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Photodegradation of 2,2',5,5'-Tetrachlorobiphenyl in Hexane

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Polychlorinated biphenyls(PCBs) are of continuing concern due to their ubiquitous occurrence in the environment and potential health impacts on the mankind. For the environmental degradation of PCBs, photolysis may be one of the major pathways regardless of their chemical stabilities. Previous studies noted that PCBs degrade mainly with stepwise dechlorination in both aqueous and organic media. When ortho and other positions are simultaneously substituted by chlorines, it is the ortho chlorines that are lost preferentially (Bunce 1982; Ruzo et al 1972; Lepine and Masse 1990;).

The photochemical behaviour varies obviously for different PCB congeners, which may have different pathways of photodecomposition. In our study, trace amount of 2, 2' , 5, 5' – tetrachlorobiphenyl was exposed in hexane under xenon lamp to study its pathway of photodegradation.

MATERIALS AND METHODS

2 , 2 ' , 5 , 5 ' — tetrachlorobiphenyl was synthesized and purified (99%) in our laboratory according to the previous report (Mullin et al 1984). Biphenyl(99.5%) was purchased from the Petroleum Works of Beijing. Hexane and other solvents of analytical grade were redistilled in an all glass system.

A solution of 1.71 X 10^{-3}mmol/L 2,2' 5,5' — tetrachlorobiphenyl in n—hexane was photolyzed in model NDC — 3 photoreactor (made in Radio Works of Changning, Nanjing, China) with a 300 — W xenon lamp for 36 hours. The photolyzed solutions for different times were analyzed by Varian 3740 GC apparatus, equipped with a Ni^{63} electron capture detector. The column was SE—54 (18m X 0.25 mmi. d.) (J. &. W. Scientific Inc.) with N_2 as carrier gas. Initially temperature was set at 50°C for 2 min then programmed to 280% at 4°C /min. The injector and detector temperatures were 300°C and 350 °C respectively.

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The photoproducts were identified by the retention time of PCB congeners in gas chromatography and confirmed by GC—MS (VG TRIO 2000) equipped with a SE —54 column (15m X 0.25mm i. d. , film thickness 0.25μm) (J. & W. Scientific Inc.).

With the relative response factors of PCB congeners in accord with the previous study (Mullin et al 1984) , the quantity of these photolyzed products could be calculated.

A solution of 6. 48 X 10^{-2} mmol/L biphenyl in n—hexane was photolyzed at the same conditions of 2,2' ,5,5' —tetrachlorobiphenyl for 14 hours. The photolyzed solutions for different times were analyzed by HP 5890 GC apparatus, equipped with a FID and a SE—52 column (25m X 0. 25mm i. d.) (Research Institute of Petroleum Processing of China) . Initially temperature was set at 50°C for 2 min then to 280°C at 10 °C/mm. The injector and detector temperatures were 250°C and 300 °C respectively.

RESULTS AND DISCUSSION

Figure 1 is the gas chromatogram of photodegraded solution after 16 hours. The products include not only less chlorinated biphenyls but also small amounts of chlorobenzenes, while biphenyl is not found. Figure 2 shows the concentration changes of photodegraded products at different times. It can be seen that the concentration change trend of 2, 2' , 5— trichlorobiphenyl is very similar to that of 2, 3' , 5—trichlorobiphenyl , or we can also say that the ortho chlorines are not lost preferentially under our experimental conditions.

Our results suggest that the observed production of less chlorinated biphenyls and chlorobenzenes in this system does not completely proceed by previously studied mechanism of PCBs photolysis (Ruzo et al 1974 ; Chang LW and Giam CS 1992) , which reported that PCBs lost ortho chlorines preferentially and no chlorobenzenes were found. It is more similar to the results of laser—induced dissociation of PCBs in the liquid phase, which produced chlorobenzenes (Fantoni et al 1988).

Because biphenyl is not found, and no obvious photodegradation of biphenyl is observed after 14 hours irradiation in the same experimental system of 2,2' ,5,5' — tetrachlorobiphenyl. So the suggestion that 2,2' 5,5' — tetrachlorobiphenyl only undergo stepwise dechlorination to completely form biphenyl can not be proved. Our results show that 2,2' ,5,5' — tetrachlorobiphenyl may be photodegraded both by dechlorination and cleavage of inter—ring bond to form less chlorinated biphenyls and chlorobenzenes , when the photolysis is conducted in hexane with the xenon lamp.

Toxicity of PCB congeners is affected evidently by their ortho chlorines, whether the ortho chlorines lose may affect the toxicity of photoprcducts. Besides, the results of

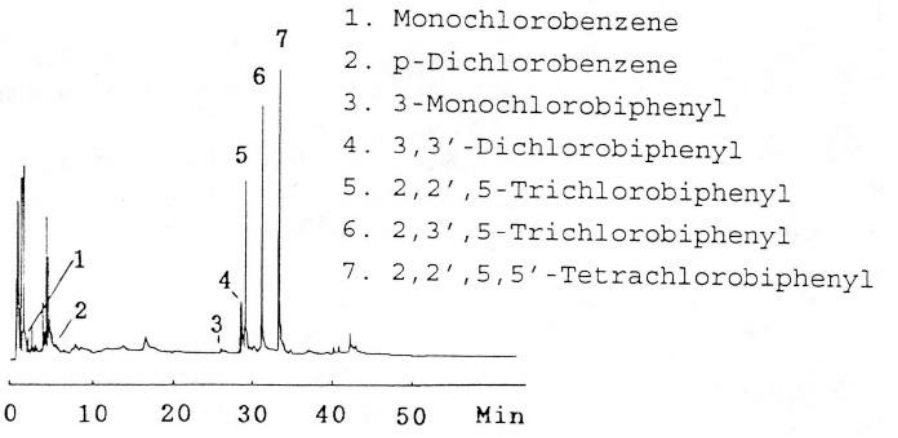
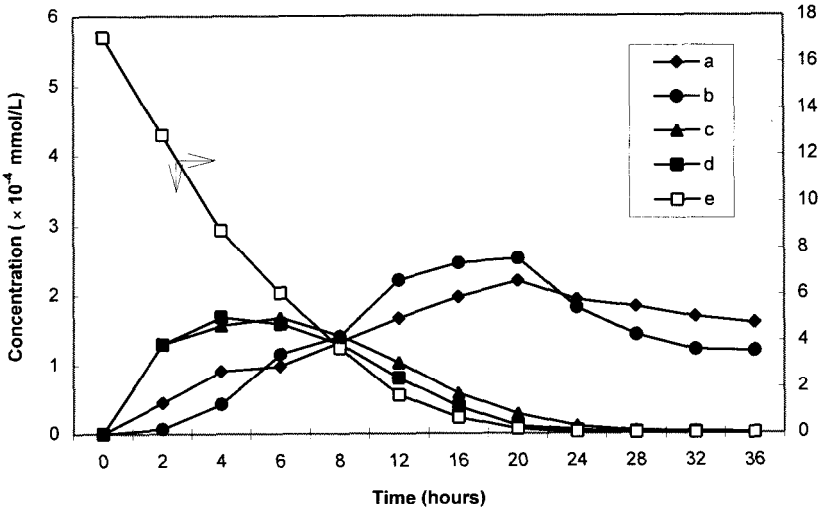


Figure 1. Gas chromatogram of photodegradation products of 2,2' ,5,5' — tetrachlorobiphenyl in hexane after 16 hrs irradiation



a 3—Monochlorobiphenyl b 3 , 3 '—Dichlorobiphenyl
d 2,3' ,5—Trichlorobiphenyl c 2,2 ' ,5—Trichlorobiphenyl
e 2 , 2 ' , 5 , 5 '—Tetrachlorobiphenyl

Figure 2. The concentration of 2, 2 ' , 5, 5 ' — tetrachlorobiphenyl and some photoproducts in hexane after different times of irradiation

our experiment showed inter—ring bonds of 2,2' ,5,5' — tetrachlorobiphenyl could also be cleaved to produce chlorobenzenes , which are different from PCBs both in the toxicity and photodegradation. So the pathway of photolysis may vary obviously for different PCB congeners and irradiation conditions. The differences between previous reports and our results show that photodegradation of different PCB congeners should be studied in depth to understand the thorough mechanism of photodegradation and effects of this class of contaminants on the environment.

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