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Pathway of diethyl phthalate photolysis in sea-water determined by gas chromatography–mass spectrometry and compound-specific isotope analysis

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HIGHLIGHTS

- The major intermediates were mono-ethyl phthalate and phthalic anhydride.
- ^{13}C-enrichment ($\Delta\delta^{13}C = 12.3‰$) in residual DEP was a direct evidence of photolysis.
- Results of CSIA indicated the initial reaction step was cleavage of a C—O bond.
- The degradation pathway was proposed for DEP photolysis.

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ABSTRACT

The degradation mechanism of diethyl phthalate (DEP) in natural seawater under UV irradiation was investigated using a combination of intermediates detection and determination of stable carbon isotopic fractionation. Typical intermediates identified with gas chromatography–mass spectrometry (GC–MS) were mono-ethyl phthalate (MEP) and phthalic anhydride. Stable carbon isotope signature was determined by gas chromatography coupled with isotope ratio mass spectrometry through a combustion interface (GC–C–IRMS). A profound ^{13}C enrichment, with a δ^{13}C isotope shift of 12.3 ± 0.3‰ ($f = 0.09$) in residual DEP molecule, was clearly an indicator to its photolysis. The reactive position isotope enrichment factor ($\varepsilon_{\text{reactive position}}$) and apparent kinetic isotope effects (AKIE) were −35.25 ± 2.26‰ and 1.075, respectively, indicating that the initial reaction step was cleavage of a C—O bond in DEP photolysis. Based on these observations, a degradation pathway was proposed. First, a C—O bond in DEP molecule was broken to form MEP. Then, MEP was further degraded to phthalic anhydride. Our work demonstrates that compound-specific isotope analysis (CSIA), when combined with intermediates analysis, is a reliable measure to deduce the mechanism of DEP photolysis. This approach might be extended as a reference for mechanism investigation in complicated environment systems.

1. Introduction

Phthalic acid esters (PAEs) are widely used industrial chemicals serving as additives in plastics manufacturing, paints, adhesives, cardboard, lubricants and fragrances. Owing to their low solubility in water and high octanol/water partition coefficients, PAEs have been identified in marine environment (Saeger and Tucker, 1976). Previous studies of aquatic toxicity indicated that PAEs with alkyl chain lengths <6 pose intrinsic toxicity to aquatic organisms (Staples et al., 1997; Qiu and Wang, 2005) and the toxicity increases with increasing alkyl chain length (Bradlee and Thomas, 2003). Hence, an increasing attention was focused on the fates of these compounds in the environment (Huff and Kluwe, 1984). The United States Environmental Protection Agency (US EPA) and some of its international counterparts have classified the most common PAEs as priority pollutants and as endocrine disrupting compounds (Barlow et al., 2003).

The study on the degradation mechanisms of PAEs is of great importance to understand their environmental fates and to design effective environmental remediation strategies. The traditional method for mechanism investigation was commonly based on the relationship of molecule structure between substrate and intermediates identified by GC–MS (Balabanovich and Schnabel, 1998; Lau et al., 2005; Young and Phelps, 2005; Kim and Lee, 2005; Xu et al., 2006, 2007; Chang et al., 2007). There are some shortcomings in traditional method. For instance, a few specific intermediates formed during transformation process were mainly polar material and degraded more easily than the parent compound, which was difficult to be detected (Mancini et al., 2002).

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Moreover, the same degradation products may be obtained by different degradation pathways (Zwank et al., 2005a).

In recent years, stable carbon isotope analysis using GC–C–IRMS has become a promising tool to assess degradation processes of organic pollutants in the environment (Hunkeler et al., 1999). Owing to kinetic isotope effect (KIE), an enrichment of heavier isotopes in the residual fraction is usually observed after chemical reaction. The relative abundance of the heavy isotope (e.g., ^{13}C) in a molecule determined with GC–C–IRMS is expressed by the ratio $\delta^{13}C$.

$$\delta^{13}C = \frac{R_{sample} - R_{standard}}{R_{standard}} \cdot 1000‰ \quad (1)$$

where R_{sample} is the $^{13}C/^{12}C$ ratio in a given sample, and $R_{standard}$ is the $^{13}C/^{12}C$ ratio in a standard reference material, Vienna-Pee Dee Belemnite (V-PDB).

It has been found that isotope fractionation varies greatly depending on the type of bond being broken (Huskey, 1991) and the reaction mechanism (Shiner and Wilgis, 1992). Thus, isotope fractionation might be used as an indicator for different degradation pathway. For a general mechanism interpretation of isotope discrimination, $\varepsilon_{\text{reactive position}}$ has to be converted to AKIE. Compared to the AKIE value reported in the literature, the initial reaction step in molecule during the degradation course could be speculated, and specific reaction mechanisms might be obtained (Elsner et al., 2005). CSIA has been successfully applied to investigate the reaction mechanism on both biodegradation and abiotic degradation (Hirschorn et al., 2004, 2007; Zwank et al., 2005b; Elsner et al., 2007; Hartenbach et al., 2008; Vanstone et al., 2008; Abe et al., 2009; Mckelvie et al., 2009; Morasch et al., 2011). To date, few studies have investigated the photolysis mechanism of organic compound by CSIA.

In the present work, DEP, a priority pollutant listed by both China National Environmental Monitoring Center and the US EPA, was chosen as a target compound. The goal of this work was therefore to investigate the degradation mechanism of DEP under 254 nm UV condition with both GC–MS analysis and CSIA. First, typical intermediates of DEP photolysis were identified with GC–MS, and obtained a plausible mechanism. Second, the initial reaction step was further confirmed according to the result of CSIA. These two methods work complementarily to help elucidate the photolysis mechanism of DEP in natural seawater.

2. Materials and methods

2.1. Chemicals

DEP with 99.0% analytical grade (Guoyao Chemical Reagent Co., China) was used without further purification. HPLC grade hexane, dichloromethane and acetone were purchased from Dima Chemical Co., China. Hexamethylbenzene was purchased from Sigma Chemical Co. (St. Louis, MO, USA). The derivatizing reagent, bis(trimethylsilyl)trifluoroacetamide (BSTFA), was obtained from Sigma–Aldrich Co., Supelco, USA.

2.2. Sampling

Natural seawater samples were collected in August 2010 in Licun River, an urbanized marine inlet in Qingdao. The total organic carbon (TOC) of seawater, as determined by direct injection of the radiation samples into a TOC analyzer (Shimadzu TOC-4100) and calibrated with standard solutions of hydrogen potassium phthalate, was 1.903 mg L^{-1}. The salinity and pH value of seawater, determined with multi-parameter water analyzer (Hach sension 156), were 32.5% and 7.63, respectively. Before adding target compound, the sea-water samples were autoclaved by γ-ray for 30 min, and filtered with 0.45 μm polypropylene syringe filters. Then DEP was added to sea-water sample and the initial concentration was about 60 mg L^{-1}.

2.3. Irradiations

Irradiation experiments in laboratory were carried out in a stainless steel cylinder. A low pressure mercury lamp (Philips, 35W), emitting 254 nm monochromic UV light, was placed at the central axis of the cylinder. The reactors, water jacketed Pyrex tube (diameter 2.8 cm), were distributed around the cylinder and parallel to the UV lamp. The distance between the reactors and the UV lamp was about 5 cm. The UV light intensity was monitored by light intensity meter and the value was about 73.2 μW cm^{-2}. The dark control test was also conducted in the cylinder by wrapping the tube with aluminum foil to prevent exposure to UV light.

All experiments were carried out at room temperature (23.0 ± 2 °C).

2.4. Treatment of irradiated samples

The irradiated seawater sample (10.00 mL) was first adjusted to pH ⩾ 12.00 with 1.0 mol L^{-1} NaOH. After adding 5.0 mL of NaCl (5%), the sample was extracted three times with 10.0 mL hexane for 5 min each time by a rotating shaker. The combined extracts were pre-concentrated in a vacuum rotary evaporator to a final volume of about 1 mL, and transferred into amber glass vials to dry at room temperature under gentle nitrogen stream.

To remove interfering compounds, extracts were introduced onto a silica gel chromatographic column after redissolved in 1 mL hexane. Silica gel (100–200 mesh) was activated by heating at 180 °C for 12 h and partially deactivated with Milli-Q water (5% w:w). The glass column (inner diameter, 1.0 cm; length, 18.0 cm) was packed with glass wool at its base and filled with 7.0 g of deactivated silica gel slurry in hexane under gravity. In order to prevent disturbance by eluting solvent, 1.0 g of anhydrous sodium sulfate was added on the top. A volume of 20.0 mL hexane was added and drained to the top of the sodium sulfate to condition the silica gel column prior to sample loading. Then extracts were quantitatively transferred to column and eluted consecutively with 20.0 mL hexane, 15.0 mL dichloromethane–hexane (3/7 v:v), and 30.0 mL acetone–hexane (2/8 v:v). The third eluate contained DEP was concentrated to dry under a gentle stream of high purity nitrogen (Zeng et al., 2005), and then added 50.0 μL hexane and 50.0 μL standards for GC analysis.

For identification intermediates, the irradiated sample (10.00 mL) was first adjusted to pH ⩽ 2.00 with 1.0 mol L^{-1} HCl. The sample was extracted following the procedures described above. After that, the dried extracts were redissolved in 0.5 mL hexane and subsequently derivatized with BSTFA (50.0 μL) for 80 min at 40 °C. The solution contained derivative products was again dried under a continuous nitrogen stream and redissolved in 1.0 mL of hexane for subsequent intermediate analysis.

2.5. Samples analysis

2.5.1. Gas chromatograph conditions

Extracts were analyzed using a gas chromatograph (Shimadzu GC-2010) equipped with flame ionization detector (FID) and HP-5 capillary column (film thickness, 0.25 μm; inner diameter, 0.32 mm; length, 30 m). The initial column temperature was set at 130 °C for 1 min, increased by 5 °C min^{-1} to 220 °C, then increased by 3 °C min^{-1} to 275 °C and maintained for 13 min. Injector and detector temperatures were set at 290 °C and 320 °C, respectively. Nitrogen was used as both a carrier gas (flow rate