ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

Organized by

T. Zachry

Symposia Papers Presented Before the Division of Environmental Chemistry
American Chemical Society
Anaheim, CA March 28 – April 1, 2004

OVERCOMING BARRIERS TO THE REMEDIATION OF CARBON TETRACHLORIDE THROUGH MANIPULATION OF COMPETING REACTION MECHANISMS

Paul G. Tratnyek[1], James E. Amonette[2] and Eric J. Bylaska[2]
[1]Oregon Health & Science University, 20000 NW Walker Road, Beaverton, OR 97006
[2]Pacific Northwest National Laboratory, Richland, WA 99352
tratnyek@ebs.ogi.edu, Fax: 503-748-1273

A great deal of research has been published on the degradation of CCl_4 due to the combination of its convenience as the prototypical chlorinated alkane and its relevance as an environmental contaminant. However, the majority of this work has focused primarily on disappearance of the parent compound, without characterization of the reaction products beyond preliminary verification of the expected reaction pathways[1-4]. Other studies have attempted exhaustive product identifications in order to develop detailed reaction pathways, but with limited quantification of the distribution of products or investigation of the factors that control product-branching ratios. Comparatively few studies have gone so far as to quantify product branching ratios and/or to model the variability in product branching ratios with experimental conditions.

Among the studies that have addressed product distributions in some detail, most offer evidence for variations in product-branching ratios that might be significant in environmental remediation applications. For example, an early study by Criddle and McCarty used a simple electrolysis cell to demonstrate that more cathodic potentials (at a Ag electrode) favor hydrogenolysis of CCl_4 beyond $CHCl_3$ to CH_2Cl_2 and somewhat more reaction by the alternative pathway that produces CO[5]. More recent studies of controlled electrolysis have shown more complete dechlorination of CCl_4 using electrodes made from other metals[6] and Fe(0) electrodes protected with high cathodic overpotentials[7]. In suspensions of granular zero-valent metals—without an externally supplied cathodic overpotential—the type of metal[8], photoexcitation[9], presence of H-

donors [9], and the composition of the passive film[10] have all been shown to influence the distribution of products from reduction of CCl_4.

More detailed studies of product-branching ratios are available for just a few systems. A kinetic model has also been presented that describes product-formation pathways for abiotic reduction of CCl_4 on biotite, vermiculite and pyrite[11,12], but this work did not involve systematic testing of the effects of experimental conditions on product-branching ratios. In recent work on reduction by mineral surfaces where Fe(II) is present we have shown little difference in product-branching ratios among different halogenated methanes[13], but large changes in product-branching ratios have been observed with different preparations of the adsorbing mineral surface (Fig. 1).

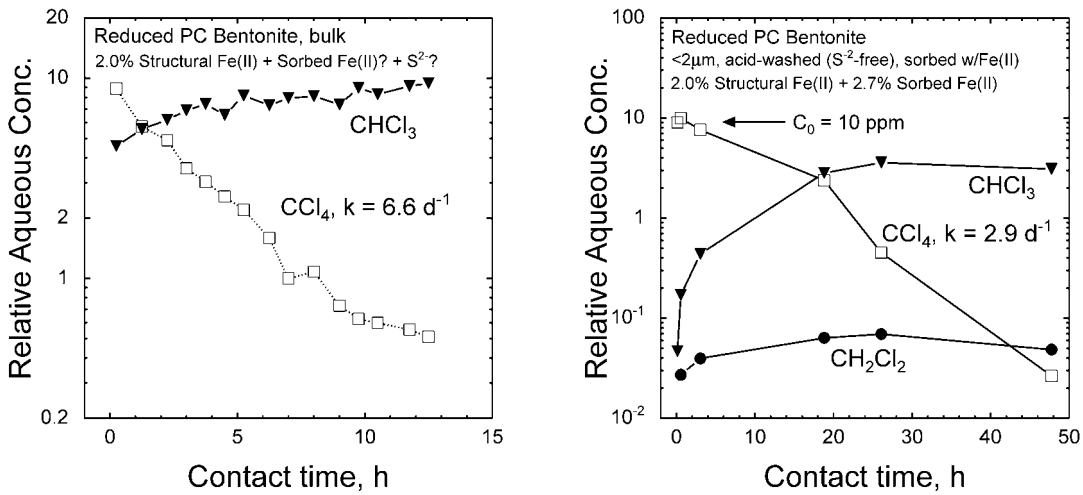

Figure 1. Analysis of products obtained from reaction of CCl_4 with a dithionite-reduced clay suggests that reduction mechanisms vary with the surface properties of the clay. Reduction of the bulk bentonite clay (left) leaves an unknown quantity of sorbed Fe(II), $FeCO_3$ and possible sulfide minerals as solid reductants (in addition to the structural Fe(II) in the smectite) and yields nearly complete conversion of CCl_4 to $CHCl_3$. If the bentonite clay is size-fractionated (<2 µm) to isolate the smectite mineral, acid-washed after dithionite reduction to remove sulfides and the exchange sites saturated with Fe(II) (right), only 35% of the CCl_4 is converted to $CHCl_3$. The remainder, presumably, is converted to CO and eventually $HCOO^-$ and CO_2 *via* the dichlorocarbene intermediate.

Consideration of our own preliminary results (*e.g.*, Fig. 1) and the published literature suggests that the product-branching ratio depends on the nature of the reducing surface as well as the composition of the aqueous phase. Amonette *et al.*[1], Pecher *et al.*[13], and unpublished data from PNNL (D. J. Workman and Y. A. Gorby) show that Fe(II) sorbed to hematite and hydrous ferric oxide surfaces strongly favors the two-electron pathway, whereas sorption to goethite surfaces leads to as much as 90% reaction by the one-electron pathway (as evidenced by formation of $CHCl_3$). Pecher *et al.*[13] also noted a significant beneficial effect of aging (8-24 h) on the reactivity of the Fe(II) sorbed to

goethite surfaces and they speculate that this aging results in the formation of high-density clusters of sorbed Fe(II) or Fe(II) surface precipitates. A similar process was implicated by Amonette *et al*.[1] who demonstrated a second-order dependence of degradation rate on sorbed Fe(II) and suggested that the catalytic role of the surface resulted from the fixing of two Fe(II) atoms in close proximity for simultaneous (or rapid sequential) reaction with CCl_4.

The presence in solution of readily available H donors can affect the product-distribution ratio. Pecher *et al*.[13] demonstrated that protons from solution do not affect the branching ratio and speculated that trace amounts of methanol or the organic pH buffers (*e.g*., MOPS) used in their experiments with sorbed Fe(II) could supply H atoms for the one-electron reaction. However, Balko and Tratnyek[9] found that isopropanol increased the amount of CCl_4 degraded by the one-electron pathway under photochemical stimulation. They noted that this might be an underappreciated source of variation in product-distribution ratios because experiments are often performed in the presence of significant concentrations of organic buffers (which would be strong H-donors). This hypothesis might also apply to the interpretation of field data, since variable amounts of natural organic matter might provide an uncontrollable source of variability in product-branching ratios.

Manipulation of solution pH also affects product distribution. With sorbed Fe(II) systems, *increasing* the pH above 6 enhances the amount and density of Fe(II) sorbed and this, in turn, increases both the overall rate[1] and the proportion of reactant following the two-electron pathway[13]. Similar enhancement at high pH was reported for photochemical degradation of CCl_4 at TiO_2 surfaces[14] and attributed to the base-catalyzed hydrolysis of the dichlorocarbene. At pH of 8.5 and above, however, hydrolysis of Fe(II) leads increasingly to its oxidation by water and precipitation of mixed-valence green-rust phases in which the Fe(II) density is less and the dichlorocarbene pathway is less favored[13]. With Fe(0) systems, on the other hand, we have observed that *decreasing* the influent pH below 7 favors the desirable two-electron pathway (Fig. 2). This is presumably due to solubilization of the oxide film and thereby depassivation the Fe(0) toward corrosion.

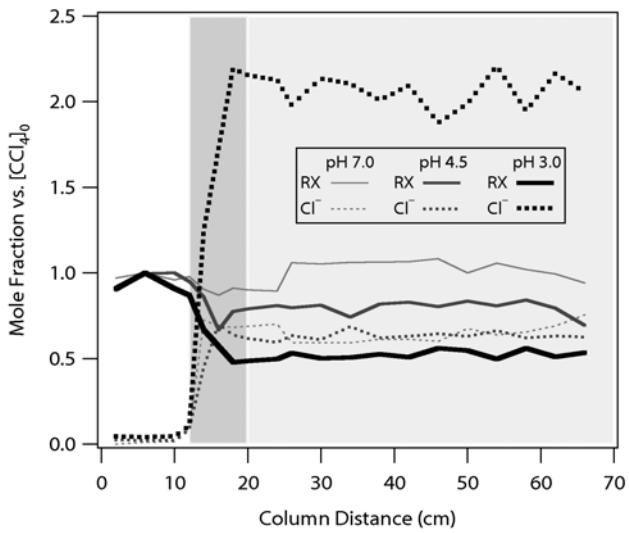

Figure 2. Mole balance of chlorinated methanes ($[RX]/[CCl_4]_0$ where RX = CCl_4+$CHCl_3$+CH_2Cl_2) and chloride ($[Cl^-]/[CCl_4]_0$) along a column packed with 12 cm of sand (unshaded) followed by a zone of granular Fe(0) (shaded). The darkly shaded area is the interfacial region where accumulation of precipitates on the Fe(0) is greatest. The influent pH was adjusted by titration with HCl to the pH values indicated in the caption. The pH adjustment apparently resulted in more complete dechlorination of CCl_4, perhaps due to a shift from the one-electron to the two-electron product-formation pathways.

ACKNOWLEDGEMENTS

This research was supported by the Environmental Management Science Program of the Office of Science, U.S. Department of Energy, grant DE-FG07-02ER63485.

REFERENCES

1. Amonette, J. E.; Workman, D. J.; Kennedy, D. W.; Fruchter, J. S.; Gorby, Y. A. (2000) Dechlorination of carbon tetrachloride by Fe(II) associated with goethite. *Environ. Sci. Technol*., **34**(21), 4606-4613.
2. Johnson, T. L.; Fish, W.; Gorby, Y. A.; Tratnyek, P. G. (1998) Degradation of carbon tetrachloride by iron metal: Complexation effects on the oxide surface. *J. Contam. Hydrol*., **29**(4), 377-396.
3. Kim, S.; Picardal, F. W. (1999) Enhanced anaerobic biotransformation of carbon tetrachloride in the presence of reduced iron oxides. *Environ. Toxicol. Chem*., **18**(10), 2142.
4. McCormick, M. L.; Bouwer, E. J.; Adriaens, P. (2002) Carbon tetrachloride transformation in a model iron-reducing culture: Relative kinetics of biotic and abiotic reactions. *Environ. Sci. Technol*., **36**(3), 403-410.
5. Criddle, C. S.; McCarty, P. L. (1991) Electrolytic model system for reductive dehalogenation in aqueous environments. Environ. Sci. Technol., 25(5), 973-978.
6. Liu, Z.; Arnold, R. G.; Betterton, E. A.; Festa, K. D. (1999) Electrolytic reduction of CCl_4—Effects of cathode material and potential on kinetics, selectivity and product stoichiometry. *Environ. Eng. Sci*., **16**(1), 1-13.
7. Li, T.; Farrell, J. (2000) Reductive dechlorination of trichloroethene and carbon tetrachloride using iron and palladized-iron cathodes. *Environ. Sci. Technol.,* **34**(1), 173-179.

8. Boronina, T.; Klabunde, K. J.; Sergeev, G. (1995) Destruction of organohalides in water using metal particles: Carbon tetrachloride/water reactions with magnesium, tin, and zinc. *Environ. Sci. Technol*., **29**(6), 1511-1517.
9. Balko, B. A.; Tratnyek, P. G. (1998) Photoeffects on the reduction of carbon tetrachloride by zero-valent iron. *J. Phys. Chem. B*, **102**(8), 1459-1465.
10. Agrawal, A.; Ferguson, W. J.; Gardner, B. O.; Christ, J. A.; Bandstra, J. Z.; Tratnyek, P. G. (2002) Effects of carbonate species on the kinetics of 1,1,1-trichloroethane by zero-valent iron. *Environ. Sci. Technol*., **36**(20), 4326-4333.
11. Kriegman-King, M. R.; Reinhard, M. (1994) Transformation of carbon tetrachloride by pyrite in aqueous solution. *Environ. Sci. Technol*., **28**(4), 692-700.
12. Kriegman-King, M. R.; Reinhard, M. (1992) Transformation of carbon tetrachloride in the presence of sulfide, biotite and vermiculite. *Environ. Sci. Technol*., **26**(11), 2198-2206.
13. Pecher, K.; Haderlein, S. B.; Schwarzenbach, R. P. (2002) Reduction of polyhalogenated methanes by surface-bound Fe(II) in aqueous suspensions of iron oxides. *Environ. Sci. Technol*., **36**(8), 1734-1741.
14. Choi, W.; Hoffmann, M. R. (1996) Kinetics and mechanism of CCl_4 photoreductive degradation on TiO_2: The role of trichloromethyl radical and dichlorocarbene. *J. Phys. Chem*., **100**(6), 2161-2169.