Titanium dioxide mediated photocatalytic degradation of dibutyl phthalate in aqueous solution—kinetics, mineralization and reaction mechanism

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Abstract

The photocatalyzed degradation conditions of di-*n*-butyl-ortho-phthalate, a representative endocrine disruptor, in aqueous titanium dioxide (TiO_2)-suspended solution were optimized. The effect of various factors, such as photocatalyst dosage, initial substrate concentration, temperature, pH and co-existing organic substance, on the photocatalytic degradation of dibutyl phthalate was investigated. The final mineralization product was carbon dioxide during the degradation of dibutyl phthalate in aqueous solution. The intermediate products were identified by GC–MS technique. On the basis of the detected intermediate species and the calculated frontier electron densities of dibutyl phthalate structure, the photocatalytic degradation reaction pathways were proposed. The photocatalytic degradation treatment for the wastewater including phthalic acid esters is simple, easy handling and low cost.

1. Introduction

Esters of 1,2-benzenedicarboxylic acid (phthalic acid esters, PAEs, phthalates) have a wide variety of industrial, agricultural and domestic applications, but so far the most important is their use as plasticizers that improve the flexibility and workability of polymeric materials. Release of phthalates into the ecosystem or wastewater effluent occurs during the production phase and via leaching and volatilization from plastic products during their usage and/or after disposal [1]. PAEs have been reported to be etiological agents in several human diseases, including disorders of the male reproductive tract, breast and testicular cancers, disruptors of the neuroendocrine system, and skeletal effects [2,3]. As a result, several regulatory bodies, such as the US Environmental Protection Agency (US EPA) [4], the European Union [5] and China National Environmental Monitoring Center [6] classified phthalate esters as a top priority pollutant for risk assessment, mandating the reduction and control of phthalate pollution.

Since phthalate esters are becoming a class of concerning water pollutants and they are still accumulating in the environment though they can be biological degraded within 1–100 days [7], there is a strong need to look for alternative and faster treatment processes for such pollutants. The photocatalytic oxidation is one of the emerging technologies for the elimination of organic micropollutants because of the efficiency in their mineralization, ideally producing as end products carbon dioxide, water, and inorganic mineral ions [8–20]. Among the semiconductors used, titanium dioxide (TiO_2) is considered a very efficient catalyst that, unlike other semiconductors, is non toxic, stable to photocorrosion, low cost and suitable to work using sunlight as energy source. However, very few works related to the use of TiO_2 in the photocatalytic degradation of PAEs have been reported [21–24]. In these studies, the detailed kinetic studies and reaction mechanism in the photocatalytic degradation of PAEs in the aqueous TiO_2 suspension were not evaluated.

In the present work, the photocatalytic degradation conditions of di-*n*-butyl phthalate (DBP) in water with TiO_2 were optimized, and the photocatalytic degradation kinetics of DBP was studied. The final degradation product was investigated in order to evaluate the mineralization of DBP. Furthermore, the

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photocatalytic degradation pathways were speculated on the base of the evidence of the oxidative intermediate formation.
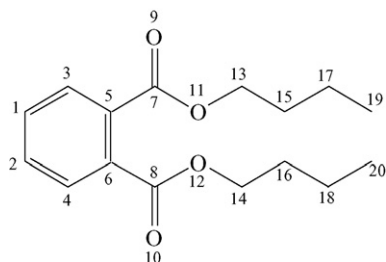
di-*n*-butyl-ortho-phthalate (DBP)

2. Experimental

DBP (di-*n*-butyl-ortho-phthalate, *o*-C_6H_4-[COO(CH_2)$_3$ CH_3]$_2$, CAS #84-74-2) used in this study was purchased from Nacalai Tesque Inc., Kyoto, Japan (GC grade >98%). DBP aqueous solutions were prepared with ultrapure water, which was purified by an ultrapure water system (Advantec MFS Inc., Tokyo, Japan) resulting in a resistivity >18 MΩ cm. A 100 mL aqueous solution containing 5 μg/mL (18 μM) DBP was put into a Pyrex reaction vessel (200 mL capacity). TiO_2 powder (anatase, purity 99.9%, diameter 230 nm, surface area 8.7 m^2/g, Wako Pure Chemical Industries Ltd., Osaka, Japan) was added to the solution to produce a given concentration of TiO_2 suspension. The temperature was kept constant with a water bath. The detailed experimental conditions were shown in Table 1. The TiO_2 suspension containing DBP was irradiated with a Xe lamp (990 W, Ushio Electronics CO., Tokyo, Japan). In this case, the short ultraviolet radiation ($\lambda < 300$ nm) was filtered out by the vessel wall. The intensity of light was measured by a UV radio meter with a sensor of 320–410 nm wavelengths (UVR-400, Iuchi Co., Osaka, Japan).

After illumination, TiO_2 was separated through the 0.45 μm Advantec membrane filter. The amount of DBP in the aqueous solution was measured using a high-performance liquid chromatograph (HPLC, JASCO Co., Tokyo, Japan), equipped with a JASCO UVIDEC-100-VI optical detector and a Chromospheres 5 Poly C18 column (Chrompack, VARIAN Inc., California, USA). The elution was monitored at 276 nm. The eluent used was a mixed solvent of acetonitrile and water (1/1, v/v). The flow rate of the mobile phase was 1.5 mL/min. The degradation efficiency of DBP was calculated with the following equation.

$$\text{Dedradation efficiency (\%)} = \frac{100 \times (q_0 - q_1 - q_2)}{q_0 - q_1}, \quad (1)$$

Table 1
Degradation conditions

DBP	5 μg/mL (100 mL)
TiO_2	0–30 mg (0–300 μg/mL)
Temperature	10–40 °C
pH	1–10
Light intensity	1.8 mW/cm^2
Illumination time	60 min

where q_0, q_1 and q_2 were the initial amount of DBP, the amount adsorbed onto the catalyst at equilibrium and the residual amount undegraded after the treatment, respectively.

The evolution of CO_2 was evaluated with a GL Science GC-353B equipped with a methanizer and an FI detector, combined with a Porapack Q using nitrogen carrier gas. The intermediate products were extracted by means of solid-phase extraction. The extraction disk (C18 disk, 3 M Empore) was placed in the conventional filtration apparatus and washed with 10 mL of solvent mixture, dichloromethane and ethyl acetate (1:1), 10 mL of methanol and 10 mL of ultrapure water. Then, the sample was percolated through the disk with a flow rate of 5 mL/min under vacuum. The compounds trapped in the disk were collected by using 4 mL × 5 mL of solvent mixture, dichloromethane and ethyl acetate (1:1), as eluting system. The fractions were evaporated under a gentle stream of nitrogen to 50 μL into conical vials, and 1 μL was injected into GC–MS instrument in splitless mode. For the analysis of intermediate products, a Shimazu Gas Chromatograph and Mass Spectrometry (GC–MS 5050A) equipped with a DB5 J&W Scientific capillary column (30 m × 0.25 mm i.d.) was used at the following chromatographic conditions: injector temperature 220 °C, column temperature program 40 °C, 40–200 °C (5 °C/min), 200–210 °C (1 °C/min), 210–280 °C (20 °C/min) and 280 °C (3 min). Helium was used as the carrier gas at 1.5 mL/min. The interface was kept at 280 °C. Qualitative analyses were performed in the electron-impact (EI) mode, at 70 eV using the full scan mode.

Molecular orbital calculations were carried out at the single determinant (Hartree–Fock) level for optimization of the minimum energy obtained at the AM1 level. All semi-empirical calculations were performed in MOPAC Version 6.01 with a CAChe package (Fujitsu Co. Ltd.). An initial position for a possible •OH radical attack was estimated from calculations of frontier electron densities of the DBP structure. The mode by which DBP might adsorb onto the TiO_2 surface was estimated from calculated partial charges of DBP [8,9,25].

3. Results and discussion

In the primary experiments [24], the complete disappearance of DBP was observed in <3 h, working with moderate amounts of TiO_2 (5 mg) with the Xe lamp illumination. In the photocatalytic degradation of DBP, different TiO_2 materials such as P25 (Degussa), ST-01 (Ishihara Techno Corp.) and ones supplied by Wako Pure Chemical Industries were evaluated. The TiO_2 materials obtained from Wako Pure Chemical Industries (efficiency: 86%) were more efficient for the photocatalytic degradation of DBP in water, compared with 61% of P25 and 70% of ST-01. Therefore, the TiO_2 photocatalyst supplied by Wako Pure Chemical Industries was applied to the subsequent degradation studies.

Nakai et al. [26] has investigated the conformation of dialkyl phthalate. From ^{1}H-NMR measurements, di-*n*-butyl phthalate was found to be in a C2 symmetry conformation, in which two ester-alkyl chains are not distinguished spectrometrically from each other. The chemical shift of the methyl and methylene groups of alkyl chains emerged at the ordinary regions in [1]H-
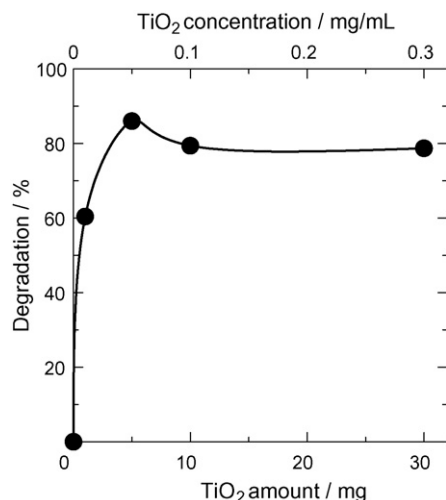
Fig. 1. Effect of TiO$_2$ amount on the photocatalytic degradation of DBP in water. DBP: 5 μg/mL; illumination time: 60 min; temperature: 20 °C; pH: 6.

Fig. 2. Effect of initial substrate concentration on the photocatalytic degradation of DBP in water using TiO$_2$. TiO$_2$: 5 mg (50 μg/mL); illumination time: 60 min; temperature: 20 °C; pH: 6.

NMR spectra, suggesting that the methylene chains are extended straightforwardly. This was supported by ab initio molecular orbital (MO) calculations to estimate the most energetically stable conformation of di-*n*-alkyl phthalates. In the estimated conformation, two alkyl groups linked by the ester bond to the adjacent carboxyl groups are extending to the different directions, which are deviated from the benzene plane to the upward and downward, respectively.

3.1. Effect of photocatalyst dosages

To optimize the TiO$_2$ suspension concentration, the effect of photocatalyst dosages on the degradation of DBP in aqueous solution was studied. The results were illustrated in Fig. 1. The degradation efficiency increased with increasing the amounts up to 5 mg. Then, the efficiency decreased slightly, and above 10 mg of TiO$_2$ became nearly flat. The increase in the efficiency seems to be due to the increase in the total surface area, namely number of active sites, available for the photocatalytic reaction as the dosage of photocatalyst increased. However, when TiO$_2$ was overdosed, the number of active sites on the TiO$_2$ surface may become almost constant because of the decreased light penetration, the increased light scattering and the loss in surface area occasioned by agglomeration (particle–particles interactions) at high solid concentration [10]. Therefore, 5 mg of TiO$_2$ was selected as the optimal amounts of photocatalyst for the sequential experiment. The TiO$_2$ amounts corresponded the suspension concentration of 50 μg/mL (630 nmol/mL).

3.2. Effect of initial substrate concentration

It is very signficant, from the application point of view, to investigate the dependence of the photocatalytic degradation on the substrate concentration. Therefore, the influence of initial substrate concentration on the photocatalytic decomposition using TiO$_2$ was investigated, as shown in Fig. 2. With increasing the initial substrate concentration, the degradation amounts
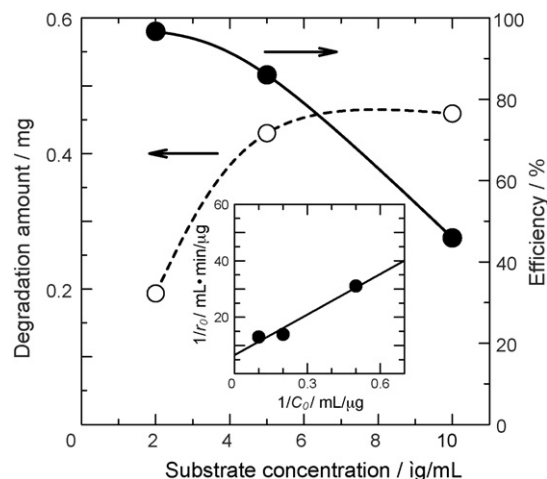
of DBP increased greatly, although the degradation efficiency decreased gradually. Therefore, 5 μg/mL of DBP solution was used because it was an appropriate concentration for evaluating the photocatalytic degradation.

The photocatalytic oxidation kinetics of many organic compounds has often been modeled with the Langmuir–Hinshelwood (L–H) equation, which also covers the adsorption properties of the substrate on the photocatalyst surface. This model was developed by Turchi and Ollis [11] and expressed as Eq. (2):

$$r_0 = -\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{kKC_0}{1 + KC_0} \tag{2}$$

where r_0 is the degradation rate of the reactant, k is the reaction rate constant, K is the adsorption coefficient of the reactant and C_0 is its concentration. The transformation of the L–H equation (Eq. (2)) into its inverse function results in a linear relationship with an intercept of k^{-1} and a slope $(kK)^{-1}$:

$$\frac{1}{r_0} = \frac{1}{k} + \frac{1}{kKC_0} \tag{3}$$

The intercept and the slope can be obtained from a plot of the inverse of r_0 as a function of the reciprocal C_0, as illustrated in the insert in Fig. 2. Eq. (3) shows a good fit for the data with a correlation coefficient 0.980. The reaction rate constant (k) was 0.152 μg/mL min (7.05×10^{-4} mol/L s).

3.3. Effect of temperature

Very little information on the temperature effect on the photocatalytic degradation of pollutants in aqueous solution with TiO$_2$ has been presented. Therefore, the effect of temperature on the photocatalytic degradation of DBP in water using TiO$_2$ was investigated in the range of 10–40 °C. The results were shown in Fig. 3. Although the degradation efficiency of DBP gradually increased as the temperature increased, the appreciable change was not observed in the temperature range. In the photocatalytic degradation of imazaquin in an aqueous suspension of titanium
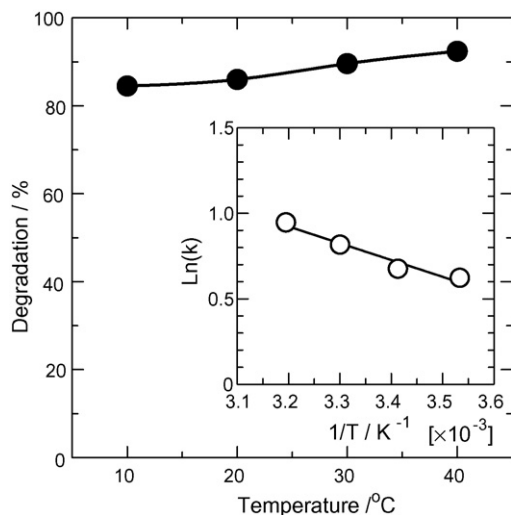
Fig. 3. Effect of temperature on the photocatalytic degradation of DBP in water using TiO$_2$. TiO$_2$: 5 mg (50 μg/mL); DBP: 5 μg/mL; illumination time: 60 min; pH: 6.

Fig. 4. Effect of initial pH concentration on the photocatalytic degradation of DBP in water using TiO$_2$. TiO$_2$: 5 mg (50 μg/mL); DBP: 5 μg/mL; illumination time: 60 min; temperature: 20 °C.

dioxide [12], the effect of temperature was studied in the range 20–40 °C, and the rate constants increased with increasing temperature. Ishiki et al. [13] have investigated the photocatalytic degradation of imazethapyr herbicide at TiO$_2$/H$_2$O interface. The temperature effect was studied using a suspension between 20 and 40 °C, and the herbicide was more easily degraded at lower temperatures in the TiO$_2$ suspension, due to the decrease in the physisorption between the TiO$_2$ surface and the imazethapyr molecules. By plotting the natural logarithm of the rate constant as a function of reciprocal absolute temperature, a linear behavior was obtained with the correlation coefficient 0.980, as drawn in the insert in Fig. 3. The activation energy (E_a) was relatively low and was estimated to become 0.814 kJ/mol. Wu et al. [15] have investigated the kinetic modeling of promotion and inhibition of temperature on the photocatalytic degradation of benzene vapor, and have presented the apparent activation energy of 0.76 kcal/mol. As a consequence, all subsequent illuminations were performed at 20 °C because of the operating cost for the photodegradation system.

3.4. Effect of initial pH

The amphoteric behavior of most semiconductor oxides affects the surface charge of the photocatalyst. Therefore, the role of initial pH on the degradation efficiency for DBP was investigated in the pH range 1–10, as illustrated in Fig. 4. The degradation efficiency increased with increase in pH. The pH value of zero point charge (zpc) pH$_{zpc}$ of TiO$_2$ particles is equal to around six as Ti^{IV}–OH [16]. This means that the TiO$_2$ surface becomes positively charged, Ti^{IV}–OH$_2^+$, when the pH is lower than this value and becomes predominantly negative, Ti^{IV}–O$^-$, for a pH value above about six. Generally, the pH changes can have a non-insignificant result not only on the mode of adsorption of the DBP substrate on TiO$_2$ surface, but also on the selectivity of the photodegradative reaction occurring on the particle surface since redox reactions are very sensitive to changes
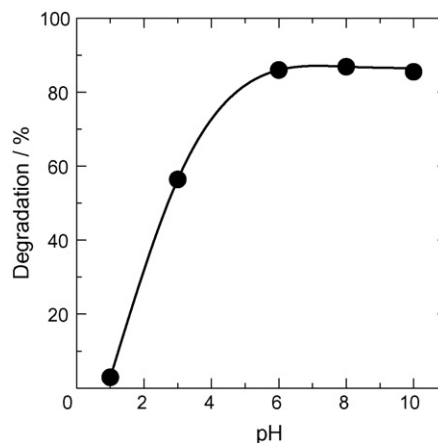
in the surface potential [16]. The adsorption of the DBP on the TiO$_2$ surface was estimated from the simulation of molecular partial charges (Table 2). The most negative partial charge atoms in the DBP structure were the two carbonyl oxygen atoms (9O and 10O), with the next ones being two ether oxygen atoms (11O and 12O). Therefore, we deduce that in alkaline media (pH > 6) the DBP substrate is likely adsorbed on the negatively charged particle surface through all positive hydrogen atoms in such a way that the DBP molecule lies relatively flat against the particle surface, and in acidic condition (pH < 6) on the positively one through the four negative oxygen atoms that the side-chain parts of DBP molecule are adsorbed onto the surface. On the other hand, at high initial pH, more hydroxide ions (OH$^-$) in the solution induced the generation of hydroxyl free radicals (HO$^\bullet$), which came from the photooxidation of OH$^-$ by holes forming on the titanium dioxide surface. Since hydroxyl free radical is the dominant oxidizing species in the photocatalytic process, the photocatalytic decay of DBP may be accelerated in an alkaline medium. Similar reaction has been suggested by a number of researchers [10,17–20]. Consequently, pH 6 was selected for the optimal experimental conditions, because of the unnecessary of chemical treatment including neutralization process.

3.5. Effect of co-existing organic substance

Generally, the wastewater from the industrial plant has contained not only DBP, but also other organic substances. Therefore, the influence of the co-existing organic substance on the DBP degradation efficiency was investigated, as shown in Fig. 5. Acetone was selected as the co-existing compounds since it is one of the normal solvents. The photocatalytic degradation efficiency for DBP decreased gradually with an increase in the concentration of acetone. These phenomena mean that hydroxyl free radicals also attacked acetone because its concentration was much larger compared with that of DBP. As a consequence, in the case of the present of other organic substances, longer illumination time may be needed in order to achieve the same efficiency as that obtained in the case of DBP only.

Table 2
Calculations of partial charge (PC) and frontier electron density (FED) for DBP

| Atom	PC	FED
1C	−0.119	0.263
2C	−0.119	0.263
3C	−0.097	0.221
4C	−0.097	0.221
5C	−0.050	0.340
6C	−0.050	0.340
7C	0.344	0.048
8C	0.344	0.048
9O	−0.365	0.071
10O	−0.365	0.071
11O	−0.226	0.022
12O	−0.226	0.022
13C	−0.014	0.006
14C	−0.014	0.006
15C	−0.161	0.005
16C	−0.161	0.005
17C	−0.154	0.003
18C	−0.154	0.003
19C	−0.209	0.001
20C	−0.209	0.001
1H	0.145	0
2H	0.145	0
3H	0.170	0
4H	0.170	0
13H-1	0.088	0.005
13H-2	0.088	0.005
14H-1	0.088	0.005
14H-2	0.088	0.005
15H-1	0.091	0.002
15H-2	0.091	0.002
16H-1	0.091	0.002
16H-2	0.091	0.002
17H-1	0.080	0.002
17H-2	0.080	0.002
18H-1	0.080	0.002
18H-2	0.080	0.002
19H-1	0.075	0
19H-2	0.072	0.001
19H-3	0.072	0.001
20H-1	0.075	0
20H-2	0.072	0.001
20H-3	0.072	0.001
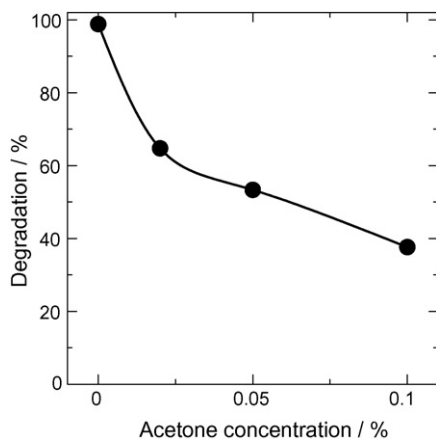
Fig. 5. Effect of the concentration of acetone on the photocatalytic degradation of DBP in water using TiO_2. TiO_2: 5 mg (50 μg/mL); DBP: 5 μg/mL; illumination time: 180 min; temperature: 20 °C; pH: 6.
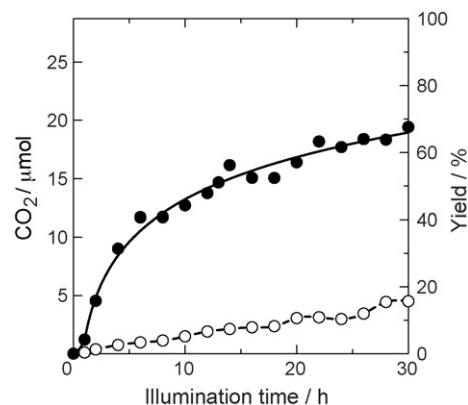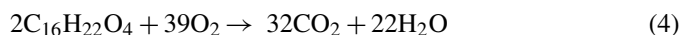

Fig. 6. Carbon dioxide formation during the photocatalytic degradation of DBP in water using TiO_2. Air atmosphere: (●); Helium atmosphere (without oxygen): (○); TiO_2: 5 mg (50 μg/mL); DBP: 5 μg/mL; Temperature: 20 °C; pH: 6.

3.6. Mineralization

Halmann [22] has described the release of CO_2 during the photocatalytic degradation of DBP using mercury lamp. For the photocatalytic degradation of DBP with TiO_2 semiconductors, the total mineralization reaction can be estimated as follows:

$$2C_{16}H_{22}O_4 + 39O_2 \rightarrow 32CO_2 + 22H_2O \qquad (4)$$

Therefore, the evolution of CO_2 during the photocatalytic degradation of DBP in water using TiO_2 was investigated under air and helium (without oxygen) atmospheres. The results were illustrated in Fig. 6. Under the air atmosphere, the yield of CO_2 evolution increased sharply until 6 h illumination time, and after 6 h the yield increased gradually. On the other hand, the CO_2 evolution rate in the helium atmosphere was very slow relative to that observed in the air atmosphere. This fact indicates that oxygen species dissolved in the sample solution play a significant role in the photocatalytic degradation of DBP with TiO_2. Taking into account the fact that complete disappearance of the DBP in the irradiated cells occurred after relatively short illumination time (<3 h) in the photocatalytic degradation [24], whereas the formation of CO_2 was observed after the 3 h illumination, it could be deduced that transient organic intermediate products are likely to be present in the reaction system after the complete destruction of DBP. In consequence, in the photocatalytic degradation of DBP in the aqueous TiO_2 suspension, the mineralization reaction to CO_2 could proceed with the reduction in estrogenic activity.

### 3.7. Intermediate products and photodegradation mechanism

The intermediate products formed in the photocatalytic degradation of DBP in the aqueous TiO_2 suspension for 30 min were investigated by GC–MS analysis. Six products were identified by the molecular ion and mass fragment peak and also through comparison with GC/MS NIST library data. Table 3 lists retention time, molecular weight and structure obtained for six intermediate products. The similarities of these four products to the NIST library data were more than 85%. Bajt et al. [27]

Table 3
GC–MS–EI retention time, molecular weight of intermediate products

Peak no.	Retention time (min)	Molecular weight (m/z)	Molecular structure
1	27.4	294	
2	28.4	264	
3	28.6	276	
4	28.7	276	
5	29.1	276	
6	29.3	264	

have investigated the similar DBP degradation technique to the present work. In the degradation of DBP by homogeneous photocatalysis with Fe(III) in aqueous solution, they have identified intermediate products (g)–(m) in Scheme 1 by HPLC/ES/MS and GC/MS, which could not be detected in this study.
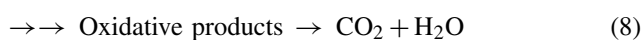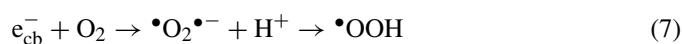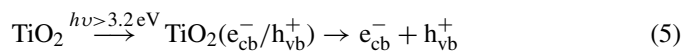
The photocatalytic degradation of DBP is, apparently, a very complex process whose mechanism is not yet fully clarified. The present experimental data and literature reports [21–24,27] suggest the photocatalytic degradation pathway of DBP in water with titanium dioxide, as illustrated in Scheme 1. Two carbon
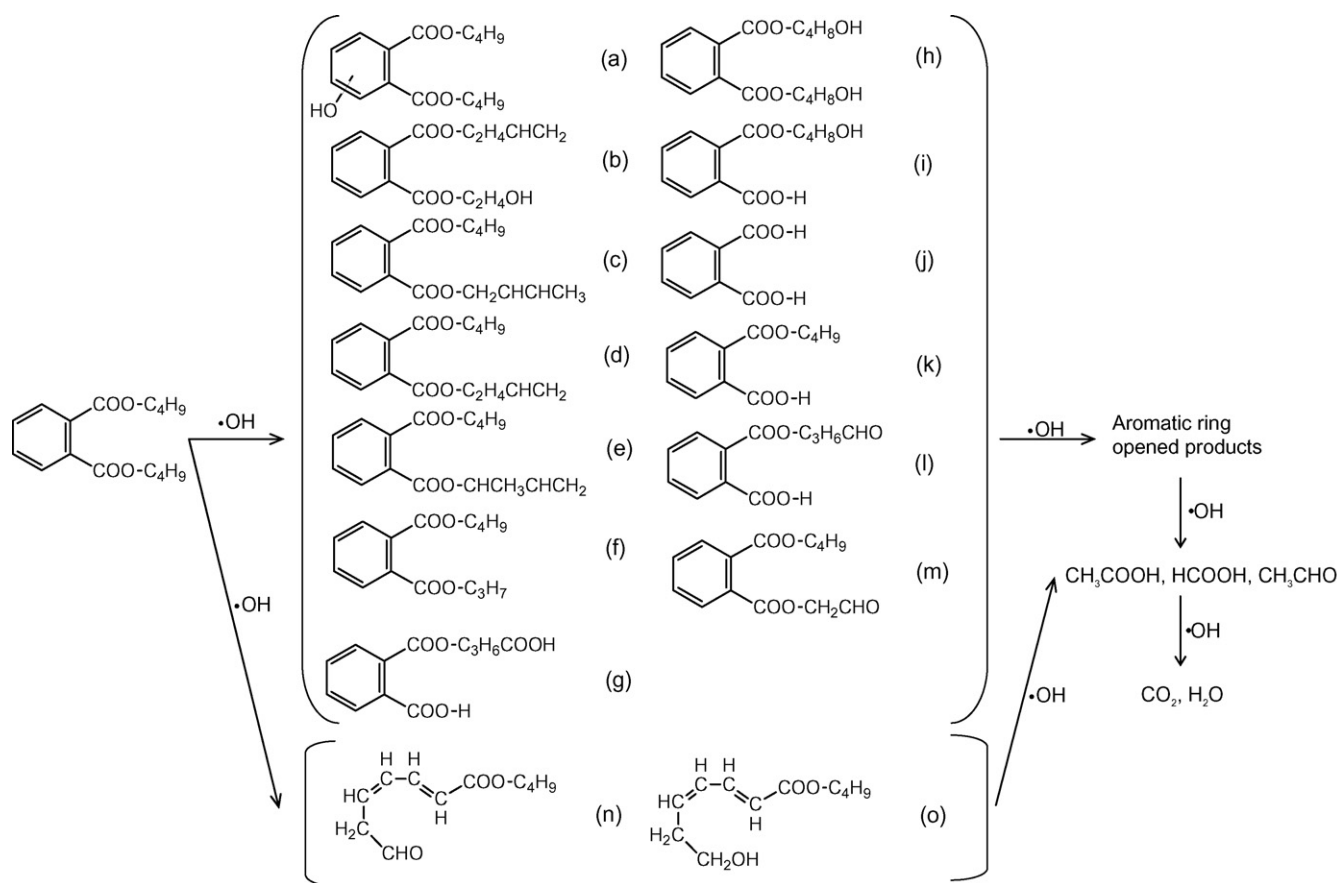
Scheme 1. Proposed photocatalytic degradation pathway of DBP.

atoms (5C and 6C) in α-position with respect to carboxyl group have the largest frontier density according to the MOPAC simulation (see Table 2). Therefore, these sites would become one of the most likely sites of attack by neutral •OH radicals, although the other sites may be attacked by them.

A general TiO_2 photocatalytic mechanism is concluded as follows: TiO_2 particulates absorb UV light with an energy greater than 3.2 eV (wavelengths below 387 nm) to generate electron/hole pairs (Eq. (5)). The holes (h^+) are ultimately trapped with OH^- ions or with H_2O_{ads} on the TiO_2 particulate surface to yield H^+ and •OH radicals (Eq. (6)). Concomitantly, dioxygen molecules react with conduction band electrons (e^-_{cb}) to yield superoxide radical anions, •O_2•$^-$, from which protonation generates the hydroperoxide radical •OOH (Eq. (7)).

$$TiO_2 \xrightarrow{h\upsilon > 3.2\,eV} TiO_2(e^-_{cb}/h^+_{vb}) \rightarrow e^-_{cb} + h^+_{vb} \tag{5}$$

$$h^+_{vb} + OH^- (\text{or } H_2O)_{surf} \rightarrow {}^\bullet OH(+H^+) \tag{6}$$

$$e^-_{cb} + O_2 \rightarrow {}^\bullet O_2{}^{\bullet -} + H^+ \rightarrow {}^\bullet OOH \tag{7}$$

$${}^\bullet OH \,(\text{or } {}^\bullet OOH) + DBP$$
$$\rightarrow\rightarrow \text{ Oxidative products } \rightarrow CO_2 + H_2O \tag{8}$$

There are two possible sites for the attack of •OH radicals, the aliphatic chain and the aromatic ring in the DBP structure. When the •OH radicals attack the aliphatic chain, a number of interme-

diate products (b)–(m) may be formed during the photocatalytic degradation of DBP. These single aromatic intermediates are presumably further oxidized through ring-rupturing reactions into aliphatic compounds containing formic acid, acetic acid and acetaldehyde [8,9]. The attack of •OH radicals to the aromatic ring, except for 5C and 6C, leads to the formation of hydroxy and dihydroxy photoproducts (hydroxylated on the aromatic ring) for DBP, as shown in Scheme 1(a). The further attack of •OH radicals would be given to the aliphatic chain of the hydroxylated products. When •OH radicals attack two carbon atoms (5C and 6C) in α-position with respect to carboxyl group, the positions would be cleaved, producing intermediates with a long chain structure (n) and (o). If intermediates with the long chain structure could be produced, their phtocatalytic degradation may be more difficult compared to that of the ring moiety. The formation of these long chain intermediates will lead to slow CO_2 mineralization in the photocatalytic degradation of DBP.

4. Conclusion

The optimization of the photocatalytic degradation conditions of DBP in water using titanium dioxide was investigated. The final degradation product was carbon dioxide. The identification of intermediate products formed during the photocatalytic degradation of DBP in water and the calculation of frontier

electron density for the DBP structure could become a useful source of information on the degradation reaction pathways.

Acknowledgment

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