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Chemosphere 70 (2008) 2060–2067

CHEMOSPHERE

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Comparison of PCE and TCE disappearance in heated volatile organic analysis vials and flame-sealed ampules

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Received 24 May 2007; received in revised form 31 August 2007; accepted 6 September 2007
Available online 22 October 2007

Abstract

The rates of hydrolysis reported for tetrachloroethylene (PCE) and trichloroethylene (TCE) at elevated temperatures range over two orders-of-magnitude, where some of the variability may be due to the presence of a gas phase. Recent studies suggest that volatile organic analysis (VOA) vials provide a low-cost and readily available zero headspace system for measuring aqueous-phase hydrolysis rates. This work involved measuring rates of PCE and TCE disappearance and the corresponding appearance of dechlorination products in water-filled VOA vials and flame-sealed ampules incubated at 21 and 55 °C for up to 95.5 days. While PCE and TCE concentrations readily decreased in the VOA vials to yield first-order half lives of 11.2 days for PCE and 21.1 days for TCE at 55 °C, concentrations of anticipated dechlorination products, including chloride, remained constant or were not detected. The rate of PCE disappearance was 34 times faster in VOA vials at 55 °C compared to values obtained with flame-sealed ampules containing PCE-contaminated water. In addition, the concentration of TCE increased slightly in flame-sealed ampules incubated at 55 °C, while a decrease in TCE levels was observed in the VOA vials. The observed losses of PCE and TCE in the VOA vials were attributed to diffusion and sorption in the septa, rather than to dechlorination. These findings demonstrate that VOA vials are not suitable for measuring rates of volatile organic compound hydrolysis at elevated temperatures.

Keywords: Tetrachloroethylene; Trichloroethylene; Hydrolysis; Heat; VOA vials; Dechlorination

1. Introduction

Heating subsurface environments contaminated with chlorinated solvents such as tetrachloroethylene (PCE) and trichloroethylene (TCE) is thought to increase the rate at which these contaminants undergo dechlorination reactions. For example, TCE was reported to be transformed into chloride during the thermal treatment of a field site after heating to between 60 and 95 °C (Truex et al., 2007). One of the potential dechlorination mechanisms involves hydrolysis, in which water substitutes into a chlorinated compound and eliminates chlorine. Although the rate of PCE and TCE hydrolysis is slow at ambient temperatures (10–25 °C), the rate increases with temperature as described by the Arrhenius equation (Jeffers and Wolfe, 1996). The rate at which PCE and TCE are dechlorinated due to hydrolysis has been determined using experimental systems operated at temperatures between 70 and 170 °C for periods of up to 40 days. However, the dechlorination rates determined by independent research groups range over two orders-of-magnitude, leading to uncertainty when estimating the fraction of mass that can potentially be degraded due to hydrolysis. For example, the time for 50% of the initial TCE mass to be dechlorinated was reported to be ca. 2 days at 90 °C by Knauss et al. (1999), while Costanza et al. (2005) reported a half-life ca. 200 days at 120 °C. Jeffers and Wolfe (1996) reported Arrhenius rate parameters that predict a TCE half-life of ca. 17 800 days at 90 °C and ca. 860 days at 120 °C. One difference between these experiments was that Knauss et al. (1999) used a single-phase system containing only

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0045-6535/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2007.09.007

an aqueous-phase, while the slower rates reported by Costanza et al. (2005) and Jeffers and Wolfe (1996) were determined using a two-phase system containing aqueous and gas phases. Reliable rates of dechlorination are needed so that in situ destruction of chlorinated ethenes can be predicted during thermal treatment, and can be considered as a complimentary means to achieve mass reduction.

Recently, Brown et al. (2005) and Brown (2006) reported results from a single-phase aqueous system that was used to determine the rate of PCE and TCE hydrolysis at 35, 45, and 55 °C. The half-life for the disappearance of TCE at 45 °C was 17 days based on data reported in Brown (2006), which is 129 times faster than the half-life at 45 °C based on Arrhenius rate parameters reported by Knauss et al. (1999). The faster rate reported by Brown (2006) was obtained using a system, which was completely filled with aqueous-phase, consisting of glass volatile organic analysis (VOA) vials sealed with Teflon®-lined silicone rubber septa. The advantage of the VOA vials is that the flexible rubber septa can accommodate the expansion of liquid water which occurs with increasing temperature. This feature allows the vials to be completely filled with water at room temperature and then incubated at elevated temperatures without the glass enclosure breaking due to liquid water expansion. Knauss et al. (1999) overcame this problem by using a custom made apparatus consisting of a variable volume, gold-walled vessel that was contained within a water-filled steel enclosure pressurized to 1000 kPa. Thus, the VOA vials appear to offer a relatively low-cost and readily available alternative to the custom made gold-walled system employed by Knauss et al. (1999) for the study of aqueous-phase dechlorination reactions in a zero headspace enclosure at elevated temperatures. However, Brown (2006) only analyzed the VOA vial contents for the parent compound, either PCE or TCE, and did not demonstrated that these compounds were being dechlorinated by analyzing for hydrolysis products such as chloride.

Volatile organic analysis vials are the recommended container for transporting aqueous samples containing dissolved-phase volatile organic compounds from the field to the laboratory (ASTM, D3694). However, the samples must be stored at 4 °C and analyzed within 14 days of collection to avoid loss of volatile organic compounds, such as PCE and TCE. Even with these precautions, PCE and TCE have been shown to be sorbed by Teflon®-lined septa, leading to losses in contaminant mass from the aqueous-phase (Kovacs and Kampbell, 1999). The integrity of the seal between the Teflon®-lined septa and the vial rim also suffers from imperfections in the glass surface that can lead to additional losses of PCE and TCE from VOA vials (Schumacher et al., 2000). Although VOA vials are routinely used for low temperature storage of volatile organic compounds, there are no reports regarding their adequacy for use as enclosures at elevated temperatures.

The objective of this study was to determine if (1) VOA vials were suitable for the study of aqueous-phase dechlorination reactions at elevated temperatures and (2) using single-phase containing VOA vials resulted in faster dechlorination rates compared with the rates obtained from two-phase containing flame-sealed ampules. These experiments involved measuring the rate of PCE and TCE disappearance along with the corresponding dechlorination products in water-filled VOA vials and flame-sealed ampules. Thirty-six VOA vials were filled with water that contained only dissolved-phase PCE and an additional 36 VOA vials were filled with water that contained only dissolved-phase TCE. Each batch of 36 vials was then divided in half, with 18 vials incubated at 21 °C and the remaining 18 vials incubated at 55 °C. The ampule experiments were performed in a similar manner, but involved 40 ampules with dissolved-phase PCE and 13 ampules with dissolved-phase TCE. VOA vials and ampules were collected from each temperature subset at selected times, with the vial or ampule sacrificed to determine the compounds present.

2. Experimental

2.1. VOA vial experiments

Volatile organic analysis (VOA) vials, made from clear borosilicate glass with average volume of 43 ml, were obtained from EP Scientific Products (Miami, OK). The vials were sealed with open-top polypropylene screw-caps fitted with 3.175 mm thick Teflon®-lined silicone septa. The vials were certified clean and used as delivered. The aqueous stock for the VOA vial experiment was prepared using water treated with a Milli-Q deionization system (Gradient A10, Millipore Corp., Billerica, MA) to an electrical resistance of 18.2 $\mathrm{M\Omega\,cm^{-1}}$ and a total organic carbon content of less than 2 $\mathrm{\mu g\,l^{-1}}$. The Milli-Q deionized (DI) water was sparged with nitrogen gas for 45 min until the dissolved oxygen concentration was less than 0.4 $\mathrm{mg\,l^{-1}}$ based on the Rhodazine D method (CHEMetrics, Inc. Calverton, VA). Each of the 72 VOA vials were filled to capacity with de-oxygenated Milli-Q DI water and temporarily sealed with a screw-cap. PCE or TCE was added to each vial by removing the screw-cap and injecting a 20 μl aliquot of methanol stock. The PCE-methanol stock had a concentration of 0.024 $\mathrm{mg\,\mu l^{-1}}$ resulting in an initial VOA vial concentration of 11.1 $\mathrm{mg\,l^{-1}}$, while the TCE-methanol stock had a concentration of 0.020 $\mathrm{mg\,\mu l^{-1}}$ resulting in an initial VOA vial concentration of 9.2 $\mathrm{mg\,l^{-1}}$. After adding the solvent spike, each vial was immediately sealed so that no gas bubbles were present to achieve a zero headspace aqueous-phase system. Of the 72 vials prepared, 36 contained PCE and 36 contained TCE, of which half (18 vials) were placed in a dark cabinet maintained at 21 ± 3 °C, and 18 were placed in a water bath maintained at 55 ± 3 °C. The vials incubated in the water bath were completely submerged so that the heated bath water covered the septa during incubation.

Six VOA vials were collected from each temperature subset at selected times, allowed to reach room temperature,