



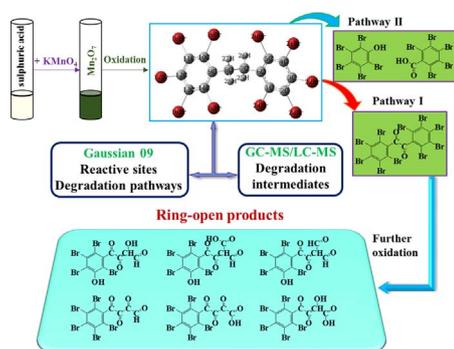
Mechanism insights into the oxidative degradation of decabromodiphenyl ethane by potassium permanganate in acidic conditions



Jing Chen, Xinxin Xu, Xiaoxue Pan, Jiayi Yao, Chenguang Li, Ruijuan Qu*, Zunyao Wang

State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, Jiangsu, Nanjing 210023, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

The KMnO_4 degradation of decabromodiphenyl ethane (DBDPE), an additive in brominated flame retardants (BFRs), was investigated in a sulfuric acid system. The degradation tests showed that DBDPE reacted completely with KMnO_4 in sulfuric acid, and a removal rate of 99.71% seems realistic. Many products were detected by liquid chromatography-quadrupole-time-of-flight-mass spectrometry (LC-Q-TOF-MS) analysis and gas chromatography-electron ionization-mass spectrometry (GC-EI-MS) analysis. The degradation initially forms 1,2-bis(perbromophenyl)ethane-1,2-dione (P_1), pentabromophenol (P_2), 2-(perbromophenyl)ethanol (P_3) and pentabromobenzoic acid (P_{28}), and the subsequent transformation of these primary intermediates generates ring-opening, five-membered ring and six-membered heterocycle products over time. Two main reaction pathways involving the direct oxidation of the C–C bond of the ethyl group and the cleavage of the C–C bond between ethyl carbon and the adjacent carbon were proposed, and were further confirmed by point charges analyses and Wiberg bond order calculations. Furthermore, the toxicity of DBDPE and its degradation products were evaluated using the ECOSAR program. DBDPE was found to be a toxic substance that could cause great damage to three kinds of organisms in different trophic levels, while all the transformation products were less toxic than parent compound.

1. Introduction

Decabromodiphenyl ethane (DBDPE), first introduced in the mid-1980s, is an additive in brominated flame retardants (BFRs) [1]. It has

become commercially important as an alternative to decabromodiphenyl ether (deca-BDE) for wide use in plastic, textile, electronic equipment, wire, polystyrene and polyolefin-based thermoplastic formulations [2–4]. Since the processing of deca-BDE-containing

* Corresponding author.

E-mail address: quruijuan0404@nju.edu.cn (R. Qu).

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polymers produces highly toxic polybrominated dibenzo-*p*-dioxins and furans, the use of deca-BDE-based BFRs was restricted in 2008 by the European Court of Justice [5,6]. To meet stricter international regulations on BFRs formulations, DBDPE is being developed in accordance with fire product standards as a replacement [7–10]. For example, the production volume of DBDPE increased rapidly in Japan and has exceeded that of deca-BDE since the late 1990s [11–13]. China, one of the world's largest manufacturers of electrical equipment, consumed approximately up to 1.2×10^4 tons of DBDPE in 2006, which has increased at a growth rate of 80% per year [1,14]. Given the widespread use of DBDPE, this emerging BFR has been widely detected in environmental samples of Sweden, Germany, North America, China and Japan [15–17], including in tree bark [18], air [15,19], house dust [20,21], sediments [22], sewage sludge [23], as well as in birds [24,25] and captive pandas [26].

To date, some researchers have investigated the chemical transformation and biodegradation of DBDPE [7,27,28]. Wang et al. evaluated the photolytic degradation of DBDPE under UV irradiation; they found that the degradation rates of DBDPE vary in different matrices, and nona-, octa-, and hepta-BDPE congeners were identified as reaction products [7]. Grause et al. reported the efficient removal of DBDPE from high-impact polystyrene (HIPS) using NaOH/ethylene glycol solution (NaOH_(EG)), and they detected various hydroxylated brominated compounds containing phenanthrene and other condensed aromatic structures [27]. Oxidation is a widely used method to remove organic contaminants, and numerous studies have shown that common oxidants such as Mn(VII), hydrogen peroxide and ozone can be employed to treat emerging micropollutants [29,30]. However, little information is available on the transformation of DBDPE in such an oxidation system, due to its very low water solubility.

Potassium permanganate (KMnO₄) has an especially strong ability to degrade various organic pollutants [31–33]. However, efficient removal of DBDPE cannot be achieved by KMnO₄ alone. In 1958, Hummers and Offeman prepared graphitic oxide by treating graphite in concentrated sulfuric acid/sodium nitrate/KMnO₄ system [34]. Since then, potassium permanganate in acidic medium has been employed for purification of carbon nanotubes and preparation of graphene nanoribbons [35,36]. Especially, Shi et al. have demonstrated that KMnO₄ can efficiently degrade deca-BDE, a similar BFR to DBDPE, in acidic conditions [37]. Hence, we propose that DBDPE can also be oxidized by KMnO₄ in acid medium.

In this work, degradation mechanism of DBDPE by KMnO₄ in sulfuric acid was systematically investigated. The transformation products were identified by liquid chromatography-quadrupole-time-of-flight-mass spectrometry (LC-Q-TOF-MS) analysis and the gas chromatography-electron ionization-mass spectrometry (GC-EI-MS) analysis, and two degradation pathways are tentatively proposed. Moreover, by using the Gaussian 09 program, we calculated total charges and frontier orbital densities to further confirm these reaction pathways. The toxicity of DBDPE and its transformation products was evaluated using the ECOSAR program. This study is the first report on the degradation of DBDPE by KMnO₄ in acid and the achieved results could provide new insights into the reaction mechanism of DBDPE.

2. Materials and methods

2.1. Chemicals

Decabromodiphenyl ethane (DBDPE, C₁₄H₄Br₁₀, 98%) was purchased from Adamas Reagent Co., Ltd. (Shanghai, China) and was used as received. KMnO₄ was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Chromatographic grade dichloromethane, toluene and methanol were supplied by Merck KGaA (Darmstadt, Germany). Other chemicals were of at least analytical grade and used as received. A DBDPE stock solution (20 mg/L) was prepared in dichloromethane and stored at 4 °C. NaHSO₃ solution was prepared with

ultrapure water at a concentration of 30 g/L and then stored in the dark.

2.2. Oxidation procedures

Oxidation reactions were conducted in KMnO₄/sulfuric acid at room temperature, and the oxidant was in excess. In a standard experiment, 1 mL of stock solution (20 mg/L) was added to each centrifuge tube. Then, the tubes were heated at 30 °C until the solvent evaporated completely. After cooling, 1 mL of sulfuric acid and 6 mg of KMnO₄ were added to the tubes in turn. The mixture was agitated with a vortex stirrer to ensure a uniform reaction. After 0.5, 1, 2, 4, 8, and 10 min, the samples were immediately quenched with 500 μL of NaHSO₃ solution to terminate the reaction. These samples were transferred to the separatory funnel and then extracted by 5 mL of toluene for 0.5 h. The average recovery was $89.4 \pm 5.0\%$.

The product identification tests were initiated by adding 5 mg of KMnO₄ into each centrifuge tube containing 5 mg of DBDPE and 1 mL of 98% concentrated sulfuric acid. After 0.5, 1, 2, 5, 30, 60, and 240 min, the samples were quenched with 3 mL of NaHSO₃ solution while constantly stirring with a vortex stirrer.

2.3. Analysis method

2.3.1. GC analysis

The concentrations of DBDPE were measured on an Agilent 6890A gas chromatograph equipped with a micro electron capture detector (ECD). The analytical column was a DB-XLB column (15 m × 0.25 mm × 0.25 μm). The GC-ECD was operated at an injection temperature of 280 °C and a detector temperature of 315 °C. Nitrogen (UP grade) was used as carrier gas at a flow-rate of 2.0 mL/min, and 2 μL of the sample was injected in splitless mode. The temperature was programmed as follows: initial temperature 120 °C held for 5 min, ramped at 30 °C/min to 280 °C (2 min), followed by a ramp of 5 °C/min to 315 °C, which was held for 15 min. The total run time was 42 min.

2.3.2. SPE-LC/GC-MS analysis

Product identification was performed using the SPE-LC/GC-MS method. The solution at different reaction times was purified with a solid phase extraction (SPE) workstation using CNWBOND LC-C18 SPE cartridges (2.CA0955.0001, 1 g, 6 mL) (CNW, ANPEL Laboratory Technologies (Shanghai), Int., China). The procedure was slightly modified from previous approaches. After activation with 5 mL methanol and 5 mL ultrapure water, each column was loaded with 3 mL of sample, washed with 5 mL ultrapure water, and then dried under vacuum. After eluting with 4 mL methanol, the degradation products in the extracts were subjected to LC-MS analysis. A similar SPE-GC-MS method was also employed to identify transformation products, in which the samples were eluted with 4 mL of toluene.

The LC-MS analyses were conducted on a high resolution hybrid quadrupole time-of-flight mass spectrometer (Triple TOF 5600, AB Sciex, Foster City, CA) equipped with an electrospray ion source. 5 μL of sample was injected into the source using an Agilent 1260 infinity high performance liquid chromatography (HPLC) system. Chromatographic separation was performed on a Thermo BDS Hypersil C₁₈ column (2.1 mm × 100 mm, particle size 2.4 μm) (Thermo Fisher Scientific, Waltham, MA), and the column temperature was maintained at 30 °C. The mobile phase consisting of 0.1% formic acid in water (A) and methanol (B) was eluted at a flow rate of 200 μL/min. The linear gradient decreased from 90% A (2 min) to 10% A in 1 min, which was held for 23 min, then returned to the starting condition in 1 min, and followed by an 8 min equilibration. Mass spectra (*m/z* 70–1000) were recorded in negative ion mode with the following ion source parameters: ion source gas 1, 55 psi; ion source gas 2, 55 psi; curtain gas, 35 psi; temperature, 550 °C; ionspray voltage floating, –4500 V;

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