detected in ice thanks to aggregation of the starting molecules. They, remarkably, showed no reactivity toward water molecules of the solvent cavity walls. Since chlorobenzene irradiation produced unexpectedly much more toxic compounds than the starting material it is obvious that the results of those experiments bring will be of a broad public interest.

Our main effort is focused on the study of photodegradation reactions of various environmentally important compounds in ice. For this study, a series of substituted chlorobenzenes (1-4 chlorine atoms) were irradiated with quartz filtered UV light in frozen water samples of various concentration. Photochemical efficiency and the product distribution were followed. The photolysis of chlorobenzenes in ice was found to be entirely different than that observed in liquid water where phenol derivatives – products of the radical nucleophilic substitution reaction with the solvent - were almost exclusively isolated.

Thus, only mono- and polychlorinated biphenyls (PCBs) and many other coupling photoproducts were detected in ice thanks to the intermolecular reactions of the starting molecules. Table 1 shows a list of the most important photoproducts that were detected after 24-hour irradiation of two chlorobenzene derivatives. In addition, the photoproduct distribution obtained after ice photolysis of tri- and tetra-substituted chlorobenzenes resembled those shown in the Table.

Table 1. Ice Photochemistry of Chloro- and Dichlorobenzene

hotoproduct	Number of isomers detected	Irradiation of chlorobenzene[a]	Irradiation of *o*-dichlorobenzene[a]
Benzene	1	h	H
Chlorobenzene	1	N/A	H
Dichlorobenzene	3	h	N/A
Trichlorobenzene	3	0	H
Biphenyl	1	h	M
Chlorobiphenyl	3	h	H
Dichlorobiphenyl	7	m	H
Trichlorobiphenyl	17	0	H
Tetrachlorobiphenyl	22	0	H
Terphenyl	3	h	S
Chloroterphenyl	14	h	M
Dichloroterphenyl	24	m	M
Trichloroterphenyl	28	0	M
Triphenylene	1	h	0

[a] Relative abundance (h = high, m = medium, s = small, 0 - under the detection limit, N/A - not rated) of the photoproducts formed by irradiation of the ~0.1 % (w/w) chlorinated benzenes mixtures in ice.

Irradiated diluted solutions (up to 4 x 10^{-5} M concentration) provided same higher-mass photoproducts, only the abundance of the coupling compounds having only two phenyl rings was higher[10].

Photoreactivity and Aggregation.

Photochemical C-Cl fission in aryl halides may be defined as any photochemical process leading to cleavage of a carbon-halogen bond. We assume that the homolysis and reactions of the free radicals take part in most of the transformations in ice (Scheme 1). Chlorobenzene derivatives described in this paper have a minimal absorption in the region of the tropospheric solar spectrum but they certainly serve as appropriate laboratory models for some other environmentally relevant pollutants. Table 1 shows that 0.1 % mixtures (one order of magnitude higher concentration than that of the saturated solution) of either chlorobenzene or *o*-dichlorobenzene are photochemically degraded into a large number of photoproducts. When irradiated, concentration of the starting material slowly dropped in the course of the reaction along with simultaneous formation of higher-mass compounds. Their formation was clearly caused by the aggregation of molecules in the frozen solvent before and/or during the process of ice solidification. For experiments with a lower chlorobenzene concentration (up to three orders of magnitude lower), many of the photoproducts were still surprisingly detectable, which means that aggregation still plays an important role. The detailed analysis data and kinetic measurements are described in the forthcoming paper[10].

Conclusion

Global transport of persistent chloroorganics to the polar region is well-known. The photochemical degradation in ice leading to very broad spectrum of various chlorinated aromatics and polyaromatics can be a secondary source of these compounds in these regions. After melting of snow, which can connected with global warming process, these pollutants can input to the polar ecosystem.

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Scheme 1.