Sonochemical degradation of various monocyclic aromatic compounds: Relation between hydrophobicities of organic compounds and the decomposition rates

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Abstract

Various aromatic compounds, i.e., nitrobenzene, aniline, phenol, benzoic acid, salicylic acid, 2-chlorophenol, 4-chlorophenol, styrene, chlorobenzene, toluene, ethylbenzene and n-propylbenzene were decomposed under identical ultrasonic irradiation conditions. The relationships between the initial rates of degradation of these aromatic compounds and their physicochemical parameters were systematically investigated. It was revealed that some correlations between the degradation rates and parameters of volatility, Henry’s law constant and vapor pressure, were observed only in the limited high range of parameters. It was suggested that the Henry’s law constant and vapor pressure had influenced on the rate of degradation for some of the tested aromatic compounds. In contrast, better correlations between the initial rates of degradation and hydrophobic parameters, water solubility and Log P (water–octanol partition coefficient), were observed over the wide range of chosen parameters. These results meant that the hydrophobicity of the compounds significantly affected their accumulation at the gas–liquid interface of the bubbles and it was the most important factor for the sonochemical degradation of aromatic compounds. In particular, for the sonolysis of water-insoluble organic compounds, Log P was found to be the representative parameter for understanding the hydrophobic properties of water-insoluble compounds.

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1. Introduction

A large number of chemical compounds have been produced along with advances in technologies and industries, in which multiple by-products are also concomitantly produced [1,2]. In general, most of the aromatic compounds, which did not originally exist in the environment, are toxic and carcinogenic, therefore they are not easily biodegraded and are persistent under various environmental conditions [3,4]. It is well known that polychlorinated biphenyl, dioxin and alkyl phenol are extremely hazardous aromatic compounds [5,6]. To treat such wastes, many types of techniques are being actively studied: adsorption treatments with activated carbon, biological treatments and advanced oxidation processes (AOP) such as ozonation treatment, Fenton reactions, photolysis and radiolysis are reported [7–9].

Ultrasonic irradiation in water brings about the formation and collapse of small gas bubbles. During the collapse, local reaction site of several thousand degrees and several hundred atmospheres are produced due to the quasi-adiabatic collapse [10,11], while the bulk liquid temperature hardly changes. This process is known as cavitation which accompanies the generation of a shockwave, the emission of light, etc. During the cavitation, it is expected that specific chemical reactions proceed so that the application of ultrasonic cavitations to waste water treatments are being intensively evaluated as the development of a new technique.
In general, sonochemical degradation of organic pollutants proceeds via a reaction with OH radicals, which are formed from water pyrolysis in the collapsing hot bubbles and/or at the interface region of the hot bubbles. For the volatile or hydrophobic pollutants, the degradation proceeds not only via the OH radical reaction, but also via a direct pyrolysis reaction in the collapsing hot bubbles and at the interface of the bubbles. Wu and Ondruschka [12] studied the aquasonolysis of volatile substrates, such as cyclic C₆H₅, aliphatic C₆H₅, thioethers, thiophenes, and N-heterocyclic compounds. Based on their report, it was concluded that the transfer process of organic substrates from the bulk liquid to cavitational bubbles and their aquasonolytic kinetics are both controlled by the hydrophobicity and volatility of their substrates. Their report was in good agreement with our previous results [13].

The sonochemical degradation rates of a number of aromatic organic compounds have been shown to be strongly dependent upon their hydrophobicity. While such a dependency has already been proposed in previous reviews [14,15], a systematic study has not yet been performed. Each monocyclic aromatic compound has individual properties specific to its functional groups, so it is difficult to predict their rates of sonolysis. In this study, the sonochemical degradation of various kinds of monocyclic aromatic compounds in an aqueous solution was investigated, and the degradation mechanism was also elucidated. Our result is the first example to clarify systematically the relationship between the properties of the compounds and the degradation rates of the aromatic compounds. In addition, we propose how to predict the rates of sonochemical degradation of aromatic compounds in water.

2. Experimental

Nitrobenzene, aniline, phenol, benzoic acid, salicylic acid, 2-chlorophenol, 4-chlorophenol, styrene, chlorobenzene, toluene, ethylbenzene and n-propylbenzene were chosen from a variety of aromatic compounds. All the aromatic compounds were supplied by Wako Pure Chemical Industries, Ltd., and used as received. Table 1 shows their physicochemical parameters which were obtained from the SRC PhysProp Database [16]. All of the sample solutions containing aromatic compound were prepared with Milli-Q water. To minimize some effects of the aromatic compound molecules and their reaction products on the cavitation phenomena, the sonolysis were carried out at a very low concentration solution (100 μM) of aromatic compounds.

Ultrasonic irradiation was carried out using a 65 mmϕ oscillator (Kaijo 4611type; MFG. No.37G4) and an ultrasonic generator (Kaijo TA-4021type; Lot. No.19G9, frequency; 200 kHz), which was operated at 200 W. The details of the irradiation set-up and the characteristics of the reaction vessel are described elsewhere [17]. A 60 mL Ar-saturated aqueous solution containing each aromatic compound was sonicated in a water bath, which was maintained at 25 °C by a cold water circulation system (TAITEC CP-150R). The reaction vessel was sealed during the irradiation in the Ar atmosphere.

The concentration of each aromatic compound in aqueous solution was monitored by a high-performance liquid chromatograph (HPLC) (Shimadzu LC-20AT, SPD-20AV) with UV detection at 223 nm using a C18 column with a mobile phase of acetonitrile/water (40:60 v/v) flowing at 0.3 mL min⁻¹. The initial rate of degradation (within 3 min) was estimated on the basis of the average of several experimental runs. Since it was reported that the rate of sonolysis does not obey zero- and first-order kinetics [18], the initial rate of degradation was used for the analysis of the obtained data.

3. Results and discussion

The prompt degradation of solutes was observed during the sonolysis of aromatic compounds in aqueous solution. These results correspond with the report by Nagata et al. [19] for the sonolysis of chlorophenol, chlorobenzene, etc. The initial degradation rates of the aromatic compounds and their physicochemical parameters such as the rate constant, volatility; hydrophobicity, etc. are described in Table 1. It was observed that there are significant differences in...
the degradation rates among the aromatic compounds from 2 to 14 μM/min. There are two pathways for the sonochemical reactions in aqueous solution. One is the thermolytic reactions that occur in the hot cavitation bubbles and/or at the gas–liquid interface of the bubbles. The other is the reactions involving hydroxyl radicals at the gas–liquid interface of the bubbles and in the bulk liquid [20,21]. Okuno et al. reported that chlorobenzene and dichlorobenzene were mainly pyrolyzed in the cavitation bubbles and at the interface of the bubbles [22]. On the other hand, Berlan et al. reported that the degradation of phenol and its chloro/nitro derivatives occurs mainly in the bulk solution by hydroxyl radicals [23]. To discuss the effect of hydroxyl radical reaction, the correlation between the initial rates of sonochemical degradation and the rate constants of the OH radical with selected aromatic compounds in aqueous solution was investigated.

Fig. 1 shows the relationship between the initial rates of degradation and the rate constants of the OH radicals, which were obtained from the literature [24]. As seen in Fig. 1, the initial rates of degradation were not simply dependent on the rate constants of the OH radicals with organic solutes. The results are due to that the accumulation of the aromatic solutes occurs in the bubbles and/or at the gas–liquid interface of the bubbles, indicating that the concentration of organic solutes becomes inhomogeneous in solution as previously reported [18]. It was considered that most of the aromatic compounds are relatively hydrophobic compared with water, so they tend to accumulate at the gas–liquid interface of the bubbles and decrease the surface free energy of the bubbles. In fact, this tendency was in good agreement with the report by Okitsu et al., [18] where the sonolysis of organic compounds predominantly occurs at the gas–liquid interface of the bubbles.

To discuss why the rates of the sonochemical degradation are different among the various aromatic compounds, we considered several parameters of the organic compounds taking into account the properties of the cavitation reaction field. At first, in the case of the pyrolytic decomposition of aromatic compounds which were reported by Ciawi et al. [25] and Okuno et al. [22], the Henry’s law constant and the vapor pressure should be considered because such parameters affect the condensation of solutes inside the cavitation bubble. The Henry’s law constant of a compound, at the air–water distribution equilibrium, is defined as,

\[ K_H = \frac{P}{C} \]

where \( K_H \) (atm m\(^3\) mol\(^{-1}\)) is the Henry’s law constant, \( P \) is the partial pressure of the chemical species in the gas phase, and \( C \) is the aqueous phase concentration of the solute.

Fig. 2 shows the relation of the Henry’s law constant of organic solutes to the rate of degradation. It was revealed that some correlations between them are observed only in the limited high range of the Henry’s law constant. It is considered that there would be a threshold value for the pyrolysis of solutes. Fig. 3 shows the relation of the vapor pressure of the organic solutes to the rate of degradation. In the case of vapor pressure, similar relationship was observed as in the case of the Henry’s law constant (Fig. 2), because both parameters are comparable physico-
chemical indicator for organic solutes. That is, the more these parameters increase, the more the solutes diffuse into the bubbles inside and undergo pyrolytic decomposition during bubble collapse. It was also suggested that some aromatic compounds with a high volatility are rapidly decomposed in comparison with low volatile compounds. Accordingly, the effects of the Henry’s law constant and vapor pressure might be one of the predominant parameters that control the rate of degradation of all the tested aromatic compounds.

It has been reported that the hydrophobicity of an organic solute is one of the most important parameters for sonochemical reactions, because highly hydrophobic compounds tend to concentrate at the gas–liquid interface [26,27] in which the concentration of OH radicals is very high [28]. The water solubility and Log $P$ (water–octanol partition coefficient) are considered as hydrophilic and hydrophobic parameters of organic compounds, respectively. The octanol/water partition coefficient ($P$) is defined as the ratio of a chemical’s concentration in the octanol phase to its concentration in the aqueous phase of an octanol/water binary system. The common logarithm of $P$ is synonymous with Log $P$.

The relationship between the water solubility of the organic solutes and the initial rate of degradation is shown in Fig. 4. It can be seen that there are some mutual relations only in the limited low range of water solubility and the degradation rates increase with decreasing the water solubility. Fig. 5 shows the relationship between Log $P$ and the initial rates of decomposition of the corresponding organic solutes. It was found that Log $P$ was the clearest correlation parameter in all the relationships between the properties of the organic solutes and the initial rates of degradation. Therefore, it can be interpreted that there is a little difference between water solubility and Log $P$. The correlation between the water solubility and Log $P$ is shown in Fig. 6. This result shows that Log $P$ incompletely has a linear relation with the water solubility. These mean that the Log $P$ of the compounds significantly affects the sonochemical degradation rates and Log $P$ is the most important parameter of aromatic compounds for
concentrating onto the gas–liquid interface of bubbles during the ultrasonic degradation. Then the accumulated organic compound on the gas–liquid interface and/or inside the gas bubble is effectively decomposed by the direct pyrolysis [22], the reaction with OH radicals [23] and the direct hydrolysis with water molecules [29].

It has been proposed that the surface excess can be used as a hydrophobic parameter in sonochemistry by Price et al. [30] and Yang et al. [31]. The chemical effects of the ultrasound result from the quasi-adiabatic collapse of the cavitation bubbles. When the reaction occurs at the gas–liquid interface of the bubbles, the surface excess should directly affect the sonochemical degradation. In general, the surface excess can be calculated for water-soluble organic compounds: The surface excess can be calculated from the change in the surface tension using the Gibbs–Duhem equation [32], where the measurement of the surface tension is needed for the aqueous solution of the organic solutes. Therefore, if hydrophobic compounds are hard to dissolve in water, the surface tension and the surface excess of their aqueous solutions could not be obtained. On the other hand, \( \log P \) can be readily calculated for many organic compounds. Therefore, for the sonolysis of water-insoluble organic compounds, \( \log P \) is the representative parameter for understanding the hydrophobic properties of water-insoluble compounds.

The ultrasonic power and frequency affect on the size and number of cavitation bubbles as well as cavitation dynamics. In addition, the initial concentration of aromatic compound and bulk temperature would also affect the cavitation phenomena. Therefore, further studies would be needed to clear the relation between the rate of sonochemical degradation and cavitation phenomena.

4. Conclusions

The good correlation between the hydrophobic parameter and the initial rates of degradation of selected aromatic compounds was observed, suggesting that the aromatic solutes concentrate at the gas–liquid interface of the bubbles, and the concentration of the solution become inhomogeneous at the interface region. In addition, the aromatic compounds with a high volatility would be pyrolyzed in the hot bubbles and their surface. Accordingly, it was confirmed that the gas–liquid interface and/or inside the bubbles were the main reaction sites, and it was found that the accumulation of aromatic compounds at the interface of the bubbles is important for their effective degradation. The hydrophobic parameter, especially \( \log P \), significantly affected the sonolysis of the aromatic compound in aqueous solution. The rates of degradation of aromatic compound could be estimated using the known \( \log P \) value without determining the surface excess value.

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