



## Mechanism and kinetics of reductive dehalogenation of PBB (polybrominated biphenyl) in the sonolytic and ketyl radical system

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### ABSTRACT

The kinetics and mechanism of reductive destruction of aqueous polybrominated biphenyl (PBB) were studied. Complete degradation was achieved within 30 min of ultrasound-assisted chemical process (UACP), which involved sonication, ketyl radical and its anion, and metal catalyst (ferrous ion). Reductive dehalogenation of PBB is a first-order reaction between PBB concentration and UACP reaction time. The kinetic condition of PBB degradation was optimized in terms of temperature, dosage of radical initiator, and metal catalyst. Mechanism of reductive debromination was also proposed to explain the function of ketyl and aryl radicals on the debromination of bromobiphenyl. Two kinetic models were studied to elucidate the debromination mechanism pathway. Laboratory observed data were found to fit model predicted values obtained from equilibrium and differential equations.

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### 1. Introduction

Polyhalogenated biphenyls including PBBs (polybrominated biphenyls) and PCBs (polychlorinated biphenyls) are widespread in the environment. Virtually, all electronic equipment and electrical products contain brominated flame retardants that have fire protection effect. These substances are also added to the manufacture of textiles, plastic materials, and building materials, which may result in spreading over the environment such as sediment where they degrade at very slow rate and in being concentrated through food chains in animal and human body. Due to the potential adverse health and environmental effect, their use had been prevented and accordingly remediation technologies for these had become a center of attention. For years, landfill disposal has been a common and deceptive practice. However, it was proved to be ineffective due to the chemical persistency and high toxicity of PBBs and PCBs. In this sense, many destructive methods had been utilized for the treatment of soil, sediment, and water contamination of these recalcitrants. Incineration was most used, while more toxic oxygenated derivatives can be produced in the system of incineration. The anaerobic degradation of microbial

activity had also been widely experimented and used [1]. Microbial method is time-consuming and requires too many factors and conditions for the appropriate removal efficiency. Oxidative method with radicals had been studied in destructing a great number of toxic chemical compounds. PCB destruction and oxidative kinetic mechanism were investigated, using UV/oxidants [2]. PCBs had been widely studied due to their commercial availability and well-known toxicity. However, studies on PBBs are somewhat rare, because bromine was considered to be easily removed. Bromine is lost from haloaliphatic compounds more readily than chlorine [3]. Not much research was conducted using ultrasound and ketyl radical in the reductive system. The kinetic study on destruction of PBBs can be important base to further understand the removal mechanism of PCBs and associated recalcitrants.

Since polyhalogenated biphenyls are resistant to the oxidative degradation, a reductive dehalogenation was induced, converting polyhalogenated biphenyls to readily biodegradable biphenyls by the cleavage of carbon–halogen bonds. For a model compound of PBB, 4,4'-DBB (dibromobiphenyls) was used in this study. PBB is more chemically reactive in the reductive process than PCB, due to the lower bond energy [4]. Others [5] found that hexabromobiphenyl was seven times more reactive than PCB.

The ultrasound-assisted chemical process (UACP) has been applied to a number of environmental recalcitrants and found to

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be a very effective method. Ultrasonic mechanisms are well documented in literatures [6–10], as follows; (a) hydrodynamic shear force created by acoustic microstreaming sufficient to cleave the large macromolecules, (b) acoustic streaming with its associated shearing force to enhance solute dispersion, and radical encountering with solute and its transport in the solution, (c) local high temperature with which reaction pathways are similar to combustion [11] and high pressure generated by collapsed microbubbles, (d) formation of free radicals at the center of a collapsing bubble for polymerization or depolymerization, and (e) surface phase transfer of target compound possibly induced by mechanical and physicochemical forces. Many UACP successful studies include the destruction of chloroform and other THMs [12], the upgrading of heavy oil; asphaltenes [13–15], the degradation of polynuclear aromatic hydrocarbons [16], the degradation of propellants [17], the destruction of porphyrin and metalloporphyrins [18], the degradation of alkylphenol ethoxylate with ultrasonic irradiation and upgrading process of asphaltenes through cavitation and surfactants [9,19], the degradation of methyl *tertiary*-butyl ether (MTBE) [20], the decolorization of chromophores of metallophthalocyanines [8], the macromolecule polymer devulcanization [6], the desulfurization in diesel fuel [21], the denitrogenation of petroleum and nitrogen containing compounds [22], and ultrasound-assisted oxidative desulfurization (UAOD) with innovative catalyst [23]. In this study, the ultrasonic effect was not mentioned thoroughly because of well-studied experiments listed above. So, the sonolytic experiments were carried out based on the fact that more effective condition of debromination including the chemical and physical reaction upgrade is expected when ultrasound is used with other chemical additives. Truly, ultrasonic reaction was found to help generate the free radicals and shorten the entire experimental time to obtain the target removal efficiency [7]. The degradation efficiency became more increased when ultrasound was in combination with free radicals [6].

Debromination of 4,4'-dibromobiphenyl (DBB) in an alkaline 2-propanol solution at moderate temperature with DTBP (di-*tert*-butyl peroxide) as a free radical initiator and ferrous chloride as a metal catalyst, was investigated. Reaction mechanism and kinetic study were emphasized in this study. Two kinetic models were compared to find the model that is more suitable for experimental results. The laboratory observed data are found to have a close match with computed values from mathematical method. This study can make a fundamental base for further studying the reductive destruction of PCB and related compounds.

## 2. Materials and methods

4,4'-Dibromobiphenyl was obtained from Eastman Kodak. Biphenyl, 4-monobromobiphenyl (4-MBB) and DTBP were purchased from Aldrich. All solvents involved in this study were purchased from Fisher Scientific. Ferrous chloride (2/4 hydrates) and ferric chloride (6 hydrates) were from Mallinckrodt. Ferrous sulfate (7 hydrates) was obtained from J.T. Baker. The reaction reagent was simply prepared by mixing 2 g of NaOH and 0.15 g of 4,4'-DBB in 500 mL of 2-propanol overnight. 2-Propanol is widely used for the domestic purpose and biodegradable, and its use is relatively safe.

Ultrasonic irradiation was performed in a high-intensity ultrasonic cleaning tank (ATH 610-6) and power generator (EMA 30-6). This unit has a 15.24 cm (W) × 25.4 cm (L) × 25.4 cm (H) dimension of stainless steel tank with a built-in thermostatically controlled heating element to maintain the liquid in the tank at constant temperature. Six piezoelectric 50-W transducers were mounted directly to the bottom of the cleaning tank. They can produce 300 W

at a fixed frequency of 40 kHz. In this study, one kind of ultrasonic frequency was used.

For the optimum condition of experiment, 25 mL of alkaline solution was distributed to a 40 mL vial of an appropriate amount of ferrous chloride. The vial was immediately capped with an airtight septum, and flushed with ultra-high pure nitrogen for 5 min at 4 psi to secure the nitrogen environment. After the addition of fixed volume (0.5 mL) of DTBP to the solution, the vial was placed in a water tub, which was preheated at 55 °C. A magnetic stirrer was placed in the vial for complete mixing during ultrasonic irradiation. An aliquot (0.5 mL) of sample was withdrawn for comparative analysis after 30 min of reaction. In addition, three different catalysts such as ferrous chloride (2/4 hydrates), ferrous sulfate (7 hydrates), and ferric chloride (6 hydrates) were tested to evaluate the optimum system under the same condition. For the optimum condition of system, the dosage of DTBP and effect of temperature were also evaluated.

Samples (0.5 mL) withdrawn from the reactor were diluted with 4.5 mL of deionized/distilled water and the mixture was extracted with 10 mL of hexane by hand shaking for 2 min. Two microliters of hexane extract were held for gas chromatographic (GC) analysis. All compounds were determined by gas chromatograph machine (Hewlett-Packard 5880A) with a flame ionization detector (DB-608 capillary column: J&W Scientific Inc.) and an integrator (3990A) manufactured by Hewlett-Packard. GC operation was as follows; the oven programmed to start at 110 °C (hold 3 min), then ramp to 280 °C (hold 3 min) at 5 °C/min, injection port temperature at 240 °C, detector temperature at 280 °C, and helium as both carrier gas (6 mL/min) and make-up gas (25 mL/min). The high sensitivity of gas chromatogram was observed for the peak separation of biphenyl, 4-MBB, and 4,4'-DBB, respectively.

Ferrous ion was determined by the phenanthroline method. Ammonium acetate buffer and phenanthroline solution were prepared as in Standard Method. Ferrous ion test solution was prepared by mixing the three solutions with DI water at a ratio of HCl (1): phenanthroline solution (40): ammonium acetate buffer (20): DI water (39). Samples of 5 mL were withdrawn from the reactor during the ultrasonic reaction and transferred to a cuvette previously loaded with the ferrous ion test solution. The concentration of ferrous ion was quantified with the UV-vis spectrophotometer (Hewlett-Packard 8452A). The wavelength of concern is 510 nm.

In the kinetic experiment, the optimal conditions that were discovered in the preliminary test, were applied for 60 min of reaction time in order to identify that a simplified kinetic expression would be acceptable as a rate reaction. An aliquot (0.5 mL) of sample was withdrawn from the reactor using a micro syringe every 5 min without any interruption of reaction. The water temperature was monitored throughout the experiment. It took 5 min for the temperature inside the reactor to reach 55 °C. Three components such as biphenyl (BP), 4-MBB, and 4,4'-DBB were measured using the GC. The total concentration of three components was to be 0.943 mM.

## 3. Results and discussion

### 3.1. Effect of catalyst

Ferrous ion in combination with hydrogen peroxide, generates hydroxyl radicals which are effective in the destruction of halogenated compounds. Ferric ion with hydrogen peroxide exhibited the same effect but to less strength. Basically, ferric ion served as a catalyst to induce the decomposition of hydrogen peroxide, yielding O<sub>2</sub>, H<sub>2</sub>O, and ferrous ion [24]. Additionally, since ferrous sulfate had been successfully used as the source of ferrous ions in the ultrasonic process with H<sub>2</sub>O<sub>2</sub>, ferrous sulfate was tested for the source

of ferrous ions in the experiment. Ferric chloride was used for the source of ferric ions as well.

Under the same condition, the addition of ferrous chloride reduced 80% of 4,4'-DBB in 15 min, while the addition of either ferrous sulfate or ferric chloride had little reduction. Both ferrous chloride and ferric chloride are soluble in the solution of 2-propanol, but ferrous sulfate is insoluble in 2-propanol. Either ferrous or ferric ion, when with ligands, cannot function as a catalyst provided all the coordination sites on the metal ions were occupied [25]. In other words, only the soluble free metal ions or metal complexes with unoccupied or available coordination sites can be effective as catalysts. In the experiment, it was observed that ferrous chloride with higher solubility in 2-propanol solution, induced more decomposition of DTBP, on the other hand, ferrous sulfate could not cause any significant reduction of 4,4'-DBB because of the lower number of ferrous ions available. Also, there was no noticeable reduction of 4,4'-DBB, although ferric chloride was soluble in 2-propanol solution. This indicates that ferric ions may not act as a catalyst like ferrous ions do. Ferric ions were also found to be hardly reduced to ferrous ions in this experiment. It is reasonable to choose the ferrous chloride for the effective catalyst with regards to decomposition of DTBP. But, the excessive amount of ferrous ions may hinder the reaction.

### 3.2. Effect of temperature

The decrease of concentration of 4,4'-DBB at different temperatures such as 35 °C, 45 °C, and 55 °C were observed. Although DTBP is unstable at temperatures in excess of 100 °C, it still showed little degradation in the solution of 2-propanol at 80 °C without any addition of ferrous ions. The reaction rate increased with increasing temperature with ferrous ions. The optimum temperature of degradation of DTBP was selected to be 55 °C, since more than 95% of bromine atoms were removed from biphenyl ring of its chemical structure within a certain ultrasonic time.

### 3.3. Effect of free radical

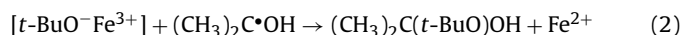
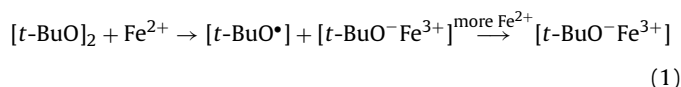
DTBP is one of the most studied dialkyl peroxides and is thermally unstable. At 80 °C it decomposes to the *t*-butoxyl radical, which gives the ketyl radical upon H-abstraction from the 2-propanol solution. It has been widely documented that metal ions such as Fe<sup>2+</sup>, Cu<sup>2+</sup>, and Co<sup>2+</sup>, accelerate the decomposition of dialkyl peroxides by one-electron transfer mechanism [26]. Therefore, the solubilized Fe<sup>2+</sup> can be expected to increase the decomposition of di-*t*-butyl peroxide, (CH<sub>3</sub>)<sub>3</sub>COOC(CH<sub>3</sub>)<sub>3</sub> (or [t-BuO]<sub>2</sub>), in 2-propanol, by breaking the relatively weak O–O bond. This is induced to generate the *t*-butoxyl radical, (CH<sub>3</sub>)<sub>3</sub>CO• (or *t*-BuO•), which is electrophilic in nature. Thus, the electron-donating OH group on 2-propanol will encourage the attack of *t*-butoxyl radical on α hydrogen of 2-propanol. Furthermore, α hydrogen on 2-propanol is a secondary hydrogen which is more reactive than primary hydrogen attached to β carbon. Therefore, the major radical produced in this system is the ketyl radical, (CH<sub>3</sub>)<sub>2</sub>C•OH, which is a nucleophilic radical with hydroxyl group. The ketyl radicals are thus regenerated in the chain reaction between the *t*-butoxyl radical and 2-propanol. The reductive debromination cycle is thermally reproduced through DTBP as a free-radical initiator.

At 0.25 mL of DTBP, regardless of the amount of ferrous chloride, 4,4'-DBB could not be completely removed in the solution after 30 min of reaction time. It was seen that complete debromination occurred with 0.5 mL and 0.75 mL of DTBP as well as 0.025 g of ferrous chloride for 30 min of the ultrasonic reaction.

### 3.4. Optimization of experimental conditions

For the reaction conditions, experiments were conducted in 25 mL of alkaline (0.1 M NaOH) 2-propanol solution for different ultrasonic times at 55 °C under the nitrogen-controlling environment. DTBP was added in the volume of 0.25 mL, 0.5 mL, and 0.75 mL with 0.0125 g, 0.025 g, 0.05 g, and 0.075 g of ferrous chloride, respectively. The largest reduction of 4,4'-DBB was found at the dosage of 0.025 g of ferrous chloride and 0.5 mL of DTBP.

For dosages of more than 0.025 g of DTBP or less, the rate of debromination was shown to be decreased in this study. Even more amount of ferrous chloride was not effective in increasing the degradation rate. This may be explained by the fact that the excessive amount of ferrous ions may react with *t*-butoxyl radicals, *t*-BuO•, to form *t*-BuO<sup>-</sup>Fe<sup>3+</sup> due to the cage effect (see Reaction (1)). This reaction will reduce available *t*-butoxyl radicals and, consequently, decrease the amount of the ketyl radical (CH<sub>3</sub>)<sub>2</sub>C•OH. Furthermore, the increase of BuO<sup>-</sup>Fe<sup>3+</sup> concentration may consume more ketyl radicals according to Reaction (2). Since ketyl radicals are essential in the process, their concentration decrease will reduce the debromination effect.



In another set of experiments, instead of freshly obtained ferrous chloride, the old and partially oxidized ferrous chloride was intentionally used to see how ferrous chloride works as a metal catalyst. The similar trend of experimental results using fresh ferrous chloride was observed for the experiment using old ferrous chloride, except for the optimum amount of ferrous chloride that is needed to reach the complete removal percentage. In Fig. 1, the debromination reaction proceeds as the dosage of old ferrous chloride increases. For the old ferrous chloride, optimum amount was 0.05 g while fresh ferrous chloride was 0.025 g for the complete removal of 4,4'-DBB. This may indicate that ferric ions cannot serve as a catalyst in the process, since ferrous ions are to become ferric ions rather than a metal initiator after oxidation. This fact is supportive of selection of ferrous ion as a reductive metal initiator.

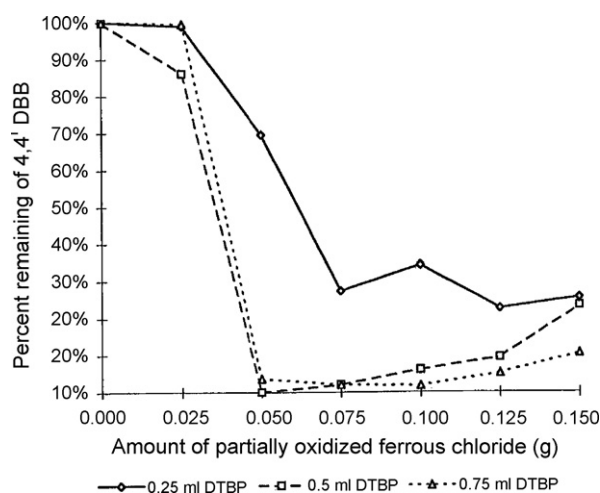


Fig. 1. The concentration variations of 4,4'-dibromobiphenyl (DBB) at different amounts of old, partially oxidized ferrous chloride with three different amounts of DTBP in the condition of 30 min of sonication time and 55 °C of temperature.

### 3.5. Reaction mechanism

The average O–O bond energy is approximately  $37 \pm 1 \text{ kcal mol}^{-1}$  ( $155 \pm 5 \text{ kJ mol}^{-1}$ ), which is the smallest when compared with other single bond energies such as C–O bond ( $84 \text{ kcal mol}^{-1}$ ), C–H bond ( $101 \text{ kcal mol}^{-1}$ ), and C–C bond ( $84 \text{ kcal mol}^{-1}$ ) [27,28]. The weak O–O bond in dialkyl peroxide can be somewhat easily cleaved upon thermolysis or photolysis to form alkoxy radicals ( $\text{ROOR} \rightarrow 2\text{RO}^\bullet$ ). Although thermal homolysis of dialkyl peroxides occurs readily at temperature in excess of  $100^\circ\text{C}$ , facile hemolytic decomposition also occurs at lower temperature in the presence of a catalytic amount of metal ions such as manganese(II), cobalt(II), copper(II), and iron(II) which readily undergo an one-electron redox reaction ( $\text{ROOR} + \text{M}^{+n} \rightarrow \text{M}^{+(n+1)} + \text{RO}^- + \text{RO}^\bullet$ ).

In the presence of ferrous ion, DTBP is readily decomposed to the *t*-butoxyl radical,  $t\text{-BuO}^\bullet$  at a moderate temperature (Reaction (3)). Subsequent hydrogen abstraction from 2-propanol by  $t\text{-BuO}^\bullet$  gives the ketyl radical  $(\text{CH}_3)_2\text{C}^\bullet\text{OH}$  (Reaction (4)). In an alkaline medium, the ketyl radical loses a proton to produce the ketyl radical anion  $(\text{CH}_3)_2\text{CO}^{\bullet-}$  (Reaction (5)). Through an electron transfer process, the ketyl radical anion reacts with  $\text{ArBr}$  (e.g., 4,4'-DBB) to generate an unstable aryl radical anion,  $\text{ArBr}^{\bullet-}$ , which upon cleavage, would provide the bromide anion,  $\text{Br}^-$  and aryl radical,  $\text{Ar}^\bullet$  (Reaction (6)). This aryl radical abstracts hydrogen from 2-propanol to help produce another ketyl radical (Reaction (7)), and would in turn start the reductive cycle of chain reactions as depicted in Fig. 2 [29]. The aryl radical is as important as the ketyl radical in the reaction. Not only aryl and ketyl radicals, debromination mechanisms also involving the formation of ketyl and aryl radical anion are relatively fast and efficient, and may serve as a basis for a PBB destruction technology.

This chain reaction can be terminated by removing intermediates such as  $(\text{CH}_3)_2\text{C}^\bullet\text{OH}$  and  $(\text{CH}_3)_2\text{CO}^{\bullet-}$  (Reactions (8–10)). The chain reaction can also be blocked by oxygen or other compounds which can compete with  $\text{ArBr}$  for the electron from  $(\text{CH}_3)_2\text{CO}^{\bullet-}$ . Generally, it is insignificant that a *t*-butoxyl radical may yield acetone and a methyl radical upon fragmentation as long as there is a reasonable amount of reactive hydrocarbon substrates in the solution [30]. Since the 2-propanol solution as a solvent in the process can amply provide the reactive hydrocarbon substrates, the fragmentation of *t*-butoxyl radical is only minor reaction. And the possible oxygen inhibitor is minimal.

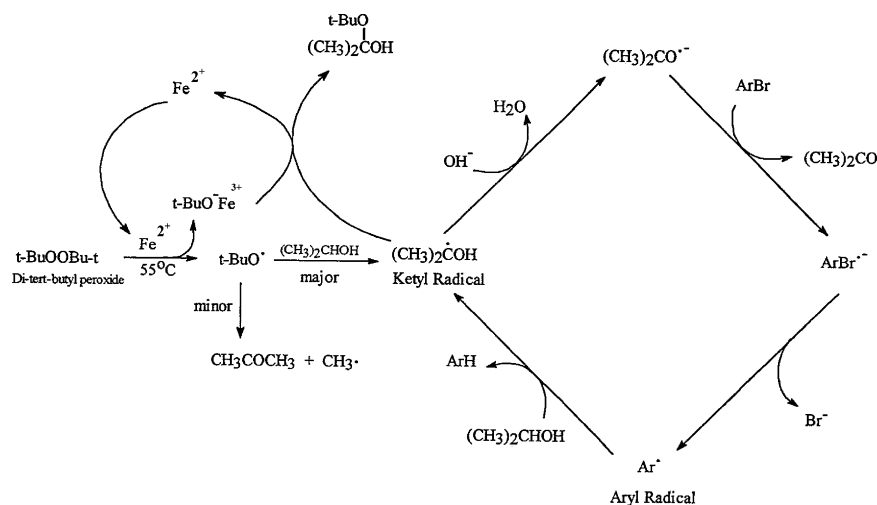
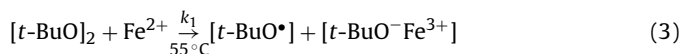
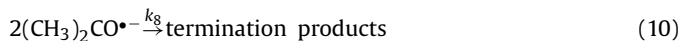
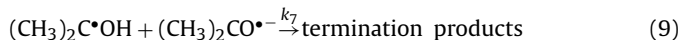
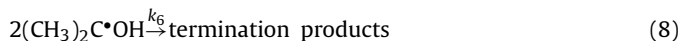
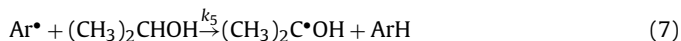
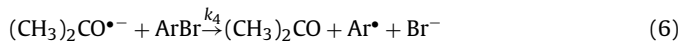
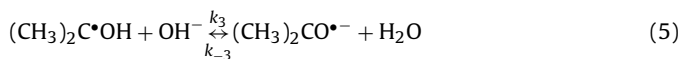
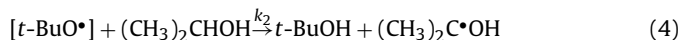


Fig. 2. The reductive debromination pathway of polybrominated biphenyl in alkaline 2-propanol, modified after [29].



### 3.6. Kinetic study

The kinetic expression was developed from proposed mechanism and compared with experimental data. The derived kinetic expression was simplified with associated assumptions. Two kinetic models were separately evaluated, plotted with observed laboratory results. The kinetic expression with Bodenstein steady state approximation was derived.

The Bodenstein approximation is that the intermediates do not accumulate to an appreciable amount during the reaction. It can be recognized that after a certain time of initial reaction, the rate of formation of intermediates is likely to be equal to their rate of destruction. The approximation is more suitable for the lower concentration of intermediates in steady state, which may commonly happen. For this approximation, non-accumulating intermediates should be noted in terms of concentrations of stable reactants and magnitudes of the rate coefficients for each step of the entire reaction. The proper kinetic expression for the mechanism can often be made, once the expression for intermediate concentrations is developed [31].

Therefore, the Bodenstein approximation is appropriate for two kinds of reaction mechanisms: (1) Transitory intermediates may either revert to reactants or proceed to products. (2) One or more intermediates do not revert to reactants but are regenerated in a subsequent chain reaction [31]. The proposed reductive dehalogenation belongs to the latter. Considering the proposed mechanism and the Bodenstein approximation for the steady state condition, the changes of rates of formation and destruction for

each propagating radical are equivalent to zero. The relationships can be stated as follows:

$$\frac{d[t\text{-BuO}\cdot]}{dt} = 0 = k_1[t\text{-BuO}]_2[\text{Fe}^{2+}] - k_2[t\text{-BuO}\cdot][(\text{CH}_3)_3\text{CHOH}] \quad (11)$$

$$\begin{aligned} \frac{d[(\text{CH}_3)_2\text{C}\cdot\text{OH}]}{dt} = 0 = & k_2[t\text{-BuO}\cdot][(\text{CH}_3)_2\text{CHOH}] \\ & + k_5[\text{Ar}\cdot][(\text{CH}_3)_2\text{CHOH}] + k_{-3}[(\text{CH}_3)_2\text{CO}\cdot^-] \\ & - k_3[(\text{CH}_3)_2\text{C}\cdot\text{OH}][\text{OH}^-] - 2k_6[(\text{CH}_3)_2\text{C}\cdot\text{OH}]^2 \\ & - k_7[(\text{CH}_3)_2\text{C}\cdot\text{OH}][(\text{CH}_3)_2\text{CO}\cdot^-] \end{aligned} \quad (12)$$

$$\begin{aligned} \frac{d[(\text{CH}_3)_2\text{CO}\cdot^-]}{dt} = 0 = & k_3[(\text{CH}_3)_2\text{C}\cdot\text{OH}][\text{OH}^-] - k_{-3}[(\text{CH}_3)_2\text{CO}\cdot^-] \\ & - k_4[(\text{CH}_3)_2\text{CO}\cdot^-][\text{ArBr}] \\ & - k_7[(\text{CH}_3)_2\text{C}\cdot\text{OH}][(\text{CH}_3)_2\text{CO}\cdot^-] \\ & - 2k_8[(\text{CH}_3)_2\text{CO}\cdot^-]^2 \end{aligned} \quad (13)$$

$$\frac{d[\text{Ar}\cdot]}{dt} = 0 = k_4[(\text{CH}_3)_2\text{CO}\cdot^-][\text{ArBr}] - k_5[\text{Ar}\cdot][(\text{CH}_3)_2\text{CHOH}] \quad (14)$$

Rearranging Eq. (11)

$$[t\text{-BuO}\cdot] = \frac{k_1}{k_2[(\text{CH}_3)_2\text{CHOH}]} [t\text{-BuOOBu-t}][\text{Fe}^{2+}] \quad (15)$$

Adding Eqs. (12) and (13), and applying Eqs. (14) and (15), the resulting equation is obtained as follows:

$$\begin{aligned} 0 = & k_1[t\text{-BuO}]_2[\text{Fe}^{2+}] - 2k_6[(\text{CH}_3)_2\text{C}\cdot\text{OH}]^2 \\ & - 2k_7[(\text{CH}_3)_2\text{C}\cdot\text{OH}][(\text{CH}_3)_2\text{CO}\cdot^-] - 2k_8[(\text{CH}_3)_2\text{CO}\cdot^-]^2 \end{aligned} \quad (16)$$

Formulating the equilibrium expression for Reaction (5) and rearranging

$$[(\text{CH}_3)_2\text{C}\cdot\text{OH}] = \frac{[(\text{CH}_3)_2\text{CO}\cdot^-]}{K_3[\text{OH}^-]} \quad (17)$$

Applying Eqs. (17) to (16)

$$\begin{aligned} & k_1[t\text{-BuO}]_2[\text{Fe}^{2+}] \\ = & \left( \frac{2k_6}{K_3^2[\text{OH}^-]^2} + \frac{2k_7}{K_3[\text{OH}^-]} + 2k_8 \right) [(\text{CH}_3)_2\text{CO}\cdot^-]^2 \end{aligned} \quad (18)$$

Rearranging in the square root

$$[(\text{CH}_3)_2\text{CO}\cdot^-] = \frac{(k_1[t\text{-BuO}]_2[\text{Fe}^{2+}])^{1/2} K_3[\text{OH}^-]}{(2k_6 + 2k_7 K_3[\text{OH}^-] + 2k_8 K_3^2[\text{OH}^-])^{1/2}} \quad (19)$$

When applying Eq. (19) to Reaction (6), overall kinetic expression can be given as

$$\begin{aligned} \frac{d[\text{ArBr}]}{dt} = & k_4[(\text{CH}_3)_2\text{CO}\cdot^-][\text{ArBr}] \\ = & \frac{k_4(k_1)^{1/2}([t\text{-BuO}]_2)^{1/2}([\text{Fe}^{2+}])^{1/2} K_3[\text{OH}^-]}{(2k_6 + 2k_7 K_3[\text{OH}^-] + 2k_8 K_3^2[\text{OH}^-])^{1/2}} [\text{ArBr}] \end{aligned} \quad (20)$$

The ultimate form of the kinetic expression mainly depends upon the relative magnitude of three terms in the denominator such as  $k_6$ ,  $k_7$ , and  $k_8$ . In other words, ultimate kinetic expression is affected by termination products as described in Section 3.5.

### 3.7. Simplified kinetic expression

The derived kinetic expression is somewhat complicated and can be reduced to a much simplified form with assumptions from previous literatures and conducted experiments. The values of the forward reaction rate constant ( $k_3$ ) and reverse rate constant ( $k_{-3}$ ) in Reaction (5) were determined as  $9 \times 10^9 \text{ (M}^{-1} \text{ s}^{-1})$  and  $1.8 \times 10^6 \text{ (M}^{-1} \text{ s}^{-1})$ , respectively [32]. Using these values of rate constants, the equilibrium constant ( $K_3$ ) in Reaction (5) can be calculated as  $5 \times 10^3$ . As for values from experiment, with conditions such as  $[\text{OH}^-] = 0.1 \text{ M}$  and  $[\text{H}_2\text{O}] = 0.022 \text{ M}$ , and assumption of 2% of 0.5 mL of DTBP added to 25 mL of reaction solution, the ratio of  $[(\text{CH}_3)_2\text{CO}\cdot^-]$  to  $[(\text{CH}_3)_2\text{C}\cdot\text{OH}]$  can be calculated as follows:

$$\frac{[(\text{CH}_3)_2\text{CO}\cdot^-]}{[(\text{CH}_3)_2\text{C}\cdot\text{OH}]} = k_3 \frac{[\text{OH}^-]}{[\text{H}_2\text{O}]} = 5 \times 10^3 \times \frac{0.1}{0.022} = 2.27 \times 10^4 \quad (21)$$

This high value in the ratio of  $[(\text{CH}_3)_2\text{CO}\cdot^-]$  to  $[(\text{CH}_3)_2\text{C}\cdot\text{OH}]$  indicates that  $(\text{CH}_3)_2\text{CO}\cdot^-$  is more abundant in the solution at the beginning of reaction. Since the variation of pH during the reaction is minimal, this ratio of two species is sustainable. For this ultrasonic destruction of PBB, the ketyl radical anions play an important role as a rate limiting factor. Comparing the big number of  $k_8$ , the rate constants of  $k_6$  and  $k_7$  in the denominator are small. Simply, the ultimate kinetic expression can be presented as follows:

$$\frac{d[\text{ArBr}]}{dt} = \frac{k_4(k_1)^{1/2}}{(2k_8)^{1/2}} ([t\text{-BuO}]_2)^{1/2} ([\text{Fe}^{2+}])^{1/2} [\text{ArBr}] \quad (22)$$

In the experiment of different concentrations of ferrous ion in the reaction mixture at various reaction times, the concentration of ferrous ion would tend to reach a constant level in approximately 10 min of reaction time. The results are shown in Fig. 3. This phenomenon was also observed at very high concentration of ferrous ion when DTBP was not applied. As to the concentrations of DTBP in the reaction, no experimental work had been successfully performed. However, the DTBP concentration can be assumed to be constant, because the molar ratio of DTBP to ferrous ion is 20:1, and DTBP is thermally stable at 55 °C. The half-life of DTBP at 120 °C is 10 h. Therefore, the kinetic expression may be shortened as

$$\frac{d[\text{ArBr}]}{dt} = K[\text{ArBr}] \quad \text{where } K = \frac{k_4(k_1)^{1/2}}{(2k_8)^{1/2}} ([t\text{-BuO}]_2)^{1/2} ([\text{Fe}^{2+}])^{1/2} \quad (23)$$

This kinetic expression can be represented as a first-order reaction in terms of ArBr. A kinetic plot of the natural logarithm of

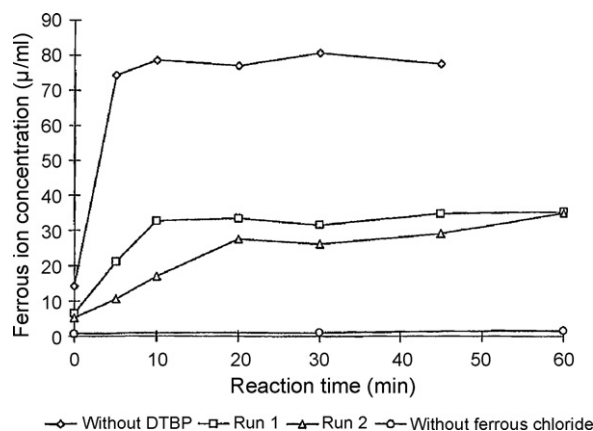


Fig. 3. The concentration variations of the ferrous ion at various sonication times in the condition of 0.5 mL of DTBP and 0.025 g of  $\text{FeCl}_2$ .

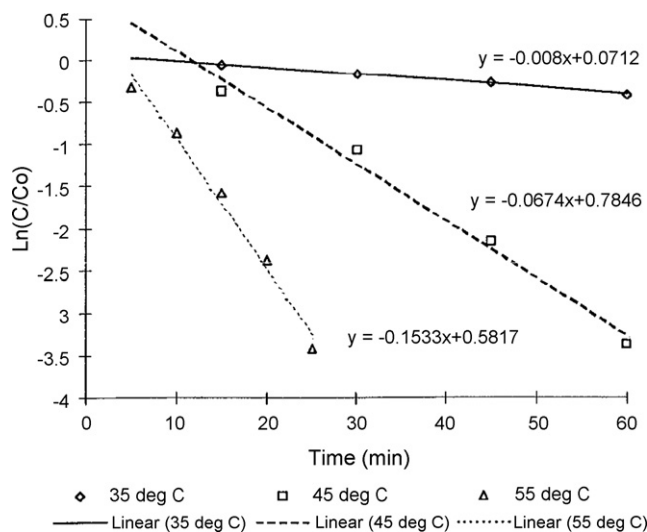


Fig. 4. Pseudo-first-order kinetic plots for the reductive debromination of 4,4'-dibromobiphenyl (DBB) in alkaline 2-propanol at three different temperatures.

4,4'-DBB concentration versus reaction time, in Fig. 4, demonstrates a linear relationship between the concentration and the UACP time. In 30 min of sonication time at optimum condition of chemical additives, 100% removal of 4,4'-DBB was observed. This linear regression with  $R^2 = 0.9868$  is well suited with a first-order reaction. The derived kinetic expression (Eq. (23)) can match with experimental findings. In order to derive the activation energy of this process, the experiments were conducted at different temperatures of 35 °C, 45 °C, and 55 °C, presented in Fig. 5, and also an Arrhenius plot using three reaction rate constants is shown. The activation energy of 29.8 kcal mol<sup>-1</sup> can be estimated in this experiment.

### 3.8. Kinetic models

Two models (Case I and Case II) were introduced to describe the kinetic mechanism and to find the better fitting model for the debromination reaction where cases are based on the developed kinetic expression with the first-order and irreversible reaction.

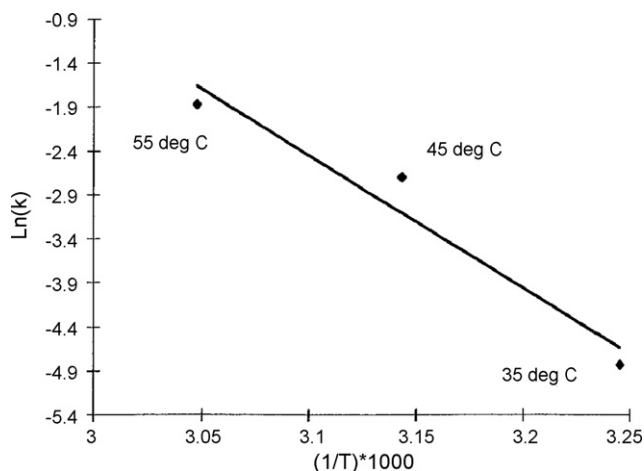


Fig. 5. An Arrhenius plot of the observed pseudo-first-order rate constants in the reductive debromination of 4,4'-dibromobiphenyl (DBB) in alkaline 2-propanol ( $y = -14.994x + 44.028$ ;  $R^2 = 0.9469$ ).

#### 3.8.1. Case I

##### 4, 4'-dibromobiphenyl (D)



This is a consecutive first-order reaction. The initial concentrations of 4,4'-dibromobiphenyl (D), 4-monobromobiphenyl (M), and biphenyl (B) are  $D_0$ ,  $M_0$ , and  $B_0$  as initial concentrations of parent compounds. The relative reaction time can be obtained by the actual reaction time minus 5 min. Three differential equations are inferred for the Case I.

$$\frac{dD_t}{dt} = -k_1 D_t \quad (24)$$

$$\frac{dM_t}{dt} = k_1 D_t - k_2 M_t \quad (25)$$

$$\frac{dB_t}{dt} = k_2 M_t \quad (26)$$

Through the integration, the general solution for each component in terms of the initial concentration and kinetic constants ( $k_1$  and  $k_2$ ), can be obtained.

$$D_t = D_0 e^{-k_1 t} \quad (27)$$

$$M_t = \frac{D_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) + M_0 e^{-k_2 t} \quad (28)$$

$$B_t = (D_0 + M_0 + B_0) - D_t - M_t \\ = (D_0 + M_0 + B_0) - \frac{D_0 k_2}{k_2 - k_1} e^{-k_1 t} - \left( M_0 - \frac{D_0 k_1}{k_2 - k_1} \right) e^{-k_2 t} \quad (29)$$

The detailed derivation procedure for Eqs. (27)–(29) is omitted. The attempts to solve for  $k_1$  and  $k_2$  using a computer program was not successful [33]. However, based on the principle of iterative non-linear regression method, the best fitting values of  $k_1$  and  $k_2$ , for experimental data were estimated using Microsoft Excel. These rate constants are presented in Table 1. The comparison of the computed values and the laboratory observed values were plotted in Fig. 6.

#### 3.8.2. Case II

##### 4, 4'-dibromobiphenyl (D)



##### 4, 4'-dibromobiphenyl (D) $\xrightarrow{k_3}$ biphenyl (B)

This is also a consecutive first-order reaction. The initial concentrations and relative reaction time are all the same as the Case I. The following differential equations are generated for the Case II.

$$\frac{dD_t}{dt} = -(k_1 + k_3) D_t \quad (30)$$

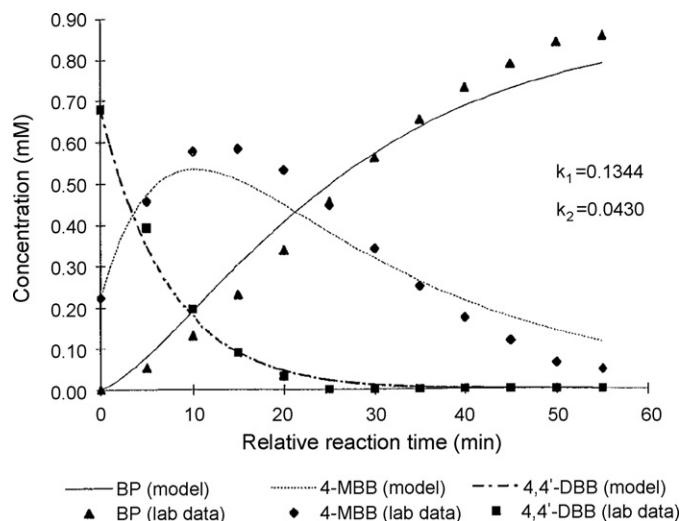
$$\frac{dM_t}{dt} = k_1 D_t - k_2 M_t \quad (31)$$

Table 1

Observed rate constants in the kinetic model study

Kinetic model	$k_1$ (min <sup>-1</sup> )	$k_2$ (min <sup>-1</sup> )	$k_3$ (min <sup>-1</sup> )	Error <sup>a</sup>
Case I ( $k_1$ and $k_2$ system)	0.1344	0.0430	N/A	0.0712
Case II ( $k_1$ , $k_2$ , and $k_3$ system)	0.1461	0.0497	-0.0206	0.0418

<sup>a</sup> Error is the sum of the squares of the difference between model predicted numbers and laboratory observed numbers.



**Fig. 6.** Comparison of laboratory observed data with model predicted values in the reductive debromination of 4,4'-DBB ( $k_1$  and  $k_2$  system, biphenyl (BP), monobromobiphenyl (MBB), dibromobiphenyl (DBB)).

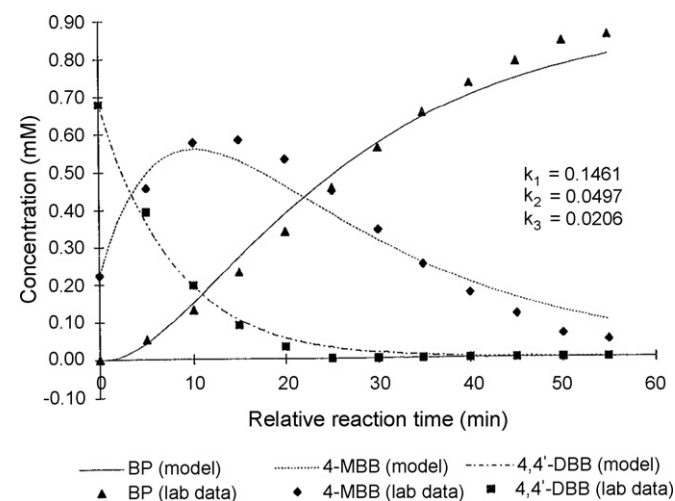
$$\frac{dB_t}{dt} = k_3 D_t + k_2 M_t \quad (32)$$

Through the integration, the general solution for each component in terms of the initial concentration and kinetic constants ( $k_1$ ,  $k_2$ , and  $k_3$ ), can be obtained. The detailed derivation procedure for Eqs. (33)–(35) is omitted. Rate constants are also presented in Table 1. The comparison of the computed values and the laboratory observed values were plotted in Fig. 7.

$$D_t = D_0 e^{-(k_1+k_3)t} \quad (33)$$

$$M_t = \frac{D_0 k_1}{k_2 - k_1 - k_3} (e^{-(k_1+k_3)t} - e^{-k_2 t}) + M_0 e^{-k_2 t} \quad (34)$$

$$B_t = (D_0 + M_0 + B_0) - D_t - M_t \\ = (D_0 + M_0 + B_0) - \frac{D_0(k_2 - k_3)}{k_2 - k_1 - k_3} e^{-(k_1+k_3)t} \\ - \left( M_0 - \frac{D_0 k_1}{k_2 - k_1 - k_3} \right) e^{-k_2 t} \quad (35)$$



**Fig. 7.** Comparison of laboratory observed data with model predicted values in the reductive debromination of 4,4'-DBB ( $k_1$ ,  $k_2$ , and  $k_3$  system).

In general, the kinetic models of Cases I and II are fitting the laboratory data in some reasonable manner. Both models provide a better fit for 4,4'-DBB than 4-MBB and biphenyl. Deviations and error may occur from assumptions of simplified kinetic model and unconsidered reactions such as dissolution of ferrous chloride and precipitation (or loss) of compounds during the reaction. Case II has lower error value in Table 1. However, Case II is not plausible due to the negative constant,  $k_3$  where reaction proceeds backward, which is against the original assumption of positive reaction progress. Thus, Case I is more acceptable kinetic model for this reductive dehalogenation of PBB.

#### 4. Conclusion

Chemical assisted ultrasonic chemistry (UACP) to remove halogens is likely to include complex pathways involving numerous reactive intermediates, their identification, and radical mechanism. Debromination mechanism pathway was elucidated in a kinetic study through the kinetic expression, the equilibrium equation, the appropriate kinetic model, and the radical dissociation in a chain reaction. Sonolytic destruction of PBBs exhibits pseudo-first-order reaction kinetics at a given initial concentration of PBBs ( $C_0$ ) with a linear regression between  $\ln(C/C_0)$  and the UACP time. Free radicals such as ketyl and aryl radicals, and their anions are also important in the chain reaction of reductive debromination technology. Sonolytic and radical system was highly effective in dehalogenation of PBB.

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