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Photolysis of Octachloronaphthalene in Hexane

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Polychlorinated naphthalenes (PCNs) are a mixture of chloronaphthalenes (CNs) with various degrees of chlorination. The sources of PCNs include the commercial product "Halowax", impurities in polychlorinated biphenyls (PCBs), and by-products from the waste incinerations (Falandysz 1998; Yamashita et al. 2000 and 2002). In comparison with PCBs and polychlorinated dibenzo-p-dioxins/furans (PCDDs/PCDFs), knowledge on the formation, distribution and toxicity of PCNs are limited. PCNs have received growing attention, especially their environmental distribution. Though average PCN levels in the environment are lower than PCBs and PCDDs/PCDFs (Falandysz 1998), PCNs were found in nearly all the environmental constituents including air, soil, sediment, animal and plant (Falandysz 1998; Loganathan et al. 2002). Various types of toxicity of PCNs including dioxin-like activities were reported (Villeneuve et al. 2001). However, the environmental fate of PCNs is not well understood. In consideration of their global distribution and potential toxicity, more detailed studies on the environmental fate of PCNs are warranted.

Sequential dechlorination was found as a major photolysis mechanism of several PCNs (Ruzo et al. 1975a and b). Only a limited number of environmental parameters have been studied for effects on the photolysis of PCNs. Photolysis studies of highly chlorinated PCN congeners have not been found. In this study, octachloronaphthalene (OCN) was selected to study several aspects of its photolysis including light, aeration, photoproduct profiles, sensitizers and quenchers. Effects of these parameters on OCN photolysis were examined for remediation and toxicity interests.

MATERIALS AND METHODS

OCN and Halowax 1000, 1014, and 1051 were obtained from Accustandard, Inc (New Haven, CT). Standard solutions of individual congeners were obtained from Cambridge Isotope Laboratory (Andover, MA) and Wellington Laboratories (Guelph, Canada). Chlorophyll a from spinach, 2-decanone, 2-pentanol, and farnesol were obtained from Sigma Aldrich (Milwaukee, WI).

A small aliquot (10 μM) of sensitizers or quenchers– chlorophyll a, acetone, 2-

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decanone, 2-pentanol or farnesol– was added to OCN hexane solution (6.0 μM). The solutions were aerated with air or deaerated by purging with nitrogen for 10 min. Control samples were prepared according to the same procedures without sensitizers or quenchers.

OCN in hexane in quartz photocells was placed in a Rayonet Photoreactor (Southern N.E. Ultraviolet Co., Branford, CT), and exposed to 300 nm (0.283 kJ/m^2 min) or 350 nm lights (3.457 kJ/m^2 min) (RPR-3500 and RPR-3000 lamp, Southern N.E. Ultraviolet Co, Branford, CT). After exposure, a small aliquot of sample was collected at different time intervals for analysis using gas chromatography-mass spectrometry (GC-MS). Sunlight photolysis was done on February 12 -14, 2003 at the University of Hawaii at Manoa, Honolulu, Hawaii. Averaged sunlight irradiation was 44.043 for 300-1100 nm, 4.488 for UV-A, and 0.100 kJ/m^2 min for UV-B regions. Aerated or deaerated OCN hexane solutions in quartz photocells (10 mm i.d. × 250 mm length) were exposed to sunlight at ambient air temperature. A small aliquot of samples (1 ml) was collected at different time intervals during the exposure. The dark control OCN solution was covered with aluminum foil and stood under the same condition as treatments.

The GC-MS consisted of a Varian CP-3800 GC, Saturn 2000 ion trap MS, Varian CP-8400 autosampler, and a ZB-1 column (60 m, 0.25 mm i.d., 0.25 μm film thickness, Phenomenex, USA). The carrier gas was helium at a flow rate of 2 ml min^{-1}. The MS was operated in electron impact mode (70 eV). Injection port and ion source temperatures were 250 °C. The column temperature started at 150 °C for 6 min, was ramped up to 270 °C at a rate of 4 °C min^{-1} and was finally held for 10 min. Photolysis products were identified and quantified by comparing elution order and concentrations of each congener in Halowax 1014 or pure standard from literature (Imagawa and Yamashita 1994; Jarnberg et al. 1994; Wiedmann and Ballschmiter 1993).

RESULTS AND DISCUSSION

Photolysis in the environment is affected by many factors including quenchers, sensitizers, oxygen levels, and adsorption on solid particles (Schwarzenbach et al. 1993). Direct photolysis of chemicals is dependent on the light sources and the absorption spectra of chemicals (Schwarzenbach et al. 1993). In this experiment, all reactions followed pseudo-first order kinetics (Table 1). OCN showed two characteristic absorption peaks at 265 (λ_{max}) and 315 nm in hexane. Although the intensity of 350 nm light (3.457 kJ/m^2 min) was approximately 12-fold of 300 nm (0.283 kJ/m^2 min), OCN was photodegradated much faster at 300 nm ($-k$ = 0.365 h^{-1}) than at 350 nm ($-k$ = 0.103 h^{-1}). OCN photolysis in deaerated hexane under sunlight followed pseudo-first order kinetics, but the reactions were approximately two times slower than that of aerated hexane – photolysis constants of 0.0531 and 0.1322 h^{-1}, respectively. The results suggest a possible involvement of reactive oxygen species in the photolysis.

Table 1. Photolytic kinetics of OCN in hexane under UV and sunlight

Light source	Sensitizer or quencher	$-k^a$, h^{-1}	$t_{1/2}{}^b$, h	$R^{2, c}$
UV (350 nm)	None (control)	0.103	6.7	0.982
UV (300 nm)	None (control)	0.365	1.9	0.988
	Acetone	1.145	0.6	0.987
	2-Decanone	0.443	1.6	0.967
	Chlorophyll a	0.827	0.8	0.994
	Farnesol	0.434	1.6	0.988
	2-Pentanol	0.296	2.3	0.994
Sunlight	Aerated	0.132	5.3	0.994
	Deaerated	0.053	13.1	0.978

[a] $-k$ is photolysis constant; [b] $t_{1/2}$ is half-life; [c] R^2 is coefficient of determination.

Hydrophobic contaminants are selectively accumulated in the waxy layer of plant leaves than in other parts (Keum et al. 2002a), since the waxy layer consists mainly of hydrocarbons, ketones, alcohols and terpenoids (Oliveira and Salatino 2000; Chachalis et al. 2001). Those chemicals can affect the photolysis of recalcitrant chemicals (Schynowski and Schwack 1996). In this study, several chemicals that mimic the components of plant wax were tested for the effect on OCN photolysis. Aliphatic ketone is known as a photosensitizer (Keum et al. 2002b). Acetone and 2-decanone enhanced the reaction (-k, 1.145 and 0.443 h^{-1}, respectively) in comparison with the sensitizer-free control (-k, 0.365 h^{-1}). A rate enhancement by chlorophyll a, a well- known singlet oxygen sensitizer, supported that active oxygen species were involved in the reaction. Aliphatic alcohols are known to affect photolysis constants (Keum et al. 2002b). Farnesol slightly enhanced OCN photolysis (-k, 0.434 h^{-1}), but 2-pentanol slightly inhibited the reaction (-k, 0.296 h^{-1}) in this experiment.

Photoproduct profiles of OCN in hexane and in the presence of sensitizers or quenchers in hexane were similar, except that with the presence of acetone. Sequential dechlorinations were a major reaction in hexane. Ruzo et al. (1975a and b) also reported the same photolysis pattern of mono- to tetra-CNs in hydrocarbon and alcohol. The concentrations of hepta-CNs reached maximum after 4 h of exposure and remained as the major photoproducts up to 9 h (Figure 1). Hexa-CNs congeners were the major products after 9 h of exposure.

The concentrations of penta- and tetra-CNs were steadily increased during the irradiation. Among the hepta- and hexa-CN congeners, lateral-dechlorination products (e.g., 1,2,3,4,5,6,8-hepta and 1,2,4,5,7,8-hexa CN) were dominant. However, PCN-52/60 (1,2,3,5,7- / 1,2,4,6,7-penta CN) and PCN-47 (1,4,6,7-tetra CN), peri-dechlorination products, were identified as the most dominant penta- and tetra-CN congeners. Jarnberg et al. (1999) reported such a preferred removal of chlorine at peri-position (Chlorine at 1, 4, 5, or 8th carbon atom) in methanol under sunlight.

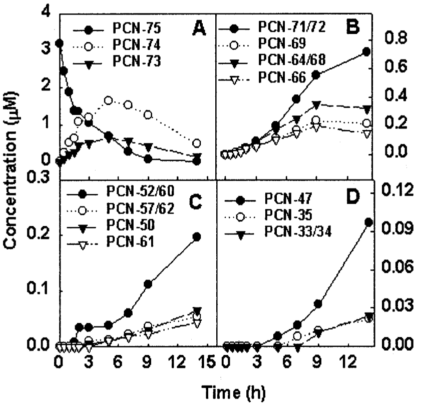


Figure 1. Photoproduct profiles of OCN in aerated hexane under 300 nm light. Octa- and hepta-CNs (**A**), hexa-CNs (**B**), penta-CNs (**C**), and tetra-CNs (**D**). All the data were average of two independent experiments.

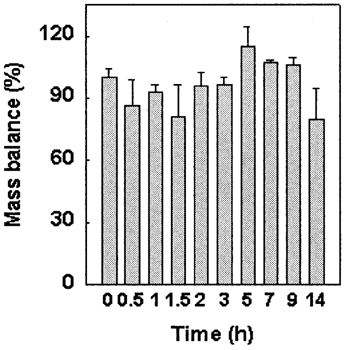


Figure 2. Mass balance of OCN photolysis in hexane under 300 nm light, which was calculated as a percent of sum of octa- (parent), hepta-, hexa-, penta-, and tetra-CNs to the initial concentration of OCN

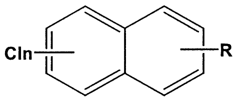
Table 2. Retention times and fragmentation patterns of tentatively identified photoproducts of OCN in aerated acetone-sensitized hexane

Class	Symbol[a]	No. of Cl[b]	Retention time (min)	Fragment ion (% Relative abundance)
Propanon-2-yl	K6	6	26.60	390 (M^+, 22), 375 (100), 355 (3)
	K5	5	24.24	356 (M^+, 25), 341 (100), 319 (4)
	K4	4	19.60	320 (M^+, 38), 305 (100), 293 (7)
2-Hydroxy-	A6	6	28.88	392 (M^+, 12), 377 (100), 355 (8)
Propyl	A5	5	25.45	358 (M^+, 19), 343 (100), 325 (8)
Hexyl	H7	7	30.01	452 (M^+, 45), 395 (100), 381 (45)
	H6	6	29.33	418 (M^+, 67), 384 (47), 347 (100)
	H6	6	27.27	418 (M^+, 45), 384 (52), 361 (100)
	H5	5	24.97	384 (M^+, 18), 343 (100), 323 (52)
	H5	5	24.69	384 (M^+, 44), 327 (100), 292 (44)
2-Propanoyl	M6	6	29.16	440 (M^+, 16), 403 (16), 383 (100)
+ hexyl	M5	5	25.63	406 (M^+, 63), 391 (80), 345 (40)

[a] Symbols stand for tentatively identified photoproducts, the Arabic numbers indicate the number of chlorines on the molecule.

[b] Number of chlorine atoms in tentative structures were estimated from the abundance of isotope peak of molecular ions.

Mass balances were calculated from the sum of tetra- to octa-chloronaphthalens and ranged from 81 to 114 % (Figure 2). In consideration of the strong dioxin-like toxicity of tetra- to hexa-CNs which were the main photoproducts in hexane,

Basic structure	Symbols	R	n
	A5 or A6	$CH_3CHOHCH_2$-	5 or 6
	H5, H6, or H7	$CH_3(CH_2)_4CH_2$-	5, 6, or 7
	K4, K5, or K6	CH_3COCH_2-	4, 5, or 6
	M5 or M6	$CH_3(CH_2)_4CH_2$- and CH_3COCH_2-	5, or 6

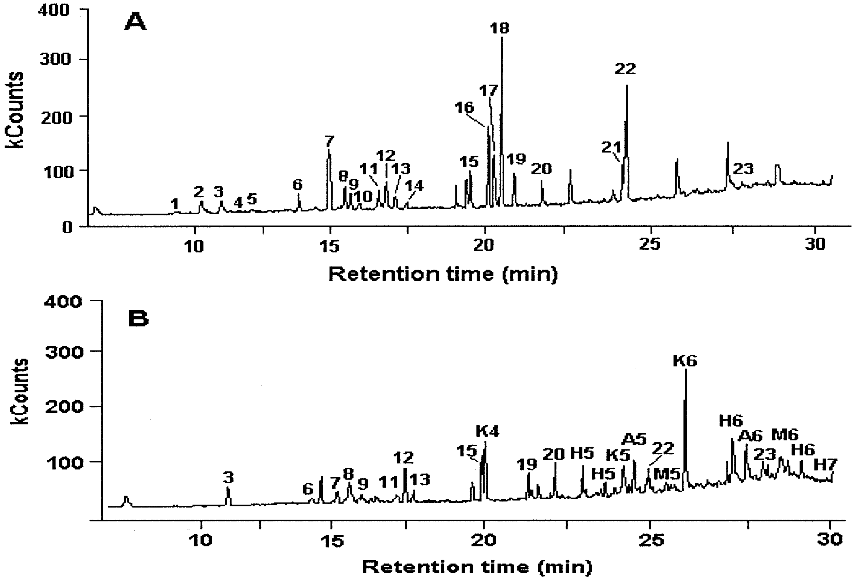


Figure 3. General structures of tentatively identified products (peaks A5 to M6 in **B**) and GC-MS total ion chromatograms of OCN photolysis in aerated hexane (**A**) and aerated acetone-sensitized hexane (**B**) at 300 nm. The Arabic numbers in the chromatograms A and B correspond to: 1, PCN-42; 2, PCN-33/34; 3, PCN-47; 4, PCN-28; 5, PCN-35; 6, PCN-46; 7, PCN-52/60; 8, PCN-61; 9, PCN-50; 10, PCN-54; 11, PCN-57/62; 12, PCN-55; 13, PCN-49; 14, PCN-56; 15, PCN-66/67; 16, PCN-64/68; 17, PCN-69; 18, PCN-71/72; 19, PCN-63; 20, PCN-65; 21, PCN-74; 22, PCN-73 and 23, PCN-75.

increase of such congeners may suggest that photolysis under simple hydrocarbon without sensitizers did not diminish (eventually increase) the dioxin-like toxicity of PCNs within the experimental period. However, a complete decomposition of PCNs was achieved within 5-6 h in chlorophyll a-sensitized hexane. No chlorinated products were found after 9 h. These results suggest that singlet oxygen mediated photolysis may efficiently attenuate the toxicity of PCNs.

In comparison with the other treatments, simple dechlorination was not the major photoreaction in acetone-sensitized photolysis. In the 1.5 h exposure samples, more than 10 peaks were identified tentatively as solvent- or sensitizer-addition products (Table 2, Figure 3). The possible substituents for chlorine atoms were hexyl-, 2-hydroxypropan-1-yl and propan-2-on-1-yl moieties. Such complex profiles of photoproducts may be derived from the fact that acetone can act as a reactive radical or transfer its energy to other chemicals, namely hexane (Koshioka et al. 1987). In spite of the complexity of the photoproduct profiles, a complete dechlorination was achieved within 5 h from an acetone-sensitized reaction in hexane. From a remediation point of view, addition of acetone or related aliphatic ketones can be an efficient means for photocatalytic removal of PCNs.

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