



Critical factors in sonochemical degradation of fumaric acid



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ABSTRACT

The effects of critical factors such as Henry's Law constant, atmospheric OH rate constant, initial concentration, H_2O_2 , FeSO_4 and tert-butanol on the sonochemical degradation of fumaric acid have been investigated. The pseudo first-order rate constant for the sonochemical degradation of 1 mM fumaric acid is much lower than those for chloroform and phenol degradation, and is related to solute concentration at the bubble/water interface and reactivity towards hydroxyl radicals. Furthermore, fumaric acid is preferentially oxidized at the lower initial concentration. It is unreactive to H_2O_2 under agitation at room temperature. However, the degradation rate of fumaric acid increases with the addition of H_2O_2 under sonication. 0.1 mM of fumaric acid suppresses H_2O_2 formation thanks to water sonolysis, while degradation behavior is also dramatically affected by the addition of an oxidative catalyst (FeSO_4) or radical scavenger (tert-butanol), indicating that the degradation of fumaric acid is caused by hydroxyl radicals generated during the collapse of high-energy cavities.

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1. Introduction

Advanced oxidation processes (AOPs) are oxidation procedures which remove both toxic and non-biodegradable pollutants from waste water [1]. Four different reagents are normally used as oxidants; ozone, hydrogen peroxide, oxygen and air. These are combined with UV irradiation and specific catalysts, such as Fenton's reagent, cause hydroxyl radicals to be formed [2]. The mineralization of carbon-containing organics is one of AOP's goals [3]. However, AOPs also yield refractory by-products, which are usually small carboxylic acids [4]. Fumaric acid ($\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$) is one of the common intermediates and can limit COD and TOC reduction to less than 5% even after several hours of sonication, even when the aromatic substrate and intermediates have degraded [5–8]. An 80% decrease in phenol concentration ($C_0 = 89 \text{ mgL}^{-1}$) has been observed at 540 kHz, while TOC was reduced by only 4% [9].

Fumaric acid is used as a food additive for its anti-oxidant and anti-microbial effects and is also employed as an acidity regulator (E297), as well as being part of the unsaturated polyester resin

manufacturing process. In earlier studies, the production of tartaric acid from the catalyzed oxidation of fumaric acid by aqueous osmium tetroxide-potassium chlorate solutions was approximately 100% [10,11]. The permanganate oxidation of fumaric acid leads to the formation of formyl(hydroxy)acetic acid, while hydroxymalonic, glyoxylic and oxalic acid are further intermediates [12]. As it is unsaturated, the ozonation of fumaric acid largely follows the Criegee mechanism (formation of carbonyl compound plus hydroxyalkylhydroperoxide) [13]. Formic acid is a major intermediate product in the subcritical aqueous-phase oxidation of fumaric acid, whereas acetic acid is formed only in the presence of oxygen [14]. The hydroxylation of the fumaric acid double bond and the abstraction of a hydrogen atom produces malic acid via the action of ultraviolet radiation/hydrogen peroxide/oxygen [15]. The photocatalytic degradation of fumaric acid occurs in the homogeneous phase at high pH by means of solvated hydroxyl radicals. The principle product is reported to be acrylic acid. Downstream intermediates include acetic, oxalic and formic acids [16,17].

Due to the numerous high energy hot-spots (high temperatures of several 1000 K and pressures of some 10 MPa) induced by sonication in aqueous solutions, the pyrolysis of water vapour occurs in the compression phase of oscillating or collapsing gas bubbles to create H^\bullet , OH^\bullet , O_2^\bullet and O^\bullet atoms, etc. [18,19]. Inside a gaseous bubble the main oxidant is H_2O_2 when the bubble temperature at the end of the bubble collapse is in the range of 4000–6500 K and O^\bullet

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atom when it is above 6500 K [19]. Such active species react with volatile solutes in the gas phase or react with dissolved solutes in an interfacial area or even in the bulk solution [20]. Hydrogen peroxide is produced via the combination of OH radicals or other radical reactions during the sonication.

The sonolyses of dicarboxylic acids (succinic acid, maleic acid and fumaric acid) in aqueous solution has been reported [21]. These acids successively transform from one to the other under sonication. Malic acid and tartaric acid have been obtained via the hydroxylation of maleic and fumaric acid. However, dicarboxylic acids were reduced very slowly under sonication. When 50 mL of 10 mM fumaric acid was sonicated in argon atmosphere at 200 W and 200 kHz ultrasound at 25 °C, only ca. 60% of fumaric acid was converted in 6 h.

In this study, we compare the sonolytic rates of chloroform, phenol and fumaric acid, as well as the degradation rates of fumaric acid with H₂O₂ under agitation and sonication. The effects of H₂O₂, Fenton's reagent and tert-butanol addition on fumaric acid sonolytic kinetics are reported to reveal the sonolytic mechanisms of hydrophilic organic pollutants.

2. Experimental

2.1. Chemicals

Fumaric acid (Fluka, 99.5%), chloroform (CHCl₃, Riedel-de Haen, 99%), phenol (Fluka, 99%), hydrogen peroxide (Sigma–Aldrich, 50 wt.%), Iron (II) sulfate heptahydrate (Sigma–Aldrich, 99%), tert-butanol (Sigma–Aldrich, 99%), phosphoric acid (Sigma, 85%) and deionised water (H₂O, conductivity ≤1.5 μS cm⁻¹) were all used as received.

2.2. Ultrasonic device and operation

This device is made up of an ultrasound generator, an ultrasound transducer and a double walled cylindrical glass reactor (Meinhardt Ultraschalltechnik, Leipzig). The ultrasonic transducer worked at 534 kHz. Applied ultrasonic power, determined by calorimetric measurement, was 15 W and acoustic intensity was 1.2 W cm⁻². The temperature of the bulk liquid was maintained at 25 °C by circulating cooling water. Hydrogen peroxide concentrations were determined iodometrically, using the method described by Kormann et al. [22] and Pétrier et al. [23].

In a typical run, a fumaric acid-containing aqueous solution (200 mL) was fed into the ultrasonic reactor. The ultrasonic transducer operated continuously at 534 kHz under air atmosphere. Aliquots (1 mL) of the processed solution were periodically extracted from the reaction system and analyzed quantitatively and qualitatively by HPLC. All data are means of a single experiment in duplicate.

2.3. HPLC analysis

The Jasco LC-2000 Plus HPLC system was used to detect the concentrations of fumaric acid and all resulting organic acids. The HPLC system contained a DG-2080-53 3-Line Degasser, PU-2080Plus intelligent HPLC-Pump, AS-2055Plus intelligent Sampler, CO-2060Plus intelligent Column Thermostat, MD-2010Plus Multi-wavelength Detector, LC-Net II/ADC and Chrompass Chromatography Data System, Vers. 1.8.6.1. A ReproSil-Pur C18-AQ (5 μm, 200 × 4.6 mm) column, provided by Dr. Maisch GmbH (Ammerbuch-Entringen, Germany), 200 mM H₃PO₄ mobile phase and UV detection at 210 nm were also used. Analyses were performed at a flow rate of 1.0 ml/min and a temperature of 20 °C.

3. Results and discussion

3.1. Comparison of sonolytic rate constants for fumaric acid, phenol and chloroform

200 mL of 1.0 mM chloroform-, phenol- and fumaric acid-containing aqueous solutions were separately sonicated for 180 min in the double-walled reactor with 534 kHz ultrasound at 25 °C. Fig. 1 shows the clear difference in their degradation rates.

The integrated rate equation for pseudo first-order kinetics is described in Eq. (1):

$$C_t/C_0 = e^{-kt} \quad (1)$$

where C_t represents the concentration of substrate at given time t and C_0 represents the initial substrate concentration, k is the rate constant for the degradation [24].

The degradation rate constant and correlation coefficient, R^2 , values are shown in Table 1, which indicates that the sonochemical degradation of the selected compounds follows pseudo first-order kinetics very well. This result is consistent with the sonochemical degradation of hydrocarbons, chlorinated hydrocarbons, phenol, methylene blue, etc. [25–30].

As seen in Table 1, the volatile, hydrophobic chloroform (entry 1) rapidly undergoes sonolysis during cavitation bubble collapse because of its particularly high Henry's Law constant (K_H : 3.67×10^{-3} atm m³/mol at 25 °C) [31–33], while hydrophilic phenol (entry 2, K_H : 3.33×10^{-7} atm m³/mol at 25 °C) [34] and fumaric acid (entry 3, K_H : 8.5×10^{-14} atm m³/mol at 25 °C) [35] are slowly oxidized by on-site formed oxidants such as OH radicals [23,36]. In addition, the oxidative degradation of fumaric acid with OH radicals is much slower than that of phenol as fumaric acid has a much lower atmospheric OH rate constant (K_{OH} : 7.949×10^{-12} - cm³/mol sec at 25 °C) [37] than phenol (K_{OH} : 2.63×10^{-11} cm³/mol sec at 25 °C) [38]. The previous study has denoted that the degradation of volatile, hydrophobic compound such as carbon tetrachloride is considered to occur in the bubble of cavitation, while the degradation of non-volatile, hydrophilic compounds such as phenol and methylene blue takes place through oxidation process in aqueous solution [30]. This is the reason why fumaric acid and other short-chain carboxylic acids exist as intermediates during the sonication of phenol-containing solutions.

However, fumaric acid is preferentially oxidized at the lower initial concentration, as shown in Fig. 2 and Table 1 (entry 4). It

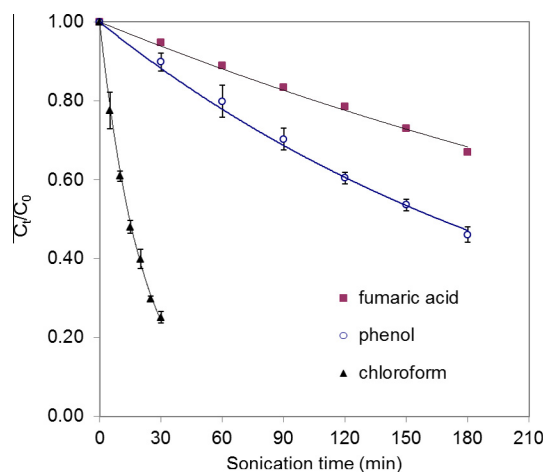


Fig. 1. Degradation of fumaric acid, phenol and chloroform as a function of sonication time (200 mL of 1.0 mmol L⁻¹ substrate, 534 kHz, 15 W, 25 °C).

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