Chemosphere 193 (2018) 861–868

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Photodegradation behaviors of polychlorinated biphenyls in methanol by UV-irradiation: Solvent adducts and sigmatropic arrangement

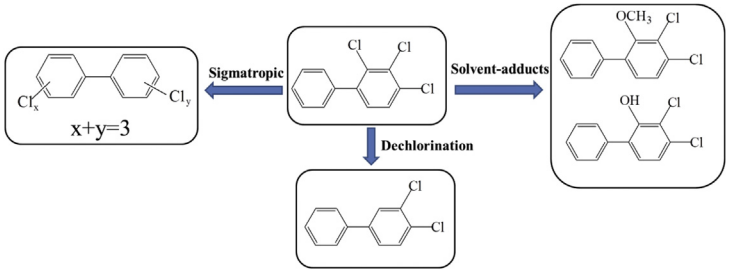
Ting Tang [a], Zhiqiang Zheng [a], Rui Wang [a], Kaibo Huang [a], Huafeng Li [a], Xueqin Tao [b], Zhi Dang [a, c], Hua Yin [a, c], Guining Lu [a, d, *]

[a] School of Environment and Energy, South China University of Technology, Guangzhou 510006, China
[b] School of Environmental Science and Engineering, Zhongkai University of Agriculture and Engineering, Guangzhou 510225, China
[c] The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, China
[d] Guangdong Provincial Engineering and Technology Research Center for Environmental Risk Prevention and Emergency Disposal, Guangzhou 510006, China

## HIGHLIGHTS

- PCBs with *ortho*-chlorine can generate both methoxylated and hydroxylated PCBs (MeO- PCBs and HO-PCBs).
- *Ortho*-chlorine plays a vital role in the sigmatropic rearrangement reaction of PCBs.
- PCBs with *ortho*-chlorine can generate solvent adducts in various solvents.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 9 March 2017
Received in revised form
26 October 2017
Accepted 18 November 2017
Available online 20 November 2017

Handling Editor: Andreas Sjodin

*Keywords:*
Polychlorinated biphenyls
Photodegradation
Solvent adduct
Sigmatropic rearrangement
Dechlorination

## ABSTRACT

This study has investigated the photolysis of polychlorinated biphenyls (PCBs) in methanol solution under UV irradiation. The results showed that the PCBs containing *ortho*-chlorine can generate both hydroxylated and methoxylated PCBs (HO-PCBs and MeO-PCBs), while the PCBs with a *meta*-chlorine but without *ortho*-chlorine can only generate MeO-PCBs as the only solvent adducts. No solvent adducts were detected during the photochemical reaction of 4-chlorobiphenyl (PCB-3), indicating the *para*-chlorine cannot be attacked by solvent molecule to form correspondent solvent adducts. The sigmatropic rearrangement was found during the photochemical reaction of *ortho*-substituted PCBs, but cannot occur in the reaction of PCBs with only *meta*- or *para*-chlorine, indicating that *ortho*—chlorine played a vital role in the sigmatropic rearrangement reaction. In addition, the seteric hindrance can also lead to the generation of sigmatropic rearrangement products. The effect of solvent was investigated in the case of photochemical reaction of 2-chlorobiphenyl (PCB-1), the results showed that sigmatropic rearrangement can occur in different solvents, and corresponding solvent adducts were generated in the photochemical reaction of PCB-1 in different solvents.



## 1. Introduction

Polychlorinated biphenyls (PCBs) are historically used as flame retardants in electrical capacitors and as hydraulic and heat

* Corresponding author. School of Environment and Energy, South China University of Technology, Guangzhou 510006, China.
*E-mail address:* GNLu@foxmail.com (G. Lu).

https://doi.org/10.1016/j.chemosphere.2017.11.095
0045-6535/

exchange fluids in electrical equipment, they are highly toxic and stable chemicals (Miao et al., 1999). The environmental contamination of PCBs has been recognized since Soren Jensen first detected PCBs in pike from Sweden (Breivik et al., 2002). Although the production of these chemicals has been banned, PCBs were continually detected in the water, fish, air and humans (Di Guardo et al., 2017; Hellman et al., 2008; Liu et al., 2017; Muller et al., 2017; Naert et al., 2006; Petro et al., 2010; Storelli and Perrone, 2010).

Various methods have been adopted to eliminate the PCBs in the environment, including nano zero valent iron (Long et al., 2014; Wu et al., 2012; Zhang et al., 2012; Zhuang et al., 2011), photodegradation (Chen et al., 2012, 2013; Izadifard et al., 2010; Lin et al., 2004; Wong and Wong, 2006; Yao et al., 2000),incineration (Akai et al., 2001; Di Guardo et al., 2017), and microbial degradation (Fava et al., 2003; Stella et al., 2017; Zanaroli et al., 2012). Thereinto, photolysis has been identified as the most important process for the degradation of PCBs. Many researchers have investigated the photolysis of PCBs in various solvents and media. Miao et al. have investigated the dechlorination of 8 PCBs in hexane under UV irradiation and found the reactivity of chlorine atoms at different positions of PCBs rings were in the order of ortho > meta > para, but no PCB-solvent adducts or sigmatropic rearrangement products were detected (Miao et al., 1999). On the contrary, an earlier study has reported that the cyclohexyl-PCBs was formed in irradiated Aroclor 1254 in aliphatic solvent (Lepine et al., 1992). Wong et al. have investigated the photodegradation of several PCB congeners in solvent methanol, ethanol, and 2-propanol and found that the major products were lower PCB congeners and the minor products include some HO-PCBs, ethylated, dimethylated and methylated biphenyls (Wong and Wong, 2006). Yao et al. have investigated the photochemistry of non-ortho substituted PCBs by UV irradiation in alkaline 2-propanol, and found that in the case of 3,4-dichlorinated biphenyl (PCB-12), the products of photorearrangement was observed. However, the mechanisms of the generation of solvent adducts and sigmatropic rearrangement products were not well elucidated in these studies. For example, the effect of chlorinated position on the generation of solvent adducts and sigmatropic rearrangement products, and the effect of different solvent on these reactions were not well investigated.

The purpose of this study was to elucidate the key factor to the generation of solvent adducts and sigmatropic rearrangement products through the case study of photochemical reaction of 2, 3, 4-Trichlorobiphenyl (PCB-21). This PCB congener was selected as target pollutant because it contains three chlorine substituents which located separately on *ortho*-, *meta*-, and *para*-positions on the same ring. The photochemical reaction of this congener has never been reported before. Moreover, its dechlorination products (i.e. 2-Chlorobiphenyl (PCB-1), 3-chlorobiphenyl (PCB-2), 4-chlorobiphenyl (PCB-3), 2,3-Dichlorobiphenyl (PCB-5), 2,4-Dichlorobiphenyl (PCB-7), 3,4-Dichlorobiphenyl (PCB-12), 2,3,4-Trichlorobiphenyl (PCB-21)) were also investigated as starting materials to investigate the effect of chlorinated position on these reactions.

## 2. Material and methods

### 2.1. Materials

PCBs standards (i.e. PCB-1, PCB-2, PCB-3, PCB-5, PCB-7, PCB-12, PCB-21) was purchased from AccuStandard, Inc, USA. HPLC grade methanol was obtained from Anpel company (Shanghai, China).

### 2.2. UV irradiation experiments

The photo-degradation experiments were conducted in a 22 mL quartz glass vessel, containing 20 mL methanol solution of different PCBs, the concentration of PCBs was set at 5 mg $L^{-1}$. The vessels were placed around a 100 W mercury lamp in a photo-reactor. The lamp was set in a cold well to keep the temperature around 25 °C. The sketch of the photo-reactor instrument and the spectrum chart of the Hg lamp are available in Fig.S1 and Fig.S2, respectively.

For the effect of different organic solvent on the generation of solvent adducts and sigmatropic rearrangement, 1 mL of the stock solution of PCB-1 (100 mg $L^{-1}$ in acetone) was added into the vessels, then the gentle nitrogen gas was used to evaporate the acetone solution, then 20 mL ethanol, acetonitrile, hexane, tetrahydrofuran were separately added into these vessels. These vessels were placed in the photo-reactor to conduct the photochemical experiment.

### 2.3. Instruments

The photoproducts analyses were performed on a gas chromatography-mass spectrometry (GC-MS) which coupled a Thermo-Trace GC Ultra instrument to a Thermo-DSQII mass spectrometer (Thermo-Electron Corporation, Waltham, USA). The electron impact ionization mode was set at electron energy of 70 eV. A 30 m DB-5MS capillary column (0.25 mm i.d., 0.25 μm film thickness) was used for separation. Helium gas (1.0 mL $min^{-1}$) was used as the carrier gas. 1 μL sample was injected into GC in splitless mode. The temperature of injection inlet was set at 280 °C. The temperature of oven was held at 100 °C for 1 min, increased by 20 °C $min^{-1}$ to 210 °C, then by 4 °C $min^{-1}$ to 260 °C for 10 min. The quantification of identified degradation products was acquired in selected ion monitoring (SIM) mode. The qualitative analysis of the solvent adducts and sigmatropic rearrangement products were acquired in full scan (50–650 *m/z*). The quadrupole temperature and ion source temperature were set at 250 °C and 280 °C, respectively. The data processing was performed by Xcalibur software (Thermo Fisher, US).

## 3. Results and discussion

### 3.1. Dechlorination pathway of PCB-21

The UV irradiation can rapidly dechlorinate PCBs, resulting to lower chlorinated PCBs and biphenyl. All the dechlorination products of PCB-21 were used as starting material to investigate the kinetics and dechlorination pathways. Fig. 1 shows the changes in the dechlorinated intermediates during the irradiation. We found that PCB-21, PCB-5, PCB-7, PCB-12, PCB-1 can be totally degraded in 60 min, while PCB-2 need 360 min to reach completely degradation, and PCB-3 only degrade to about 50% even after 12 h UV irradiation, indicating that PCB-3 was much more stable than the other two isomers. The dechlorination products were accumulated during the photochemical reaction of PCBs. When there is chlorine substituents on *ortho*-position (i.e. PCB-21, PCB-5, PCB-7), the *ortho*-chlorine tend to be preferentially removed. When no chlorine atom was substituted on *ortho*-position (i.e. PCB-12), the *meta*-chlorine tend to be preferentially removed. This results showed that the reaction activity of the substituent chlorine atom was in the order of *ortho*- > *meta*- > *para*-chlorine on the diphenyl rings, which was in agreement with the previous results (Chang et al., 2003; Miao et al., 1999), but not correlated well with the results of PCBs degradation under gamma irradiation, which was in the order of *ortho*- > *para*- > *meta*- (Lépine and Massé, 1990). The overall dechlorination pathways of PCB-21 were summarized in Fig. 2.

Mass balance was also considered during the photoreaction process. However, a severe mass loss was found during the