Sonolytic Degradation of Phthalic Acid Esters in Aqueous Solutions. Acceleration of Hydrolysis by Sonochemical Action

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The degradation of phthalic acid esters in an aqueous solution by sonochemical action was performed at an ultrasonic frequency of 200 kHz. The sonochemical degradation of phthalic acid esters followed pseudo first-order kinetics. The OH radical reaction was found to be a predominant factor of the degradation of diethyl phthalate in the pH range 4−11. However, over pH 11, the degradation rate was accelerated with an increased pH due to the increased hydrolysis. From experiments involving stirring and ultrasonic irradiation, the accelerated degradation by hydrolysis in the presence of ultrasound was also established. The accelerated hydrolysis of phthalic acid esters by sonochemical action may be due to the existence of a sphere in which a temperature higher than that in the bulk solution is present.

Introduction

Phthalic acid esters (PAEs) have been widely used as a popular and important additive to give improved flexibility, extensibility, and workability in plastic industrial processes for a long time.[1] Because PAEs are produced in very large quantities and are also released into the environment during manufacture, use, and disposal, they are considered a ubiquitous pollutant of the aquatic and terrestrial environments.[2] Numerous studies on the behavior of PAEs in soil, sludge, natural water, and wastewater and on the treatment using various transformations processes have been undertaken.[3−8] The biological process as a conventional treatment method required longer periods to degrade the PAEs due to the half-lives for the degradation of the PAEs ranging from 1 day to 2 weeks in natural waters and from one week to several months in soil.

Recently, the degradation of environmental contaminants by sonochemical action has been studied as one of the effective oxidation processes.[9−14] The chemical effects by ultrasonic irradiation in aqueous solution result from the high temperatures and pressures (up to some five thousand degrees and in the range of hundreds of bars), which are attained when the adiabatic compressed bubbles are violently collapsed.[15,16] Under these extreme conditions, the radical species, such as OH radicals and H atoms, are produced via the pyrolysis of water in the collapsing cavitation bubble and can either react with organic compounds or recombine with other radical species. The degradation pathways seem to be the direct thermal reaction inside and in the vicinity of the cavitation bubbles and the free radical oxidation by OH radicals in the vicinity of the cavitation bubbles and in the bulk solution.

In this study, we investigated the kinetics of degradation of dimethyl phthalate (DMP), diethyl phthalate (DEP), and dibutyl phthalate (DBP). The effects of pH on the sonolysis of DEP were also studied. The sonochemical reaction sites of DEP and the accelerated hydrolysis by the sonochemical effect under alkaline conditions are discussed.

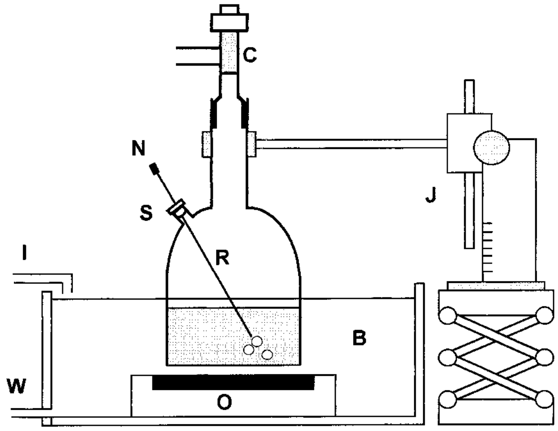

Figure 1. Schematic diagram of the experimental apparatus for ultrasound irradiation: (O) oscillator (200 kHz), (R) reactor (150 mL), (J) jacket for reactor fixation (3.8 mm), (N) syringe needle for gas purge, (S) septum, (C) stopcock, (I) cooling water inlet, (W) water outlet, and (B) water bath (20 °C).

Experimental Methods

All reagent grade chemicals were purchased from Wako and used without further purification. The water used for the preparation of the aqueous solutions was purified by a Millipore Milli-Q system (resistivity = 18.3 MΩ cm). The sample solution was purged with a high purity gas (>99.99%) before ultrasonic irradiation and the pH was adjusted with phosphate buffer and sodium hydroxide solution.

As shown in Figure 1, the experimental apparatus for the ultrasonic irradiation consisted of an ultrasonic generator, a barium titanate oscillator (65 mm i.d.) operating at 200 kHz (6 $\mathrm{Wcm^{-2}}$), and a water bath for the maintenance of the constant temperature of 20 °C. The power was determined by calorimetric

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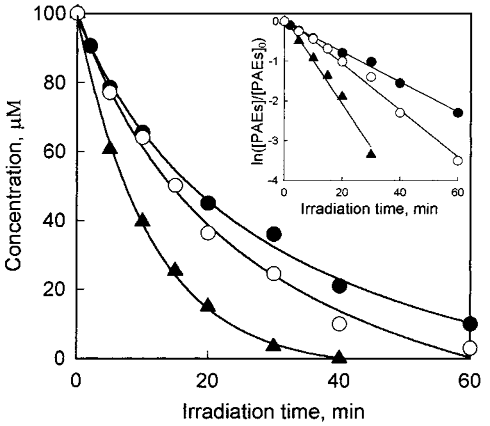

Figure 2. Change in the concentration of PAEs during the sonolysis and pseudo first-order plots (inset) of degradation of PAEs with irradiation time. The pseudo-first-order constants (k_o) of degradation rate for DMP, DEP, and DBP are 0.039 min^{-1}, 0.110 min^{-1}, and 0.059 min^{-1}, respectively. Temperature = 20 °C and pH = 7; (●) DMP, (▲) DEP, and (○) DBP.

method under optimum conditions. A cylindrical glass vessel (50 mm i.d.) with a total volume of about 150 mL had a sidearm with a septum for gas bubbling or for extracting the gaseous and liquid samples without contact of the solution to air. The bottom of the glass vessel was made as thin as possible (1 mm thickness) for good transmission of the ultrasonic waves during the irradiation. The vessel was fixed at a constant position ($\lambda/2$ from a oscillator) relative to the nodal plane of the sound wave and also closed during the experiment.

PAEs were analyzed using a high performance liquid chromatograph (Shimadzu LC-6A) equipped with a UV photodetector and a partisil-10 SAX column (4.6 × 150 mm, GL Sciences). The mixture of 0.05 M KH_2PO_3 and methanol was used as the eluent with a flow rate of 1.0 mL min^{-1}. Gaseous products such as hydrogen, carbon monoxide, and hydrocarbons (CH_4, C_2H_6, C_2H_4, and C_2H_2) were determined using a gas chromatograph (Hewlett-Packard 6890) equipped with a thermal conductivity detector and a flame ionization detector, and separations were performed using a GS-molesieve column (J & W Scientific). The hydrogen peroxide concentration was measured by the KI colorimetric method. In this method, iodide ion is oxidized by H_2O_2 in slightly acidic (pH 5.85) ammonium molybdate solution (1.6×10^{-4} M), $H_2O_2 + 3I^- \rightarrow I_3^- + 2OH^-$. The produced I_3^- was spectrophotometrically determined at 352 nm ($\epsilon = 2.6 \times 10^4$ M^{-1} cm^{-1}).

Results and Discussion

Degradation of PAEs by Sonochemical Action. The degradation of the PAEs was carried out at an initial concentration of 100 µM and at pH 7 under an argon atmosphere. Figure 2 shows the time dependence of the sonochemical degradation of the PAEs and also depicts the plots of ln([PAEs]$_t$/[PAEs]$_0$) versus irradiation time (inset). The linearity of the plots indicates that the degradation of the PAEs by ultrasonic irradiation follows pseudo first-order kinetics. The degradation of DEP was almost completed with 30 min of ultrasonic irradiation. The DEP was degraded more quickly than the other PAEs, and the degradation half-life times ($t_{1/2}$) of DMP, DEP, and DBP were determined to be 17.9, 6.9, and 11.8 min, respectively. The physicochemical properties of solutes, particularly hydrophobicity and vapor pressure, are a significant determinant of the sonolytic reaction pathway and degradation rate. The higher hydrophobicity and vapor pressure will be lead to partition of solutes into the vicinity of the cavitation bubble and to vaporization of solutes inside the cavitation bubble. The physicochemical properties of PAEs would be capable of affecting the degradation rate on the reaction with OH radicals and thermal reaction inside and/or in the vicinity of the cavitation bubble.

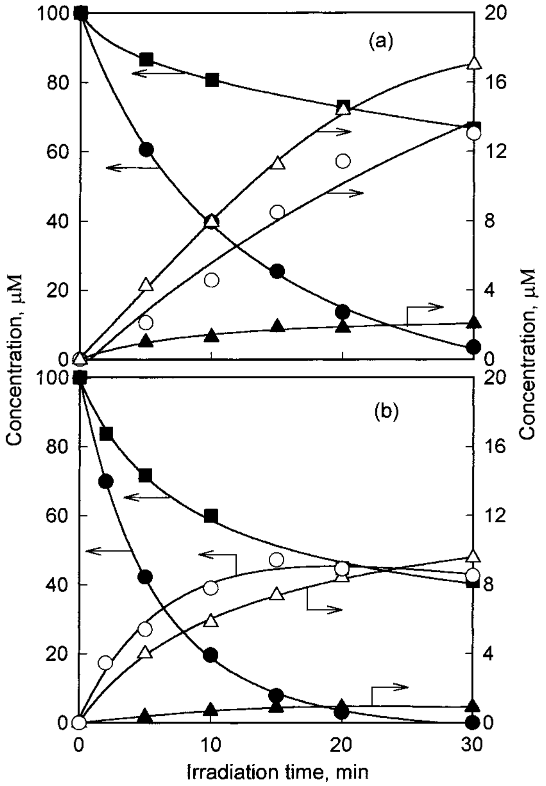

Figure 3. Profile of the degradation of DEP and the formation of products as a function of the irradiation time. (a) pH 7 and (b) pH 12. (●) DEP, (■) DEP in 3 mM 2-methyl-2-propanol solution, (○) MEP, (△) CO, and (▲) hydrocarbons (sum of CH_4, C_2H_2, C_2H_4, and C_2H_6).

The UV absorption spectra of DEP are an example of the sonolysis at pH 7 having a strong maximum at 230 nm and a weak maximum at 275 nm attributed to the aromatic ring, and these decreased with increasing irradiation time. It seems that the aromatic ring in DEP was cleaved during the degradation of the starting compound by the sonochemical action.

Sonolysis of DEP under an Argon Atmosphere at pH 7 and 12. Figure 3 shows the degradation of DEP and the formation of products as a function of the irradiation time at pH 7 and 12. The observed initial degradation rates of DEP were 7.9 µM min^{-1} (pH 7) and 11.6 µM min^{-1} (pH 12). The sonolysis of DEP in the presence of 2-methyl-2-propanol (*tert*-butyl alcohol), which is a well-known radical scavenger,[9,17] was carried out in order to evaluate the radical reaction. The degradation of DEP in the presence of *tert*-butyl alcohol was suppressed about 66% (pH 7) and 44% (pH 12) after a 30-min sonolysis.

When organic compounds are degraded by ultrasonic irradiation under argon, CO may be detected as the main gaseous product. The amount of CO continuously increased with the degradation of DEP, whereas the amount of each hydrocarbon did not show an appreciable increase with irradiation time probably due to the further decomposition of the hydrocarbons via pyrolysis.[18] The evolution of C_2H_2 showed a particularly remarkable decrease among the produced gases.

The concentration of monoethyl phthalate (MEP), which was regarded as the hydrolysis product of DEP, was approximately 3.3 times higher at pH 12 than at pH 7. It was reported that the

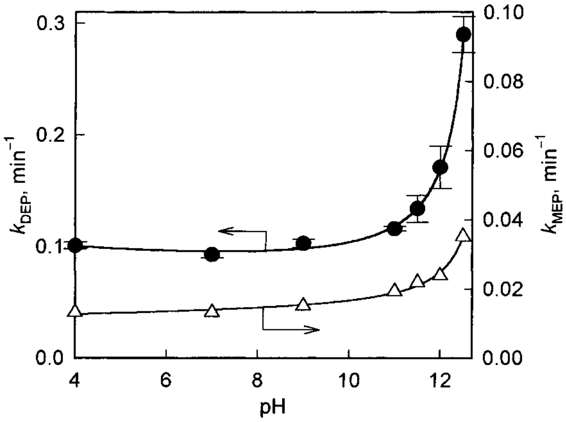

Figure 4. Comparison of degradation rate constants as a function of pH on the sonolysis of DEP and MEP. (●) DEP and (△) MEP.

monoalkyl phthalate including MEP during the test using bacterial indicators was not mutagenic.[19] As sonolysis progresses, the produced MEP began to slowly decompose during the sonolysis at pH 12.

Figure 4 shows the change in the degradation rate constants as a function of pH during the sonolysis of DEP and MEP. The DEP was degraded more quickly than MEP under every pH condition, and the ratio of the degradation rate constants (k_{DEP}/k_{MEP}) was determined to be approximately 7. This suggests that the monoalkyl phthalate with a low hydrolytic reactivity in a natural aquatic environment[20] seems to be degraded more slowly than dialkyl phthalate during the chemical reaction induced by ultrasonic irradiation.

Degradation Pathways. During the sonolysis of DEP, the degradation pathways such as the thermal reaction, OH radical reaction, and hydrolysis at the bubble interface and bulk solution may be predicted from the application of ultrasound and from the physicochemical properties of DEP, i.e., low vapor pressure, hydrophobicity, and hydrolytic reactivity. The degradation pathways for DEP in the presence of ultrasound were estimated using the following experimental processes: (a) The OH radical reaction was estimated from the results of the sonolysis of DEP in the presence of *tert*-butyl alcohol. The degradation of DEP by the OH radical reaction would be completely suppressed. The amount of DEP that reacts with the OH radicals can be calculated from the difference in the amount degraded in the presence and absence of *tert*-butyl alcohol (see Figure 3). (b) The thermal reaction was estimated from the amount of the main gaseous products (CO, CH_4, C_2H_6, C_2H_4, and C_2H_2) formed via pyrolysis during the degradation of DEP. These volatile gases are typical pyrolysis products.[21,22] (c) The hydrolysis that may be considered to be a potential reaction pathway in an aquatic system can be estimated from the amount of the hydrolysis product (MEP). The amount of phthalic acid as the hydrolysis product of MEP was negligible due to the slow reaction rate of MEP for the phthalic acid formation: that is, the rate of phthalic acid formation at high pH (0.05 M NaOH solution) was determined to be about 0.3 μM min^{-1} in the absence of ultrasound at 20 °C. It was confirmed in our experiments that the rate of MEP formation in the presence and absence of *tert*-butyl alcohol was not appreciably changed. Therefore, the possibility of the formation of MEP by OH radical was neglected.

The degradation pathways were estimated by data obtained in initial degradation step (the sonication for 5 min) in order to minimize the effect of degradation products.

Figure 5 shows the proportions of the three reaction pathways that contributed to the sonolysis of DEP as a function of pH.

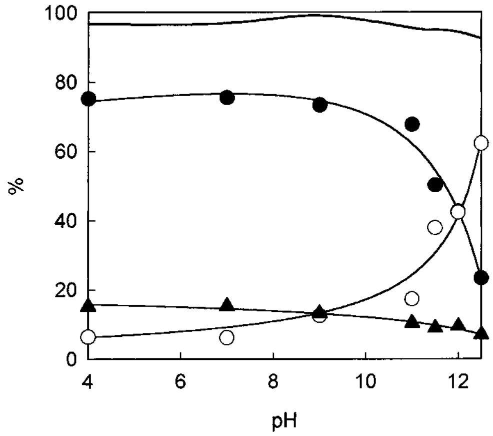

Figure 5. Reaction pathways for the sonolysis of DEP as a function of pH. (●) OH radical reaction, (▲) thermal reaction, (○) hydrolysis, and (—) mass balance.

At pH 4−11, the OH radical reaction appears to be the predominant reaction (occupancy of about 80% in all degradations) and its proportion was independent of pH.

If it is assumed that a large quantity of DEP is locally condensed around the cavitation bubble due to its hydrophobicity, the OH radicals produced from the sonolysis of water would react with DEP at the bubble interface as well as in the bulk solution. A very small amount of OH radicals would then migrate into the bulk solution. There is a competition between the OH radical addition to the aromatic molecules and the recombination of the OH radicals, which were determined have almost the same rate constants on the order of 10^9 M^{-1} s^{-1} at ambient temperature for the various pH ranges.[23] The initial concentration of H_2O_2 determined during the sonolysis of DEP was actually much lower than that of H_2O_2 produced during the sonolysis of pure water (e.g., the 90 μM H_2O_2 was formed by the sonolysis of pure water for 10 min). It appears that the sonolysis of DEP predominantly occurs via the reaction with OH radicals around the cavitation bubble. The thermal reaction and hydrolysis do not extensively contribute to the degradation of DEP, and the rate of hydrolysis was only slightly changed in these pH ranges.

On the other hand, over pH 11, the proportions of the OH radical reaction decreased with an increase in pH, whereas the contribution of hydrolysis appreciably increased. The two reaction pathways were observed to be approximately equal at pH 12, and these proportions were roughly 45% of the entire reaction. However, the degradation via the thermal reaction appears to be only slightly affected by the change of pH. The thermal reaction may occur not inside of cavitation bubble but in the bubble interface due to a low vapor pressure (0.001 mmHg, 25 °C)[2] of DEP.

These results suggest that the OH radical reaction, thermal reaction, and hydrolysis were involved in the degradation of DEP in the presence of ultrasound, and the proportions of each reaction against the whole reaction were changed by the pH of the solution.

Accelerated Hydrolysis in Alkaline Conditions. Several studies have reported that the hydrolysis reaction of esters using ultrasound was accelerated.[24−26] However, no simple description with respect to the sonochemical effect on the acceleration was offered. The existence of supercritical water proposed as an important factor in the acceleration of the sonolytic hydrolysis[27] is particularly interesting, although the possibility of the formation and the role of supercritical water during the sonolysis have been questioned.[28,29]

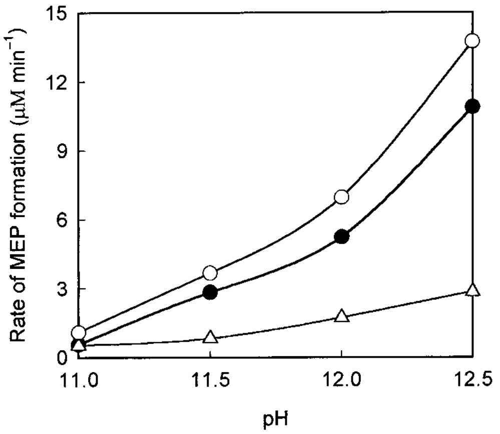

Figure 6. Plots of initial rate of MEP formation in the ultrasonic irradiation and stirring under alkaline conditions. (○) ultrasonic irradiation (R_i(sonic)), (△) stirring (R_i(stirring)), and (●) R_i(sonic) − R_i(stirring). The hydrolysis by stirring was carried out in the absence of ultrasound as a function of pH at 20 °C.

Figure 6 shows the initial rate of MEP formation in the absence and presence of ultrasound as a function of pH. The rates of MEP formation arising from the ultrasonic action alone (R_i(sonic) − R_i(stirring)) are also presented in Figure 6. The rate of MEP formation in the presence of ultrasound was about 2−5 times higher than that in the absence of ultrasound in the range of pH investigated, and these were dependent on the pH. It appears that the chemical effects of ultrasound probably play an important role in the sonolytic hydrolysis of DEP, therefore, the accelerated hydrolysis of DEP in the presence of ultrasound can be suggested.

The activation energy for the hydrolysis of DEP was estimated from the experiments in the absence of ultrasound at pH 12.

$$\ln k = \frac{-E_a}{RT} + \ln A \qquad (1)$$

where E_a is the activation energy (J mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}), and A is the preexponential factor. Using the slope ($-E_a/R$) and intercept (ln A) obtained from Arrhenius plots for solutions in the absence of ultrasound, the activation energy (E_a) and the preexponential factor (A) can be evaluated. The E_a for the hydrolysis of DEP was experimentally determined to be 50 kJ mol^{-1} from the kinetic data. Assuming that the sonolytic hydrolysis follows an Arrhenius behavior with the same E_a, the reaction temperature was calculated to be 337 K from the Arrhenius plots when the rate constants of the sonolytic hydrolysis was equal to that of the hydrolysis in the absence of ultrasound at same pH. The sonolytic hydrolysis would leads to the effect corresponding to a 44 °C rise in temperature on the hydrolysis in the absence of ultrasound. It appears that this temperature would be the average reaction temperature in this heat dissipation region containing the regions of higher and lower temperature to yield this reaction temperature. Thus, in the vicinity of the cavitation bubble, the effect of heat dissipated by the collapsing of the cavitation bubble should be an important factor for the chemical reaction using ultrasound irradiation.

The occurrence of a sphere (including interface region and supercritical temperature region) spreads from the surface of the cavitation bubble is of interest in hydrolysis reactions of environmental contaminants, since the temperature in the around of the cavitation bubble is somewhat low for the pyrolysis but sufficient for the acceleration of hydrolysis. It appears that the sonolytic hydrolysis of a substance, which tends to be concentrated at the bubble interface due to their physicochemical properties, can be achieved more effectively.

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