Stable Carbon Isotope Fractionation during Sonolysis of Di-n-butyl Phthalate

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Abstract. The degradation of di-n-butyl phthalate (DBP) at an ultrasonic frequency of 80 kHz was investigated. Ultrasonic treatment was found capable of removing DBP in water. TOC analysis showed that DBP could not be completely mineralized within radiation time of 25 h. Stable carbon isotopic fractionation in the residual DBP was evaluated. An observed $^{13}\text{C}$-enrichment, with a $\delta^{13}\text{C}$ shift of $\delta^{13}\text{C}=1.3\pm0.19‰ (f=0.07)$, provided a direct evidence for sonolysis of DBP.

1. Introduction

Ultrasonic irradiation is a promise remediation method of environmental pollutants. Specific chemical reactions proceed during the cavitation produced in sonolysis, and the application of ultrasonic cavitations to waste water treatments is being intensively concerned [1-2]. During sonolysis, the transformation degree of organic pollutants was usually evaluated by GC, HPLC and UV–vis spectrophotomete analysis [1-2]. Owing to high temperature and pressure produced due to the quasi-adiabatic collapse, physical processes such as volatilization can cause the loss of target pollutants (especially to those volatile organic pollutants) during sonolysis. Thus, the rigorous material balance is difficult to establish, making the evaluation of sonochemical reactions complicated. Compound-specific isotope analysis (CSIA) using gas chromatography coupled to isotope ratio mass spectrometry through a combustion interface (GC-C-IRMS) has become a promising tool to assess degradation processes of organic pollutants in environment [3]. To date, CSIA has been used to evaluate biodegradation [4], photolysis [5] and other abiotic degradation [6]. To the best of our knowledge, the evaluation of sonochemical degradation process by means of CSIA has not been reported according to the literature we surveyed.

In the present work, DBP was chosen as model compound. The sonolysis of DBP in water was carried out by using it as substrate. The aim was to investigate stable carbon isotopic fractionation during sonochemical degradation DBP in water.

2. Experimental Procedures

The sample solution containing DBP (200 $\mu\text{g.L}^{-1}$) was prepared with Milli-Q water. Ultrasound irradiation was carried out using an ultrasonic generator (Kamson, KG-600T;
frequency; 80 kHz), which was operated at 200 W. A 150 mL N\textsubscript{2}-saturated sample solution was sonicated in a water bath at 23 °C by a cold water circulation system. During sonolysis, the reaction vessel was sealed and covered with aluminium foil to avoid vaporization and photochemical reactions.

The irradiated sample solution (10.00 mL) was first adjusted pH ≥12.00 with 1.0 mol L\textsuperscript{-1} NaOH. After addition of 5.0 mL NaCl (5%), the sample solution 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. To remove interfering compounds, the resulted extract purified by silica gel column, and the eluate containing DBP was pre-concentrated to about 1.0 mL, then dried under a gentle stream of high purity nitrogen. Then the extract was added 50.0 µL hexane and 50.0 µL internal standards (Hexamethylbenzene) for analysis.

The concentration of DBP was monitored by a gas chromatograph (Shimadzu GC-2010) equipped with HP-5 capillary column (film thickness, 0.25 µm; inner diameter, 0.32 mm; length, 30 m). The column temperature was set at 130 °C for 1 min, increased by 5 °C min\textsuperscript{-1} to 220 °C, then increased by 3 °C min\textsuperscript{-1} to 275 °C for 13 min. Injector and detector temperatures were set at 290 °C and 320 °C, respectively. GC-C-IRMS analyses were performed on a Delta V Advantage mass spectrometer (Thermo Finnigan, Bremen, Germany) linked to a Agilent 6980 gas chromatograph. Analyses were carried out with a DB-1 fused silica capillary column (film thickness, 0.25 µm; inner diameter, 0.25 mm; length, 60 m). GC conditions were as follows: 3 min isothermal time at 60 °C, increased by 2 °C min\textsuperscript{-1} to 310 °C, splitless injector heated at 290 °C and 60 s splitless time. All data are expressed relative to the VPDB standard.

3. Results and Discussion

3.1 Sonochemical Degradation of DBP

During the course of sonolysis, the residual DBP in sample solution was monitored by GC-FID analysis (Fig.1). As can be clearly seen, DBP was degraded quickly, with more than 50% removed within initial 50 min. of sonication irradiation. After that, the removal of DBP decreased with increasing of irradiation time, especially in the stage of 150 to 200 min. The reasons for this may be related to the concentration of DBP in reaction zone and OH radicals. The reaction zone where organic pollutants destroyed in sonolysis depends on its physicochemical properties as well as on the operating conditions employed. Given that DBP used in this work is relatively non-volatile and lower octanol/water partition coefficient, the degradation of DBP occurred mainly in the interface between the bubble and the liquid. At initial stage, the concentration of DBP in reaction zone was higher, and OH radicals produced by acoustic cavitation mainly reacted with DBP. This resulted in the higher removal of DBP. At the late stages of sonolysis, the concentration of DBP in bulk solution was lower, leading to the amount of DBP diffused to reaction zone decreased significantly. On the other hand, the amount of intermediates (e.g. monoester) increased with the increasing of sonication time. Owing to some of these intermediates can further break down during sonolysis, a competitive degradation existed between DBP molecules and intermediates molecules at the late stages of degradation [7], leading to a decrease in OH concentration [8]. As a result, the amounts of OH radicals reacted with target pollutant molecules decreased, leading to the lower degradation rate of DBP.
The results of control experiment indicated that no significant loss of DBP occurred during sonolysis experiment (Fig. 1), suggesting that the loss of DBP in water was the result of sonication irradiation.

![Figure 1. Concentration–time profiles during sonolysis of DBP. Filed symbols represent sonolysis test; opened symbols represent control test.](image1)

3.2 Total organic Carbon (TOC) Analysis of DBP

The analysis by GC-FID reflected the removal of parent compound, namely apparent degradation, which could not quantitatively evaluate the total mineralization degree of target pollutant. In this study, TOC analysis was carried out to assess the extent of mineralization of DBP, since TOC can represent the total concentrations of DBP and intermediates formed in sonolysis (Fig. 2). As can be seen, the content of TOC reduced less than 30% after 15 h of sonolysis. Sonolysis of 200 µg.L⁻¹ of DBP for 25 h resulted in a TOC content of about 65%,

![Figure 2. Content of TOC over time during sonolysis of DBP.](image2)
indicating that complete mineralization of organic pollutants by sonolysis is a slow process [7].
The reason for the lower removal efficiency of TOC might be due to the accumulation of primary or secondly sonolysis products in the medium. Previous studies showed that the hydrophilic intermediates formed during the degradation of hydrophobic compounds are difficult to mineralization by sonolysis [9]. The reason might be that these compounds will tend to keep away from the hydrophobic bubble surface, decreasing the probability of interaction with OH radicals.

### 3.3 $^{13}$C Isotope Fractionation

Previous studies on sonolysis of PAEs showed that it starts with a hydrolysis of the ester group by cleavage of C-O bond to form monoester [10]. There are two types of C-O bonds in DBP molecule based on stable carbon stable isotopes ($^{12}$C, $^{13}$C). Owing to kinetic isotope effects, $^{13}$C-O bond breaks slower than $^{12}$C-O bond, which should give rise to $^{13}$C enrichment in the residual DBP. The $\delta^{13}$C values of DBP at different sonolysis stages were monitored by GC-C-IRMS (Fig. 3). It is clearly that a visible isotope enrichment, within accuracy and reproducibility associated with GC-C-IRMS ($\pm 0.5\% e)$, was observed at late stages of DBP sonolysis. The isotopic enrichment in the $\delta^{13}$C value was $+1.3\pm0.19\% e$ ($f=0.07$). The small fractionation in residual DBP was mainly because the dilution effect existed in the isotope fractionation (i.e., the higher the number of respective atoms per molecule, the more diluted becomes the extent of analyzed isotope fractionation.). In addition, stable $^{13}$C isotopic effect in a given molecule influenced by the binding partner, and tends to be greater if the element is bound to heavier atoms. For example, are generally larger in cleavage of C-O bonds than those of C-H bonds [11].

The $\delta^{13}$C values of DBP in the control test were also measured and no change from an initial $\delta^{13}$C$_0$ occurred, suggesting that the loss of DBP in water was the result of sonolysis, which was consistent with the conclusion mentioned in section 3.1.

Enrichment factor ($\varepsilon_{\text{bulk}}$) was evaluated by a linear regression of the data according to Rayleigh model for closed systems ($\ln 1000 + \delta^{13}$C$_{E} / 1000 + \delta^{13}$C$_{E0} = (a-1) \ln f = \varepsilon_{E} / 1000 \cdot \ln f$) [5]. Excellent fit was typically obtained for the regression (Fig. 4), and the value of $\varepsilon_{\text{bulk}}$ was $-0.4132\pm1.2\% e$.

![Figure 3. Stable carbon isotope fractionation during sonoolysis of DBP in water at 23ºC.](image)
4. Conclusions

The sonochemical degradation of DBP in water was investigated. The results of TOC measurement showed that DBP could not be completely mineralized in sonolysis. CSIA was first used to assess the sonolysis process of organic pollutants in water solution. The resulted $^{13}$C-enrichment in the residual DBP offered a new direct evidence of its sonolysis. Laboratory experiment results suggested that CSIA can be used to evaluate the sonochemical transformation of organic pollutants.

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References


