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Photodegradation of Dechlorane Plus in *n*-nonane under the irradiation of xenon lamp

Siwen Wang, Jun Huang, Yang Yang, Gang Yu*, Shubo Deng, Bin Wang

State Key Joint Laboratory of Environment Simulation and Pollution Control (SKJLESPC), School of Environment, POPs Research Center, Tsinghua University, Beijing 100084, PR China

HIGHLIGHTS

- Photodegradation of isomers of Dechlorane Plus (DP) as a potential persistent organic pollutant were studied.
- UV-C was found to be the main contributor to DP photodegradation.
- DP degradation followed the pseudo first-order kinetics.
- Sequential dechlorination was found as the degradation mechanism.

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ABSTRACT

Photodegradation has been regarded as the main mechanism for the removal of many halogenated organic pollutants in the environment. The photodegradation of Dechlorane Plus (DP), an emerging contaminant taken worldwide concerns in recent years, was investigated under the irradiation of a xenon lamp. Rapid photodegradation was found under the irradiation of 200–750 nm light, while the degradation became much slower when the range of light wavelength changed to 280–750 nm. DP degradation followed the pseudo first-order kinetics. The quantum yields of 200–280 nm (UV-C) were about 2–3 orders of magnitude higher than 280–320 nm, and no yields can be detected in 320–750 nm range, in an agreement with the changing photodegradation rates with wavelength. The photodegradation products were identified as lower chlorinated DPs, implicating a mechanism of reductive dechlorination. No photoisomerization or solvent adducts were observed, and the difference of photodegradation rate between *syn*- and *anti*-DP isomers was negligible.

1. Introduction

Dechlorane Plus (DP, or Dechlorane 605) is a highly chlorinated flame retardant additive, which is incorporated into industrial polymers used for coating electrical wires and cables, connectors used in computers, and plastic roofing materials [1]. As a substitute for an earlier chlorinated flame retardant (Mirex or Dechlorane), which was banned due to its toxicity to marine invertebrates [2], DP was produced thereafter with an annual world production of about 5000 tons [3] by Hooker Chemical in the 1960s. As two commercial PBDE products (penta-BDEs and octa-BDEs) have been banned by the Stockholm Convention since 2009, there is the possibility of an increase in DP production. There are mainly three types of commercial DP, namely DP-25, DP-35 and DP-515 with differences only in their particle sizes, but all have the same chemical composition and two stereoisomers (*syn*- and *anti*-DP) [4].

DP has attracted the international attention since 2006 due to its frequent detection ubiquitously in air, sediment, aquatic and also terrestrial organism from the Great Lakes [2,4–13]. High level of DP (490 pg m^{-3}) was detected in air at the Sturgeon Point site [4], and 580 ng g^{-1} (dry weight) in Lake Ontario sediment [2]. In China, DP was found in air [14–17], sediment [1,16,18,19], fish [20,21], and even in human serum [14] and hair [22]. Due to the long-range atmospheric transport, DP was even detected in the remote polar regions [23]. In addition, high level of DP was measured up to 126 ng g^{-1} in fish in Korea [24]. These results reveal that DP can be classified as a persistent organic pollutant because of its high lipophilicity, resistance to degradation, long-range transportation, bioaccumulation in aquatic species, and ecotoxicological effects on aquatic organisms [2].

A good understanding about DP's transformation and fate in the environment is the premise to assess its associated environmental risks. Despite of more and more reports on the environmental

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* Corresponding author. Tel.: +86 10 6278 7137; fax: +86 10 6279 4006.
E-mail address: yg-den@tsinghua.edu.cn (G. Yu).

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monitoring, there is rare data about the degradation of DP, especially for the photodegradation which is regarded as the main removal mechanism for many halogenated organic pollutants in the environment. Sverko et al. [2] initiated a simple UV exposure study which irradiated a 100 ng mL^{-1} isooctane solution of each DP isomer to UV light ($\lambda \geq 365$ nm) for a 30-day period, and found a decrease in parent DP concentration of 10% at 168 h and a further corresponding loss at 264 and 504 h of 40 and 65%, respectively. And *anti*-DP appeared to degrade more readily than the *syn*-DP stereoisomer. So far, this is the only available study on this topic. However, the details about DP's photodegradation are still unknown, e.g. the effects of light wavelength on the photodegradation, the degradation kinetics, the intermediates/products, as well as the reaction mechanisms.

In the present study, the photodegradation of *syn*- and *anti*-DP in *n*-nonane under the irradiation of xenon lamp was conduced. Effects of light wavelength, photodegradation kinetics, intermediates/products were investigated. In addition, the photodegradation pathway and potential reaction mechanism were discussed.

2. Method and materials

2.1. Chemicals

Commercial Dechlorane Plus 25 ($C_{18}H_{12}Cl_{12}$, purity 99%) was purchased from Jiangsu Anpon Electrochemical Co., Ltd. (Jiangsu, China). Both *syn*-DP and *anti*-DP standards with a concentration of 100 mg L^{-1} in *n*-nonane were purchased from Cambridge Isotope Laboratories Inc. (MA, USA) for quantification and photodegradation experiments. The stock solution (100 mg L^{-1}) was prepared by dissolving DP 25 in a calculated amount of solvent *n*-nonane (>99% in purity, Alfa Aesar AJohnson Matthey Company, MA, USA), while 1 mg L^{-1} *syn*- and *anti*-DP was prepared by dilution in *n*-nonane for exposure experiments. Cl10 Dechlorane Plus (aCl10DP) and Cl11 Dechlorane Plus (aCl11DP) in toluene, all with the concentration of 50 mg L^{-1}, were purchased from Wellington Laboratories Inc. (Ontario, Canada) for identifying possible intermediates.

2.2. Photodegradation experiments

The photochemical experiments were performed in a PLS-SXE300UV projector photochemical reactor (Beijing Trusttech Technology Co., Ltd., Beijing, China) using a 300-W xenon lamp. With infrared irradiation, the lamp had to be continuously cooled by air to avoid significant temperature increase. Three different filter sets, UV-CUT 280, UV-CUT 320 and UV-CUT 400 (Beijing Trusttech Technology Co., Ltd., Beijing, China) were equipped over the lamp to carry out various light sources. The reference numbers of the filter indicates the radiation below 280 nm, 320 nm and 400 nm with 50% of transmission. A UV-B radiometer (Photoelectric Instrument Factory of Beijing Normal University, Beijing, China) was used to measure the light fluxes. The continuous emission spectrum of the xenon lamp was measured with a QE65000 spectrometer (Ocean Optics Inc., FL, USA), and absorption spectra of both the filters and DP solutions in *n*-nonane were measured by a DR5000 UV–vis spectrophotometer (Hach Company, CO, USA). The absorption spectra of 100 mg L^{-1} commercial DP, 1 mg L^{-1} *syn*-DP and 1 mg L^{-1} *anti*-DP in *n*-nonane were shown in Fig. 1.

The cylindrical radiation vessel (quartz glass, 120 mm length × 16 mm inner diameter × 18 mm outer diameter) was filled with 10 mL reactive solution. A sample aliquot of 100 μL was intermittently taken from the vessel and injected into a 2-mL glass vial with insert tube for analysis. Foil-covered dark control experiments for commercial DP, *syn*- and *anti*-DP isomers in *n*-nonane were also performed for comparison with photodegradation under above-mentioned light sources. All experiments under the same condition were repeated three times, and the data reported were the average of the triplicates.

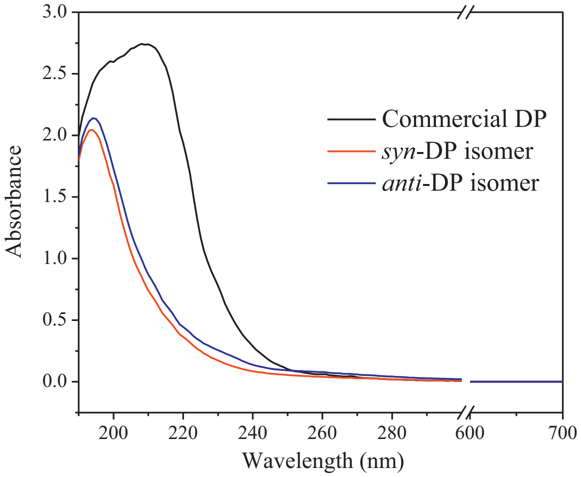

Fig. 1. Absorbance spectra of commercial DP (100 mg L^{-1}), *syn*-DP isomer (1 mg L^{-1}) and *anti*-DP isomer (1 mg L^{-1}) in *n*-nonane.

2.3. Instrumental analysis

DP and its intermediates were analyzed by an Agilent 6890 gas chromatograph equipped with an electron capture detector (μECD) and a DB-5 MS column (30 m × 0.25 mm × 0.25 μm, J&W Scientific, CA, USA). The quantification of *syn*- and *anti*-DP was carried out by comparing retention time and peak areas with those of analytical standards. GC injections (2 μL) were made in the high-pressure splitless mode with a pressure of 360 kPa for 2 min. The injector temperature was set at 265 °C to avoid the decomposition of DP. The oven temperature was programmed from 140 °C (held for 1 min) to 250 °C at a rate of 30 °C min^{-1}, to a final temperature of 285 °C (held for 5 min) at a rate of 0.8 °C min^{-1}. A GC–MS (Shimadzu QP2010 plus) was also employed for the confirmation of DP and its intermediates, where both the column dimension and the oven temperature program were identical to those of GC-μECD. The mass spectrometer was operated in negative ion chemical ionization using methane as the reagent gas. Ion source and transfer line temperatures were set to 200 and 280 °C, respectively. The full scan ($m/z = 50.0$–700.0) and selective ion monitoring mode (SIM) with m/z 653.8 and 651.8 for DP were used for confirmation, compared to those obtained from the standards. As for measurements ranging from DP~[−1Cl+1H] to DP~[−4Cl+4H] (consistent with molecular formula $Cl_{18}H_{13}Cl_{11}$, $C_{18}H_{14}Cl_{10}$, $C_{18}H_{15}Cl_9$ and $C_{18}H_{16}Cl_8$, respectively), the following ions were also selected as monitored ions: m/z 617.7 and 619.7 for *syn*-/*anti*-DP~[−1Cl+1H], m/z 583.8 and 585.8 for *syn*-/*anti*-DP~[−2Cl+2H], m/z 549.9 and 551.9 for *syn*-/*anti*-DP~[−3Cl+3H] and m/z 516.0 and 518.0 for *syn*-/*anti*-DP~[−4Cl+4H].

2.4. Calculation of quantum yields

Fundamentally, the quantum yield ϕ was defined as follows [25]:

$$\phi = \frac{\text{number of reacted molecules per time unit}}{\text{number of photons absorbed per time unit}} \quad (1)$$

where ϕ represents the reaction efficiency of a compound for a specific wavelength, and the disappearance quantum yield Φ is the sum of the single wavelength-specific ϕ values, over a range of wavelengths [26]. When the continuous light source of a xenon