

## PHOTOLYSIS OF POLYCHLORINATED NAPHTHALENE CONGENERES IN ALKALINE 2-PROPANOL SOLUTION

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### Introduction

Polychlorinated naphthalenes (PCNs) are the compounds of those naphthalene rings are substituted by chlorine atoms and consisted of 75 congeners. Because PCNs are thermally and chemically stable like polychlorinated biphenyls (PCBs), their formulations were used as insulation oils, preservatives, or flame retardants.<sup>1,2</sup> The world-wide production of PCN formulations is estimated as 150000 tons.<sup>2</sup> Though production and use of PCNs were banned in many countries in 1970-1990 because of their toxicities and environmental persistence, PCNs has been found in the environmental samples yet.<sup>2</sup> Sources of the environmental PCNs are thought as formulations formerly used in open systems or by-products in thermal processes.<sup>3</sup> PCNs which once entered into the environmental matrices are difficult to be decomposed, but they may be decomposed by chemical or biological processes little by little. Photolysis is one of the most important chemical degradation processes of the environmental PCNs.<sup>4</sup> It can be applied to the treatment of PCN contaminated wastes because photolysis is also recognized as a safe and sound treatment technique of halogenated compounds such as PCBs. To describe the environmental fate and phototreatment process behavior of PCNs, more experimental data on photolysis of PCNs are required. Therefore, we carried out the study about photolysis of PCN congeners in alkaline 2-propanol solution.

### Materials and Methods

#### Reagents

PCN congeners used for photolysis experiments were CN 1 (1-MoCN), 2 (2-MoCN), 5 (1,4-DiCN), 13 (1,2,3-TrCN), 42 (1,3,5,7-TeCN), 54 (1,2,3,6,7-PeCN), 66 (1,2,3,4,6,7-HxCN), 68 (1,2,3,5,6,8-HxCN), 70 (1,2,3,6,7,8-HxCN), 71 (1,2,4,5,6,8-HxCN), 73 (1,2,3,4,5,6,7-HpCN), 74 (1,2,3,4,5,6,8-HpCN) and 75 (1,2,3,4,5,6,7,8-OcCN). All congeners were purchased from Cambridge Isotope Labs. (US) as nonane solutions. They were diluted to 10 µg/ml with hexane. Standard solution was prepared by diluting of PCN-MXB (Wellington Lab., Canada) with Toluene. Clean up spike solution was prepared by dissolving of <sup>13</sup>C-labeled PCN congeners (Cambridge Isotope Labs.) with toluene (20 ng/ml for each congener). Sodium hydroxide, 2-propanol, and hydrochloric acid were of reagent grade and from Wako Pure Chemicals (Japan). Hexane and anhydrous sodium sulfate were of dioxin analysis grade and from Kanto Chemicals (Japan). Purified water was obtained with a Milli-Q water purification system (Millipore, US).

#### Photolysis

Alkaline 2-propanol solution was prepared by dissolving of sodium hydroxide in 2-propanol at the concentration of 3 mg/ml with sonication, and then deoxygenated by purging with nitrogen. One milliliter of individual PCN congener solution was added to 100 ml of alkaline 2-propanol solution in a glass beaker and stirred with a magnetic stirrer. A low-pressure mercury lamp (254nm, 32W) was placed over a beaker. Distance of the surface

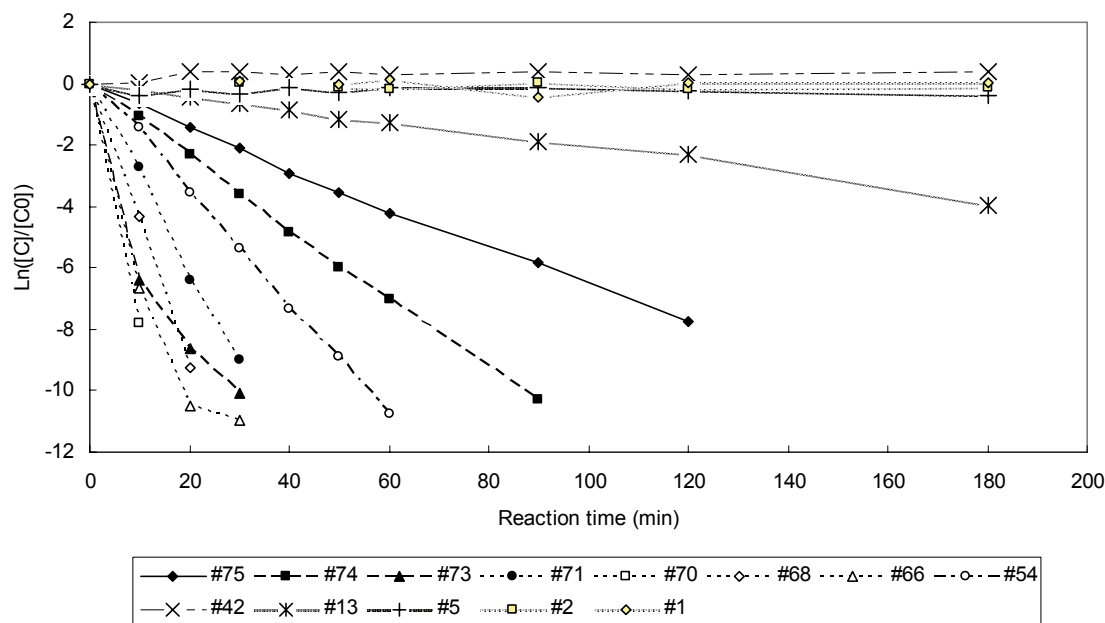


Fig. 1. Photolytic profiles of CN congeners.

of reaction solution and bottom of the UV lamp was adjusted to 2.5 cm. UV light intensity was in a range of 0.41-0.58 mW/cm<sup>2</sup> (102-144 J for 180 min reaction). A certain amount of reaction solution was initially sampled as 0 min, and then UV irradiation started. Reaction solution was sampled at 10, 20, 30, 40, 50, 60, 90, 120, and 180 min. Temperature of reaction solution was about 20 °C.

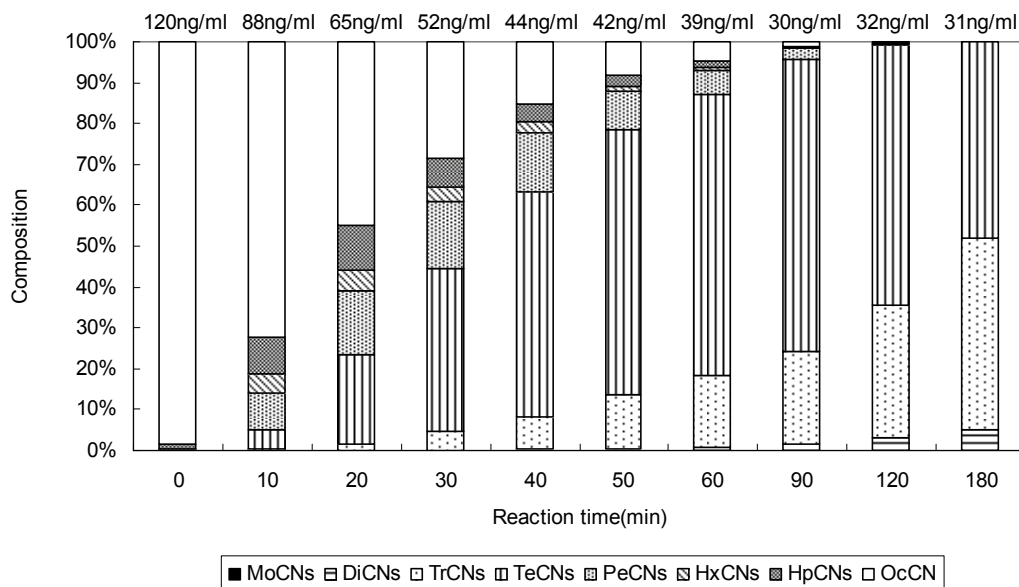
#### Analysis of PCN congeners

One milliliter of the reaction solution was transferred into a test tube. Clean up spike solution (50 µl) was added to the solution. The reaction solution was neutralized with 1 mol/l of hydrochloric acid, and then diluted with 8 ml of purified water. The neutralized solution was then extracted of hexane at twice. The extract was dried with sodium sulfate, and then concentrated to 100 µl under the flow of nitrogen. The concentrated extract was determined by HRGC/HRMS. Operating conditions of HRGC/HRMS and identification of PCN congeners were described in elsewhere.<sup>5</sup>

### Results and Discussion

#### Reaction rates

Reaction profiles of CN congeners are presented in Fig. 1. All of examined CN congeners were decomposed by UV irradiation in alkaline 2-propanol solution. Photolysis of these congeners followed in first order kinetics, and reaction rate constants were calculated. Reaction rate constant of CN 75 was  $-k=0.0645 \text{ min}^{-1}$  (3.87 h<sup>-1</sup>) and half-life of CN 75 was 10.7 min. Keum et al studied on photolysis of CN 75 by UV and sunlight in hexane with and without photosensitizer.<sup>6</sup> They reported that rate constant was  $-k=1.145 \text{ h}^{-1}$  (300nm, with acetone), and it was about one thirds of this result. As shown in Fig. 1, photolysis of penta- thorough heptaCN congeners was faster than that of CN 75, whereas photolysis of mono- thorough tetraCN congeners was much slower. Photolysis of CN 1, CN 2, CN 5 and CN 42 was extremely slow under the experimental conditions. Their rate



**Fig. 2. Composition change of photolytic product of CN 75.**

Total PCN levels are shown in the top of the bars.

constants were about one hundredth smaller than that of CN 75. From these experimental results, highly chlorinated homologues will effectively decompose, whereas lowly chlorinated homologues will hardly decompose by UV light. Therefore, in treating PCN wastes which contain lowly chlorinated homologues at high proportion, photolytic technique may be insufficient and other treatment techniques should be applied.

#### **Composition change of photolytic products of CN 75 and selectivity of position of dechlorination**

In photolysis of CN 75, the level of CN 75 declined to 53 % of the initial CN 75 concentration within 10 min and to below the detection limit (0.1 ng/ml) after 180 min reaction. Total PCN level also declined to 25.3 % of initial concentration after 180 min reaction. Composition of the sum of TeCNs and TrCNs to total PCNs was over 90 %. Because photolysis of lowly chlorinated homologues was extremely slow as noted above, photolysis of CN 75 might be terminated at the stage when TeCNs and TrCNs were formed. Change of homologue profiles of photolytic products of CN 75 is presented in Fig. 2. Concentration of HpCNs increased during in the first 10 min, and then rapidly decreased. CN 74 (1,2,3,4,5,6,8-) was more abundant than CN 73 (1,2,3,4,5,6,7-). Concentration of HxCNs also increased during 10 min, and then decreased. Major congeners were CN 66/67 (1,2,3,4,6,7-/1,2,3,5,6,7-) and CN 64/68 (1,2,3,4,5,7-/1,2,3,5,6,8-) followed by CN 69 (1,2,3,5,7,8-) and CN 71/72 (1,2,4,5,6,8-/1,2,4,5,7,8-). Concentration of PeCN rose during 20 min and then decreased. CN 52/60 (1,2,3,5,7-/1,2,4,6,7-) were the most abundant congeners followed by CN 54(1,2,3,6,7-), CN 58 (1,2,4,5,7-), CN 51 (1,2,3,5,6-), and CN 61 (1,2,4,6,8-) Concentration of TeCN increased to maximum concentration at 50-60 min, and then slowly decreased. Major congeners were CN 44 (1,3,6,7-), CN 47 (1,4,6,7-), CN 42 (1,3,5,7-), CN 37/33/34 (1,2,5,7-/1,2,4,6-/1,2,4,7-), and CN 39 (1,2,6,7-). Concentration of TrCN monotonously increased. Major congeners were CN 25/26 (1,6,7-/2,3,6-), CN 20/19 (1,3,6-/1,3,5-), CN 14 (1,2,4-), and CN 17 (1,2,7-). DiCNs were found in the samples after 30 min reaction and the level increased with reaction time. Major congeners were CN 6/12 (1,5-/2,7-), CN5/7 (1,4-/1,6-), and CN 11/8 (2,6-/1,8-). MoCNs were found in 120 and

180 min samples.

In photolysis of CN 75, CN 73 should be formed by dechlorination of *alpha*- (1-, 4-, 5-, 8-) position chlorine, whereas CN 74 should be formed by *beta*- (2-, 3-, 6-, 7-) position dechlorination. In photolysis of CN 73, CN 64/68, CN 69 and CN 66/67 were major dechlorination products. CN 64/68 and CN 69, which should be formed by *beta*-dechlorination, were more abundant than *alpha*-dechlorination products CN 66/67. In photolysis of CN 74, major dechlorination products were CN 71/72, CN 64/68 and CN 69. CN 71/72 and CN 64/68 should be formed by *beta*-dechlorination, but CN 69 was formed by *alpha*-dechlorination. In photolysis CN 66, major dechlorination products were CN 52/60 and CN 54. *Beta*-dechlorination product CN 60 (CN 52 should not be formed without rearrangement of chlorine) was more abundant than *alpha*-dechlorination product CN 54. In photolysis of CN 68, major products were CN 58, and CN 52/60. CN 58 was formed by *beta*-dechlorination, but CN 60 (CN 52 should not be formed) was formed by *alpha*-dechlorination. The amount of CN 58 was slightly higher than that of CN 60. In photolysis of CN 70, major dechlorination products were CN 54 and CN 53/55 (1,2,3,5,8-/1,2,3,6,8-). *Alpha*-dechlorination product CN 54 was more abundant than *beta*-dechlorination product CN 55 (CN 53 should not be formed). In photolysis of CN 71, major dechlorination products were CN 61 and CN 57 (1,2,4,5,6-). Both of them were *alpha*-dechlorination products. As for reaction rates of dechlorination of HpCN congeners, reaction rate of CN 73, which is *beta*-chlorine rich congener, was about three times higher than that of CN 74 (Fig. 1). This tendency was also observed in photolysis of HxCN congeners. Reaction rates of CN 66 and CN 70, which have all four *beta*-chlorine atoms, were larger than CN 68 and CN 71. From the experimental results in photolysis of hexa- through octaCNs, *beta*-dechlorination may be more favorable than *alpha*-dechlorination.

### References

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