DEGRADATION OF CHLOROETHENES IN AQUEOUS SOLUTION BY ULTRASOUND

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Among several types of pollutants, chlorinated compounds are routinely the subject of sonochemical studies to investigate the environmental applications of this technology. C1 chlorinated organocompounds (CHCl3, CH2Cl2, CCl4) and C2 compounds (1,1,1 trichloroethane, tetrachloroethylene (PCE), hexachloroethane, 1, 1, 2, 2 tetrachloroethane and specially trichloroethylene) have been also studied, particularly in respect of the influence of ultrasonic frequency on the chemical processes and their kinetics[1]. Chlorinated aromatic compounds have been also studied, including chlorotoluenes[2], p-chlorobenzoic acid [3], PCBs [4], especially chlorobenzenes [5], and chlorophenols[6].

Although perchloroethylene (PCE) remains a widely used solvent in many areas of industry and has been reported also to occur as a major intermediate in the degradation of other chlorinated compounds [7], to our knowledge, there has been no extensive study on the sonochemical degradation of this compound. In one report Bhatnagar et al. [8] related kinetics to the ultrasonic frequency (20 kHz) and vapor pressure of the compound, and showed that: (i) pH and temperature had little effect upon the destruction rate of the compound (and in any case vapor pressure does not correlate to the destruction rate for C2 compounds such PCE), (ii) nonspecificity of the process with a percent destruction higher than 72% (iii) the tetrachloroethylene can be degraded by pyrolysis jointly with radical oxidation and (iv) GC/MS analyses of the samples showed no other chlorinated products in the sonolysis of tetrachloroethylene. Inazu et al. [9] analyzed the influence of dissolved gas at 200 kHz insonation, and quantified chemical yields of products including chloride anion and carbon monoxide and/or carbon dioxide. They concluded that the main reactions were thermal decomposition or combustion in cavitation bubbles and not reactions involving OH · radicals or H atoms. Clayton J. Clark II et al. [10] studied the influence of initial substrate concentration on kinetics, and obtained no effect of concentration above 75 ppm. They reduced the concentration to below 0.9 ppm and the presence of trichloroethylene and dichloroethylene as by-products, if they occurred, were below detectable limits in solution (< 0.01 mg/L).

We have studied the effects of reaction variables such as initial concentration and ultrasonic intensity, using a 20 kHz-100W maximum power sonoreactor supplied by Undatim. This commercial sonoreactor offers variable power which can be adjusted and has been previously fully-characterized by the authors [11, 12]. The sonoreactor can operate at an optimum frequency by means of an auto-scan system. The experimental set-up used is shown in Figure 1. Special attention was paid to by-product analysis and intermediate formation during the sonochemical reactions. The aqueous phase was analyzed as a function of time using ion exchange chromatography (for chloride anion and other ions) and HPLC (for PCE and other intermediates). The gas phase over the solution during the sonochemical experiments was also monitored by Gas Chromatography-TCD for the analysis of CO/CO2 and PCE and for other intermediates by Gas Chromatography-FID. At the end of each experiment the detection and quantification of PCE and degradation products was carried out using Purge and Trap Gas Chromatography Mass Spectrometry (PT-GC-MS).
Figure 2(a) shows the concentration decay for three different initial concentrations of PCE while Figure 2(b) shows the normalized concentration decay for the same experiments. A clear superposition was obtained in Figure 2(b) showing the required reproducibility for our analysis in spite of the complex system studied. We found no influence of the initial concentration (in these experimental conditions) on the kinetics of the process, according to the volatile nature[13] of PCE.

Trichloroethylene and dichloroethylene were identified as major volatile organic intermediates throughout the sonolysis of PCE. However, other minor C₁ products at ppb level, such as CHCl₃ and CCl₄ and C₂ ones such as hexachloroethane, C₃ ones such hexachloropropene and C₄ ones such as hexachlorobutadiene were also detected at the end of the sonolysis by the P&T-GC-MS technique.

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References