Environ. Sci. Technol. **2001**, *35,* 2258−2263

Reduction of Haloacetic Acids by Fe^0: Implications for Treatment and Fate

RAYMOND M. HOZALSKI,*
LI ZHANG, AND WILLIAM A. ARNOLD
Department of Civil Engineering, University of Minnesota, Minneapolis, Minnesota 55455-0116

To predict the fate of haloacetic acids (HAAs) in natural or engineered systems, information is needed concerning the types of reactions that these compounds undergo, the rates of those reactions, and the products that are formed. Given that many drinking water distribution systems consist of unlined cast iron pipe, reactions of HAAs with elemental iron (Fe^0) may play a role in determining the fate of HAAs in these systems. In addition, zerovalent iron may prove to be an effective treatment technology for the removal of HAAs from chlorinated drinking water and wastewater. Thus, batch experiments were used to investigate reactions of four trihaloacetic acids, trichloroacetic acid (TCAA), tribromoacetic acid (TBAA), chlorodibromoacetic acid (CDBAA), and bromodichloroacetic acid (BDCAA), with Fe^0. All compounds readily reacted with Fe^0, and investigation of product formation and subsequent disappearance revealed that the reactions proceeded via sequential hydrogenolysis. Bromine was preferentially removed over chlorine, and TBAA was the only compound completely dehalogenated to acetic acid. In compounds containing chlorine, the final product of reactions with Fe^0 was monochloroacetic acid. Halogen mass balances were 95−112%, and carbon mass balances were 62.6−112%. The pseudo-first-order rate constants for trihaloacetic acid degradation were as follows: BDCAA (10.6 ± 3.1 h^{-1}) > CDBAA (1.43 ± 0.32 h^{-1}) ≈ TBAA (1.41 ± 0.28 h^{-1}) ≫ TCAA (0.08 ± 0.02 h^{-1}).

Introduction

Haloacetic acids (HAAs) are important byproducts of the chlorination of water (*1*) and wastewater (*2*). Chlorinated HAAs are formed when hypochlorous acid (HOCl) reacts with organic matter that is ubiquitous in water supplies and wastewaters. In addition, brominated HAAs are formed when free chlorine reacts with bromide to form hypobromous acid (HOBr), which then reacts with the organic matter in a fashion similar to HOCl. The nine possible chlorinated, brominated, and combined chlorinated−brominated HAAs are listed in Table 1. Some of these compounds are suspected carcinogens and pose a potential health risk to water consumers (*3*). The United States Environmental Protection Agency began regulating HAAs in drinking water as part of the Disinfectants/Disinfection By-Products (D/DBP) Rule promulgated on December 16, 1998 (*4*). This rule established a maximum contaminant level (MCL) for the sum of five HAAs (HAA5 = MCAA + DCAA + TCAA + MBAA + DBAA) of 60 μg/L (*4*).

TABLE 1. List of the Nine HAAs of Concern in Treated Drinking Water and the MDL and RSD Values Obtained for the CE Analysis Method

name	formula	abbreviation	MDL[a] (μM)	RSD[b] (%)
monochloroacetic acid	$CH_2ClCOOH$	MCAA	11.0	1.74
monobromoacetic acid	$CH_2BrCOOH$	MBAA	5.76	2.91
dichloroacetic acid	$CHCl_2COOH$	DCAA	5.36	2.06
bromochloroacetic acid	$CHBrClCOOH$	BCAA	3.94	0.49
dibromoacetic acid	$CHBr_2COOH$	DBAA	5.77	0.21
trichloroacetic acid	CCl_3COOH	TCAA	6.52	1.08
chlorodibromoacetic acid	$CClBr_2COOH$	CDBAA	4.93	3.20
bromodichloroacetic acid	$CBrCl_2COOH$	BDCAA	7.25	2.42
tribromoacetic acid	CBr_3COOH	TBAA	4.27	1.45

[a] MDL: method detection limit. [b] RSD: relative standard deviation determined from four measurements at a concentration of approximately 40 ppm.

In addition to their occurrence in chlorinated drinking water supplies, in wastewaters, and in swimming pool water (*5*), chloroacetic acids (TCAA, DCAA, MCAA) are widespread in the environment (*6*−*8*). Chloroacetic acids are plant growth inhibitors that were used as herbicides until the late 1980s (*6*). Chlorinated HAAs are believed to be formed in the atmosphere during the photochemical degradation of chlorinated solvents (*9*) and have been detected as byproducts of the oxidation of chlorinated ethylenes using the photocatalyst titanium dioxide (*10*). It appears that the chlorinated HAAs also occur naturally (*11*). Other HAAs, such as the trifluoroacetic acid and chlorodifluoroacetic acid produced upon atmospheric degradation of hydrochlorofluorocarbons and hydrofluorocarbons (*6*, *12*), are also of environmental concern. Because of their widespread occurrence, phytotoxicity, and suspected human carcinogencity, information regarding the reactivity of these compounds is needed to develop treatment methods and to predict their fate in engineered and natural environments.

Unfortunately, published research concerning the biotic and abiotic reactivity of HAAs in aquatic environments is very limited. A few studies report the biodegradation of TCAA (*13*, *14*). Yu and Welander (*14*) discovered an aerobic bacterium that was able to grow on TCAA as the sole carbon and energy source. De Wever et al. (*13*) isolated an anaerobic bacterium that was capable of growth via reductive dehalogenation of TCAA with acetate as the electron donor. The organism, named *Trichlorobacter thiogenes*, was unable to dehalogenate DCAA or MCAA, and DCAA was the ultimate product of the biotransformation of TCAA. In addition, Boethling and Alexander (*15*) demonstrated that MCAA can be mineralized to CO_2 by natural microbial communities in streamwater.

There is little or no evidence of abiotic transformations of HAAs in the literature. In particular, there are no reported investigations of the reactivity of HAAs with zerovalent iron (Fe^0). Reactions of HAAs with Fe^0 may have important implications for understanding the fate of HAAs in water distribution systems, which primarily consist of cast iron piping, and for development of HAA treatment systems. This research was performed to evaluate the reactivity of HAAs with Fe^0.

Numerous halogenated solvents are susceptible to reduction by zerovalent iron including chlorinated alkanes (e.g., methanes and ethanes) (*16*−*29*), alkenes (*19, 30*−*49*), alkynes (*48*), and aromatic compounds, such as chlorinated phenols (*50*) and polychlorinated biphenyls (*51*). Brominated com-

---

* To whom correspondence should be addressed. E-mail: hozal001@tc.umn.edu; phone: (612) 626-9650; fax: (612) 626-7750.

10.1021/es001785b CCC: $20.00

pounds, such as 1,2-dibromoethane (*52*) and 1,2-dibromo-3-chloropropane (*53*), are also reduced by Fe^0. For the alkanes and alkenes, it has been demonstrated that the reduction occurs via competing pathways: hydrogenolysis and reductive elimination (*18, 39, 40, 48*). Hydrogenolysis is the replacement of a halogen by hydrogen. Reductive β-elimination may occur when halogens are present on adjacent carbons (*39, 40, 48*). When a carbon is multiply halogenated, reductive α-elimination may occur, resulting in a carbene(oid) intermediate (*18, 48*).

Previous work with 1,1,1-trichloroethane has shown that reduction by Fe^0 occurs by a combination of hydrogenolysis and reductive α-elimination (*18*). Given the similar structure of the trihaloacetic acids to 1,1,1-trichloroethane, we hypothesized that similar pathways may be important for the HAAs. The specific research objectives of this study included the following: (1) identification of the predominant reaction pathways of the trihalogenated acetic acids (i.e., TCAA, TBAA, CDBAA, and BDCAA) with Fe^0, and (2) preliminary determination of the rates of reaction of these species.

Experimental Section

Materials. Aqueous HAA stock solutions were prepared by diluting neat chemical in distilled and deionized (DI) water (Milli-RO 12, Millipore). TCAA and TBAA were obtained from Sigma-Aldrich, and BDCAA and CDBAA were obtained from Supelco. The purity of the neat chemicals used in these experiments is as follows: TCAA (99+%), BDCAA (99%), CDBAA (99%), and TBAA (99%). The chemicals were used as received. To prepare calibration standards for all nine of the HAAs (Table 1), 1000 ppm standard solutions of HAA in methyl *tert*-butyl ether (MTBE) obtained from Supelco were dissolved in DI water and diluted to the desired concentration.

Batch Experiments. The batch experiments were performed by diluting a freshly prepared 100 mg/L trihalogenated acetic acid stock solution with deoxygenated DI water to the desired concentration (100−200 μM) and adding 36 mL of the resulting solution to a 38 mL glass serum bottle along with 0.5 g of electrolytic Fe^0 (100 mesh size; Fisher Scientific). The Fe^0 was used as received. Although the electrolytic iron may not be representative of cast iron distribution system piping, it has been demonstrated that this iron type allows detailed analyses of reaction pathways and kinetics to be performed (*18, 39, 40, 48*). The control reactors were prepared in a similar manner except that no Fe^0 was added to the bottles. The reactors with Fe^0 were prepared in duplicate along with a single control bottle. All batch bottles were filled in an anaerobic glovebag (Coy Laboratory Products), topped with PTFE-faced butyl rubber septa, and sealed with aluminum crimp caps. The bottles were then removed from the glovebag and placed on a rotator (Glas-Col) such that the bottles were mixed end-over-end at 38 rpm at room temperature. Experiments were run for periods of up to 94 h. No pH buffer was employed, leading to a rise in pH over the course of the experiments. Initial pH values ranged from 3.62 to 4.14 and rose to 5.60 to 6.23 by the end of the experiments. Experiments in which pH was monitored as a function of time revealed that much of the pH change occurred in the first hour of incubation. The bottles were periodically sampled by withdrawing 100 μL from each bottle using a syringe and then filtering the solution through a 0.45 μm pore size filter capsule (Gelman Acrodisc) into a polyethylene autosampler vial for subsequent analysis by capillary electrophoresis (CE).

Analytical Procedures. The most widely used HAA method, 6251B, involves liquid−liquid extraction with MTBE, methylation with diazomethane, and analysis by GC-ECD (*54*). The entire process is time-consuming and presents several safety concerns that arise from the methylation process. The 1-methyl-3-nitro-1-nitrosoguanidine (MNNG) used to prepare the diazomethane is a potent carcinogen (*55*). The diazomethane itself also represents a potential explosion hazard. There is a great deal of concern, therefore, about working with MNNG and diazomethane (*56*). We speculate that it is largely due to the time and difficulty of the current HAA analysis methods that little research on the fate of HAAs in aquatic systems has been performed.

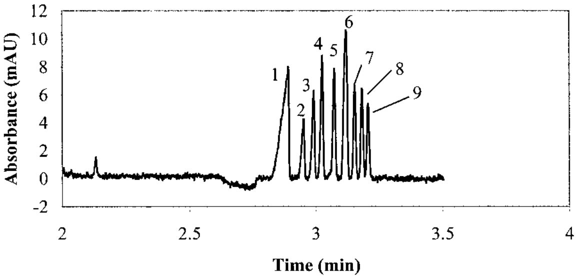

FIGURE 1. CE electropherogram from the analysis of a sample containing 10 ppm of each of the nine possible chlorinated and brominated HAAs and the internal standard trifluoroacetic acid (TFAA) in DI water. Peak identification is as follows: 1, TFAA; 2, MCAA; 3, MBAA; 4, DCAA; 5, BCAA; 6, DBAA + TCAA; 7, BDCAA; 8, CDBAA; and 9, TBAA.

To overcome the limitations of current HAA analysis methods, a new method of analyzing for HAAs using CE was developed in our laboratory. This new method is safe and rapid, so that experiments on HAA fate could be readily performed with frequent sampling and adequate replicates. Our method is similar to other CE methods recently described in the peer reviewed literature (*5, 57*).

HAA Analysis Using CE. Analyses of HAAs, chloride, and bromide were performed using a Hewlett-Packard capillary electrophoresis ion analyzer (model HP ^{3D}CE) controlled with HP Chemstation software. A 75 μm inner diameter by 56 cm (effective length) fused silica capillary was used for the separation. The separation buffer consisted of phosphate (6.25 mM NaH_2PO_4, 6.25 mM Na_2HPO_4) with 5.0 ppm of the cationic surfactant hexadimethrine hydroxide (HDMOH) as electroosmotic flow modifier. The buffer pH was adjusted to 5.7 with phosphoric acid. The HDMOH was prepared by dissolving hexadimethrine bromide (Sigma-Aldrich) in DI water and passing the solution through an anion exchange cartridge (Maxi-clean ICOH plus, Alltech Associates). The buffer solution was filtered and degassed before use with a liquid chromatography mobile phase filter/degasser (Kontes). Pressure injection (200 mbar·s) was used to introduce the sample onto the capillary. The separation voltage was −20 kV (reverse polarity), and the temperature was held constant at 25 °C. Analytes were detected by direct ultraviolet (UV) light absorbance at 191 nm with the capillary itself being the detector cell. Finally, measurements of solution pH were performed using a pH meter (Fisher Scientific).

The CE method developed in our laboratory was capable of separating and detecting the HAAs listed in Table 1, except for TCAA and DBAA, which comigrated and were unable to be resolved (Figure 1). The inability to resolve TCAA and DBAA did not create problems for the experiments in this research because these compounds were never simultaneously present in a batch bottle. In addition to analysis of the HAAs, the method was also capable of detecting the anticipated degradation products bromide, chloride, and acetate in the same run. It is also important to note that the calibration curves for all nine HAAs, acetate, bromide, and chloride were linear ($R^2 \geq 0.9966$) over the concentration ranges used in the experiments ($\leq$1 mM). The method detection limits and relative standard deviation values obtained for the nine HAAs are given in Table 1.

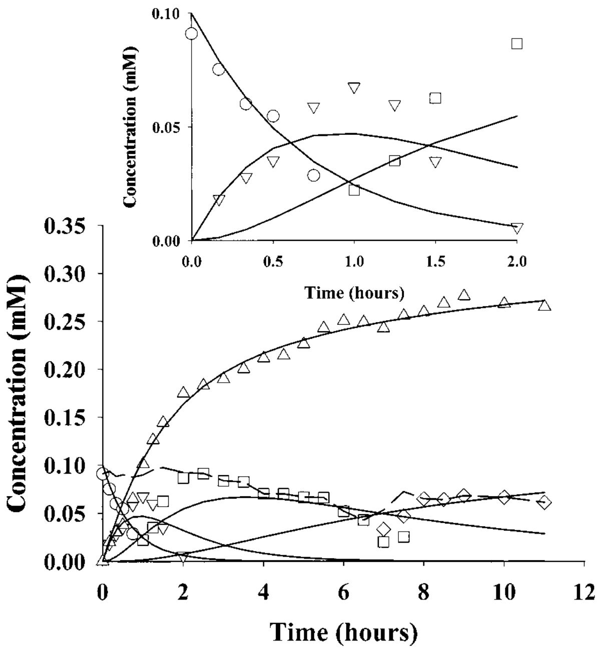

FIGURE 2. Reduction of TBAA (○) by 0.5 g of Fe(0) in 36 mL of DI water. Major products are DBAA (▽), MBAA (□), acetate (◇), and Br^- (△). The dashed line represents the observed carbon mass balance, and the solid lines are pseudo-first-order model fits. The inset figure shows the disappearance of the parent compound and the appearance of the breakdown products DBAA and MBAA during the first 2 h of incubation.

Results and Discussion

Reaction Pathways. A plot of the degradation of TBAA in the presence of Fe^0 is shown in Figure 2. The TBAA was rapidly consumed within the first 60 min of the experiment with the concomitant rise of DBAA as the product. Similarly, as DBAA was reduced, MBAA appeared, and the disappearance of MBAA was accompanied by the production of acetate. These results are consistent with the degradation proceeding via sequential hydrogenolysis from TBAA to acetate. If reductive α-elimination occurred, MBAA or acetate would have been detected at early times during the disappearance of TBAA. The total dehalogenation of TBAA was confirmed by the complete bromide mass balance (98.5%) (Figure 2). The low carbon mass balance (62.6%) in the TBAA experiment may have been due to complexation of the terminal product acetate with dissolved or solid-phase iron species, or both (*22*). In addition, there was no loss of TBAA in the control bottle (result not shown), suggesting that the TBAA degradation in the iron-containing bottles was due to dehalogenation by the Fe^0. A proposed pathway for the degradation of TBAA in the presence of Fe^0 is as follows:

Similar to the reactions of TBAA, the degradation of TCAA proceeded via sequential hydrogenolysis (Figure 3). The reductive dehalogenation of TCAA, however, was much slower than TBAA and also incomplete as evidenced by the accumulation of MCAA. The incomplete dehalogenation is also supported by the inability to detect acetate in the batch bottles and the release of only 2 mol of chloride per mole of TCAA. The carbon mass balance was 97.8%.

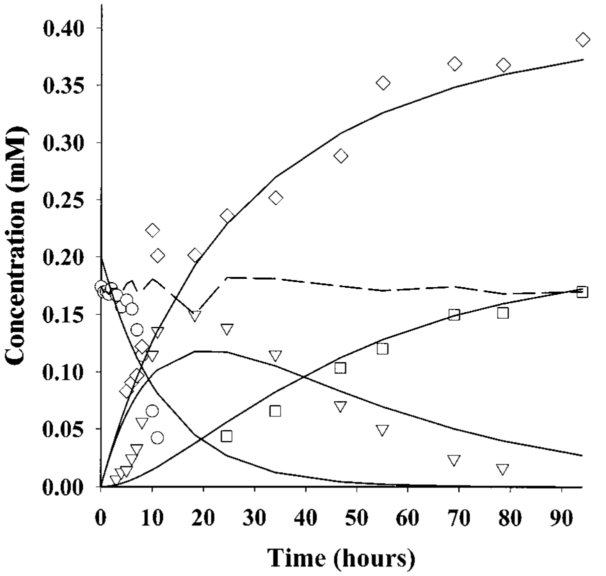

FIGURE 3. Reduction of TCAA (○) by 0.5 g of Fe(0) in 36 mL of DI water. Major products are DCAA (▽), MCAA (□), and Cl^- (◇). The dashed line represents the observed carbon mass balance, and the solid lines are pseudo-first-order model fits.

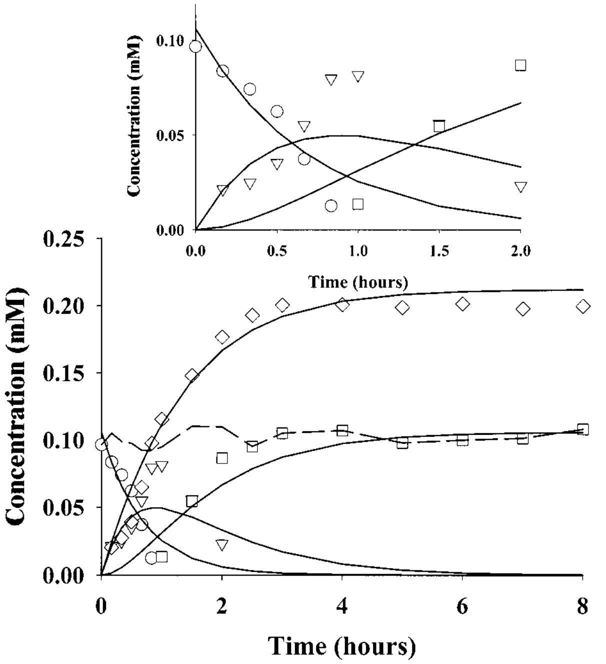

FIGURE 4. Reduction of CDBAA (○) by 0.5 g of Fe(0) in 36 mL of DI water. Major products are CBAA (▽), MCAA (□), and Br^- (◇).The dashed line represents the observed carbon mass balance, and the solid lines are pseudo-first-order model fits. The inset figure shows the disappearance of the parent compound and the appearance of the breakdown products CBAA and MCAA during the first 2 h of incubation.

For the mixed HAAs, the first step in the degradation was the loss of a bromide ion (Figures 4 and 5). Reduction of CDBAA proceeded via hydrogenolysis to form BCAA, which was subsequently reduced to MCAA (Figure 4). A plot of CE eletropherograms as a function of time clearly illustrates the destruction of the parent compound CDBAA, the production of the reaction intermediates, and accumulation of final products (Figure 6). BDCAA lost a bromide to form DCAA. A chloride was then removed to again give MCAA as the final product (Figure 5). Both carbon and halogen mass balances for the mixed HAAs ranged from 93.3 to 112%. There was no loss of either TCAA, BDCAA, or CDBAA in the control bottles without Fe^0. The results from the control bottles were not plotted in Figures 3–5 for clarity. Proposed pathways for the degradation of TCAA, BDCAA, and CDBAA, which all lead to

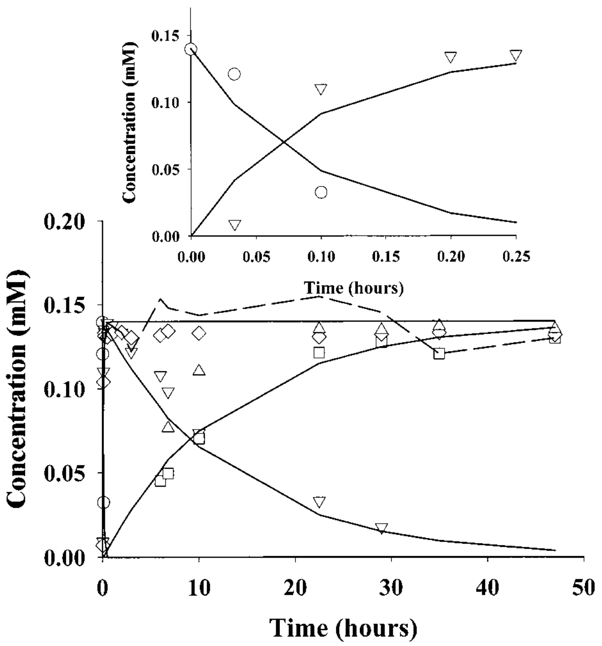

FIGURE 5. Reduction of BDCAA (○) by 0.5 g of Fe(0) in 36 mL of DI water. Major products are DCAA (▽), MCAA (□), Br$^-$ (◇), and Cl$^-$ (△). The dashed line represents the observed carbon mass balance, and the solid lines are pseudo-first-order model fits. The inset figure shows the disappearance of the parent compound and the appearance of the first breakdown product DCAA during the first 0.25 h of incubation.

MCAA as the final product, in the presence of Fe^0 are given in Figure 7.

Unlike the structurally similar 1,1,1-trichloroethane, there is no evidence that the trihaloacetic acids undergo reductive α-elimination. The work of Fennelly and Roberts (*18*) demonstrated that the reactions pathways of 1,1,1-trichloroethane can be altered by plating a catalytic metal (Cu, Ni) onto the iron. Reductive α-elimination was also increased by using Zn^0 instead of Fe^0. The reaction pathways of HAAs mediated by other reductants merit further investigation.

Degradation Rates. For each trihaloacetic acid, the concentration versus time data for the degradation of the parent compound, the formation and decay of daughter acetic acid species, and the production of the halide ions were simultaneously fit using a pseudo-first-order kinetic model for reactions in series. Rate constants were determined by a least-squares fit of numerically integrated solutions of the differential equations to the experimental data. In Figures 2−5, the solid lines represent these model fits. In general, the model captures the major features of the data well. The concentrations of intermediates (e.g., DBAA from TBAA or DCAA from TCAA) are slightly underpredicted by the model, and the predicted decay of these species is slightly slower than the experimentally observed decay rates. The overall success of this reaction-in-series model, however, provides support for the assertion that sequential hydrogenolysis is the pathway by which reactions are occurring.

The rate constants calculated for all the starting materials and intermediates that were detected are presented in Table 2. Based on these pseudo-first-order degradation rate constants, the ranking of degradation rates from fastest to slowest for the trihaloacetic acids was as follows: BDCAA (10.6 ± 3.1 h^{-1}) > CDBAA (1.43 ± 0.32 h^{-1}) ≈ TBAA (1.41 ± 0.28 h^{-1}) ≫ TCAA (0.08 ± 0.02 h^{-1}). The degradation of BDCAA is so rapid that it is likely to be mass transfer limited based on a calculation for mass transfer to suspended particles (*58, 59*). The trend in these rate constants is consistent with the trends observed for the reduction of trihalomethanes by Cr(II) (*60*) and by an iron porphyrin (*61*). For each of these reductants, the degradation rates for the bromine-containing compounds were much greater than for the trichlorinated compound. The results observed for both the trihaloacetic acids and the trihalomethanes are consistent with the preferential removal of bromine over chlorine.

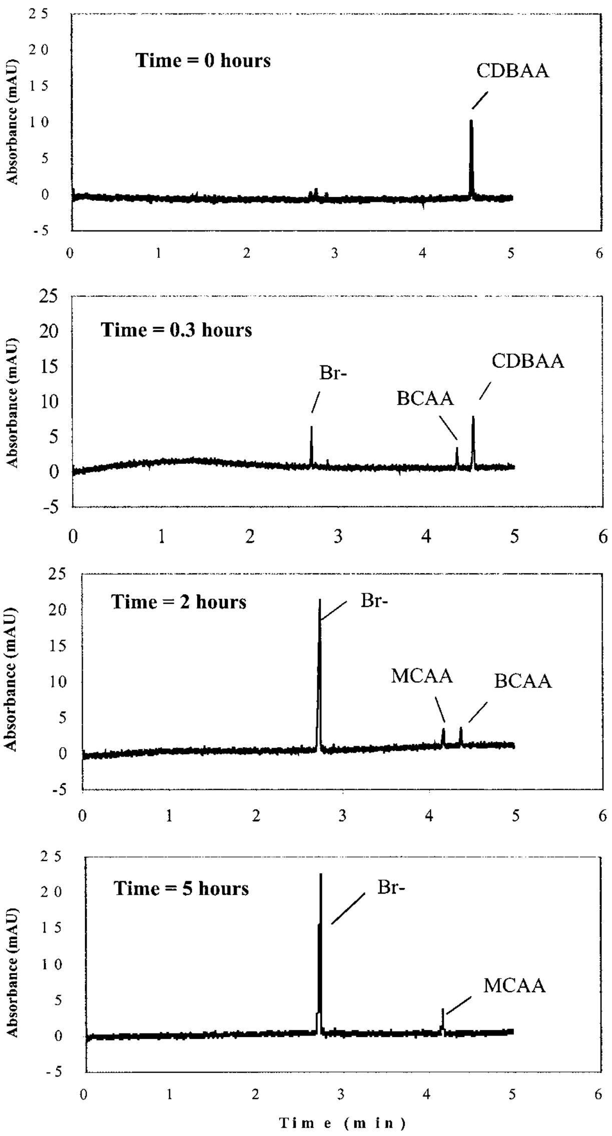

FIGURE 6. CE electropherograms as a function of time for the reduction of CDBAA in the presence of Fe(0). The electropherograms show the disappearance of the parent compound CDBAA, the subsequent appearance and disappearance of the intermediate BCAA, and the accumulation of the final products MCAA and bromide.

Although we have reported fitted rate constants for the HAAs appearing as intermediates in our experimental systems, we cannot currently make any claims about the relative reactivity of these species. The initial conditions for the trihaloacetic acids were similar (e.g., pH, iron surface oxide coating), and this allows a comparison to be made. The intermediates were produced over different time scales and thus were exposed to different solution and iron surface conditions, which may lead to changes in reactivity. The obvious example of this are the different pseudo-first-order rate constants obtained from the model fits for the intermediate DCAA produced from TCAA and BDCAA. BDCAA is completely consumed within 15 min, leading to rapid production of DCAA. The DCAA produced, therefore, is degraded under conditions very similar to those at the

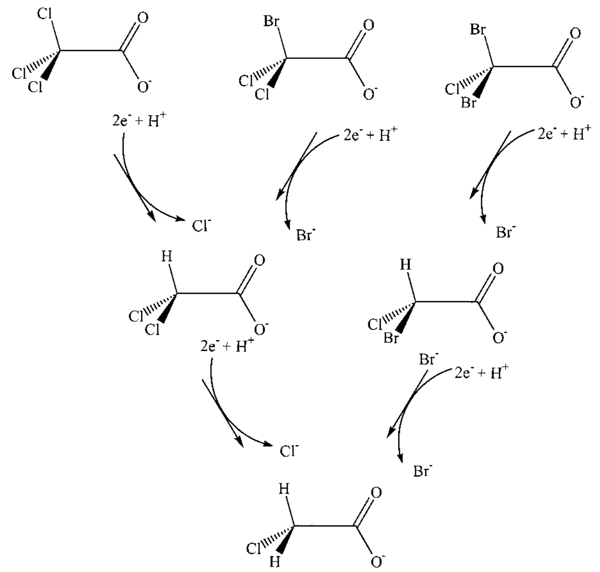

FIGURE 7. Reaction pathways of trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA), and chlorodibromoacetic acid (CDBAA) with Fe(0). For each species, reduction occurs via hydrogenolysis with chloroacetic acid (MCAA) as the terminal product.

TABLE 2. Pseudo-First-Order Rate Constants for Haloacetic Acid Reduction[a]

Figure	reaction	k_{obs} ($\mathrm{h^{-1}}$)
2	$\mathrm{TBAA \rightarrow DBAA + Br^-}$	1.41 ± 0.28
	$\mathrm{DBAA \rightarrow BAA + Br^-}$	0.82 ± 0.24
	$\mathrm{BAA \rightarrow acetate + Br^-}$	0.14 ± 0.03
3	$\mathrm{TCAA \rightarrow DCAA + Cl^-}$	0.08 ± 0.02
	$\mathrm{DCAA \rightarrow CAA + Cl^-}$	0.03 ± 0.01[b]
4	$\mathrm{CDBAA \rightarrow CBAA + Br^-}$	1.43 ± 0.32
	$\mathrm{CBAA \rightarrow CAA + Br^-}$	0.84 ± 0.28
5	$\mathrm{BDCAA \rightarrow DCAA + Br^-}$	10.6 ± 3.1
	$\mathrm{DCAA \rightarrow CAA + Cl^-}$	0.08 ± 0.01[b]

[a] Rate constants were determined for the degradation via simultaneously fitting the data for parent compounds, intermediates, and final products, including bromide and chloride. [b] The difference in these values is likely due to different pH and iron surface conditions (see text).

beginning of the experiment. DCAA is produced much more slowly from TCAA and therefore encounters different iron surface and pH conditions than the DCAA produced from BDCAA. These differences may explain why the rate constant for DCAA produced from TCAA is only 40% of that for DCAA formed via the degradation of BDCAA.

Even though the pseudo-first-order model provides a reasonable fit to our experimental data and has often been used to fit data obtained from zerovalent metal experiments, the degradation rates of TBAA, CDBAA, and TCAA appeared to undergo a subtle acceleration as the reaction progressed. The acceleration of the reaction with decreasing concentration is consistent with competition for reactive sites on the iron surface, as previously observed for carbon tetrachloride (*21*, *22*, *27*, *62*), chlorinated ethylenes (*46*−*49*), and nitroaromatic compounds (*63*). Detailed kinetic experiments to evaluate the degradation rates of all of the HAAs including the dihalogenated and monohalogenated acetic acids are currently underway in our laboratory. These studies will focus on measurement of surface-mediated reaction rate constants for each species and elucidation of the role of pH (and thus HAA speciation) on transformation kinetics.

Environmental Significance. The reduction of HAAs by $\mathrm{Fe^0}$ has important implications for the fate and treatment of these potentially carcinogenic compounds. Drinking water distribution systems primarily consist of unlined cast iron pipe. The abundance of iron metal in distribution systems may account for some of the loss of HAAs observed in full-scale distribution systems (*64*). It is expected, however, that the corroded and passivated iron surfaces in a distribution system would be much less reactive than the laboratory grade electrolytic iron used in this research. Thus, reaction rates of HAAs in the presence of cast iron filings and cast iron piping from actual distribution systems merit investigation. The roles of pH, temperature, and potential complexing agents also need to be established. In addition to impacting HAA fate in distribution systems, destruction of HAAs by $\mathrm{Fe^0}$ suggests a potential approach for in-home water treatment to eliminate these compounds from tap water. Although the observed persistence of MCAA may be of concern, we will investigate possible approaches for degrading this compound such as the use of a small amount of a catalytic metal (e.g., palladium, copper, or nickel) in combination with iron.

Acknowledgments

The authors acknowledge the funding provided by the American Water Works Association Research Foundation (Project 2644) to support the development of a method for analyzing HAAs using capillary electrophoresis. We also thank the three anonymous reviewers, whose comments and suggestions significantly improved the manuscript.

Literature Cited

(1) Krasner, S. W.; McGuire, M. J.; Jacangelo, J. G.; Patania, N. L.; Reagan, K. M.; Aieta, E. M. *J.—Am. Water Works Assoc.* **1989**, *41*−*53*, 41.
(2) Rebhun, M.; Heller-Grossman, L.; Manka, J. *Water Environ. Res.* **1997**, *69*, 1154−1162.
(3) National Academy of Sciences Safe Drinking Water Committee *Drinking Water and Health*; National Academy Press: Washington, DC, 1980; Vol. 6.
(4) Pontius, F. W. *J.—Am. Water Works Assoc.* **1999**, *91*, 46−58.
(5) Martinez, D.; Borrull, F.; Calull, M. *J. Chromatogr., A* **1999**, *835*, 187−196.
(6) Berg, M.; Muller, S. R.; Muhlemann, J.; Wiedmer, A.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **2000**, *34*, 2675−2683.
(7) Muller, S. R.; Zweifel, H. R.; Kinnison, D. J.; Jacobsen, J. A.; Meier, M. A.; Ulrich, M. M.; Schwarzenbach, R. P. *Environ. Toxicol. Chem.* **1996**, *15*, 1470−1478.
(8) Reimann, S.; Grob, K.; Frank, H. *Environ. Sci. Technol.* **1996**, *30*, 2340−2344.
(9) Frank, H.; Scholl, H.; Renschen, D.; Rether, B.; Laouedj, A.; Norokorpi, Y. *Environ. Sci. Pollut. Res. Int.* **1994**, *1*, 4−14.
(10) Glaze, W. H.; Kenneke, J. F.; Ferry, J. L. *Environ. Sci. Technol.* **1993**, *27*, 177−184.
(11) *Naturally-Produced Organohalogens, Environment & Chemistry*; Grimvall, A., deLeer, E. W. B., Eds.; Kluwer Academic Publishers: Dordrecht, Holland, 1995.
(12) Martin, J. W.; Frankilin, J.; Hanson, M. L.; Solomon, K. R.; Mabury, S. A.; Ellis, D. A.; Scott, B. F.; Muir, D. C. G. *Environ. Sci. Technol.* **2000**, *34*, 274−281.
(13) De Wever, H.; Cole, J. R.; Fettig, M. R.; Hogan, D. A.; Tiedje, J. M. *Appl. Environ. Microbiol.* **2000**, *66*, 2297−2301.
(14) Yu, P.; Welander, T. *Appl. Microbiol. Biotechnol.* **1995**, *42*, 769−774.
(15) Boethling, T. W.; Alexander, M. *Appl. Environ. Microbiol.* **1979**, *37*, 1211−1216.
(16) Balko, B. A.; Tratnyek, P. G. *J. Phys. Chem.* **1998**, *102*, 1459−1465.
(17) Boronina, T.; Klabunde, K. J.; Sergeev, G. *Environ. Sci. Technol.* **1995**, *29*, 1511−1517.
(18) Fennelly, J. P.; Roberts, A. L. *Environ. Sci. Technol.* **1998**, *32*, 1980−1988.
(19) Gillham, R. W.; O'Hannesin, S. F. *Ground Water* **1994**, *32*, 958−967.
(20) Helland, B. R.; Alvarez, P. J. J.; Schnoor, J. L. *J. Hazard. Mater.* **1995**, *41*, 205−216.
(21) Johnson, T. L.; Scherer, M. M.; Tratnyek, P. G. *Environ. Sci. Technol.* **1996**, *30*, 2634−2640.
(22) Johnson, T. L.; Fish, W.; Gorby, Y. A.; Tratnyek, P. G. *J. Contam. Hydrol.* **1998**, *29*, 379−398.

(23) Li, T.; Farrell, J. *Environ. Sci. Technol.* **2000**, *34*, 173−179.
(24) Lipczynska-Kochany, E.; Harms, S.; Milburn, R.; Sprah, G.; Nadarajah, N. *Chemosphere* **1994**, *29*, 1477−1489.
(25) Lien, H.-L.; Zhang, W.-X. *J. Environ. Eng., ASCE* **1999**, *125*, 1042−1047.
(26) Matheson, L. J.; Tratnyek, P. G. *Environ. Sci. Technol.* **1994**, *28*, 2045−2053.
(27) Scherer, M. M.; Tratnyek, P. G. Dechlorination of carbon tetrachloride by iron metal: Effect of reactant concentrations. *Prepr. Pap. ACS Natl. Meet., Am. Chem. Soc., Div. Environ. Chem.* **1995**, *35*, 805−806 (Abstr.).
(28) Scherer, M. M.; Westall, J. C.; Ziomek-Moroz, M.; Tratnyek, P. G. *Environ. Sci. Technol.* **1997**, *31*, 2385−2391.
(29) Schreier, C. G.; Reinhard, M. *Chemosphere* **1994**, *29*, 1743−1753.
(30) O'Hannesin, S. F.; Gillham, R. W. *Ground Water* **1998**, *36*, 164−170.
(31) Senzaki, T.; Kumagai, Y. *Kogyo Yosui* **1988**, *357*, 2−7.
(32) Senzaki, T.; Kumagai, Y. *Kogyo Yosui* **1989**, *369*, 19−25.
(33) Burris, D. R.; Campbell, T. J.; Manoranjan, V. S. *Environ. Sci. Technol.* **1995**, *29*, 2850−2855.
(34) Cipollone, M. G.; Wolfe, M. L.; Hassan, S. M. Kinetic studies on the use of metallic iron to reduce orgainc compounds in water under enviornmental conditions. *Prepr. Pap. ACS Natl. Meet., Am. Chem. Soc., Div. Environ. Chem.* **1995**, *35*, 812−814 (Abstr.).
(35) Mackenzie, P. D.; Baghel, S. S.; Eykholt, G. R.; Horney, D. P.; Salvo, J. J.; Sivavec, T. M. Pilot-scale demonstration of reductive dechlorination of chlorinated ethenes by iron metal. *Prepr. Pap. ACS Natl. Meet., Am. Chem. Soc., Div. Environ. Chem.* **1995**, *35*, 796−799 (Abstr.).
(36) Vogan, J. L.; Gillham, R. W.; O'Hannesin, S. F.; Matulewicz, W. H.; Rhodes, J. E. Site specific degradation of VOCs in groundwater using zerovalent iron. *Prepr. Pap. ACS Natl. Meet., Am. Chem. Soc., Div. Environ. Chem.* **1995**, *35*, 800−804 (Abstr.).
(37) Yamane, C. L.; Warner, S. D.; Gallinatti, J. D.; Szerdy, F. S.; Delfino, T. A. Installation of a subsurface groundwater treatment wall composed of granular zerovalent iron. *Prepr. Pap. ACS Natl. Meet., Am. Chem. Soc., Div. Environ. Chem.* **1995**, *35*, 792−795 (Abstr.).
(38) Orth, W. S.; Gillham, R. W. *Environ. Sci. Technol.* **1996**, *30*, 66−71.
(39) Roberts, A. L.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. *Environ. Sci. Technol.* **1996**, *30*, 2654−2659.
(40) Campbell, T. J.; Burris, D. R.; Roberts, A. L.; Wells, J. R. *Environ. Toxicol. Chem.* **1997**, *16*, 625−630.
(41) Allen-King, R.; Halket, R. M.; Burris, D. R. *Environ. Toxicol. Chem.* **1997**, *16*, 424−429.
(42) Liang, L.; Korte, N.; Goodlaxson, J. D.; Clausen, J.; Fernando, Q.; Muftikian, R. *Ground Water Monit. Rem.* **1997**, 122−127.
(43) Gotpagar, J.; Grulke, E.; Tsang, T.; Bhattacharyya, D. *Environ. Prog.* **1997**, *16*, 137−143.
(44) Gotpagar, J. K.; Grulke, E. A.; Bhattacharyya, D. *J. Hazard. Mater.* **1998**, *62*, 243−264.
(45) Su, C.; Puls, R. W. *Environ. Sci. Technol.* **1999**, *33*, 163−168.
(46) Wust, W. F.; Kober, R.; Schlicker, O.; Dahmke, A. *Environ. Sci. Technol.* **1999**, *33*, 4304−4309.
(47) Farrell, J.; Kason, M.; Melitas, N.; Li, T. *Environ. Sci. Technol.* **2000**, *34*, 514−521.
(48) Arnold, W. A.; Roberts, A. L. *Environ. Sci. Technol.* **2000**, *34*, 1794−1805.
(49) Arnold, W. A.; Roberts, A. L. *Environ. Eng. Sci.* **2000**, *17*, 291−302.
(50) Kim, Y.-H.; Carraway, E. R. *Environ. Sci. Technol.* **2000**, *34*, 2014−2017.
(51) Chuang, F. W.; Larson, R. A.; Wessman, M. S. *Environ. Sci. Technol.* **1995**, *29*, 2460−2463.
(52) Rajagopal, V. K.; Burris, D. R. *Environ. Toxicol. Chem.* **1999**, *18*, 1779−1782.
(53) Siantar, D. P.; Schreier, C. G.; Chou, C.-S.; Reinhard, M. *Water Res.* **1996**, *30*, 2315−2322.
(54) *Standard Methods for the Examination of Water and Wastewater*, 18th ed.; American Public Health Association, American Water Works Association, and Water Pollution Control Federation: Washington, DC, 1995.
(55) *Merck Index*, 10th ed.; Merck and Company: Rahway, NJ, 1983.
(56) Xie, Y.; Reckhow, D. A.; Springborg, D. C. *J.*—*Am. Water Works Assoc.* **1998**, *90*, 131−138.
(57) Urbansky, E. T. *J. Environ. Monit.* **2000**, *2*, 285−291.
(58) Harriott, P. *AIChE J.* **1962**, *8*, 93−102.
(59) Arnold, W. A.; Ball, W. P.; Roberts, A. L. *J. Contam. Hydrol.* **1999**, *40*, 183−200.
(60) Totten, L. A. Ph.D. Thesis, The Johns Hopkins University: Baltimore, MD, 1999.
(61) Perlinger, J. A.; Buschmann, J.; Angst, W.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1998**, *32*, 2431−2437.
(62) Scherer, M. M.; Balko, B. A.; Tratnyek, P. G. The Role of Oxides in Reduction Reactions at the Metal−Water Interface. In *Kinetics and Mechanisms of Reactions at the Mineral/Water Interface*; Sparks, D. L., Grundl, T., Eds; ACS Symposium Series; American Chemical Society: Washington, DC, 1998.
(63) Devlin, J. F.; Klausen, J.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **1998**, *32*, 1941−1947.
(64) Chen, W. J.; Weisel, C. P. *J.*—*Am. Water Works Assoc.* **1998**, *90*, 151−163.

Received for review October 18, 2000. Revised manuscript received February 15, 2001. Accepted February 19, 2001.

ES001785B