



Kinetics and mechanism of reductive dehalogenation of carbon tetrachloride using zero-valence metals

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Received 29 July 1994; accepted in revised form 15 November 1994

Abstract

Elemental iron and zinc reduced part-per-thousand levels of aqueous-phase carbon tetrachloride to chloroform in a few hours. Free metal ions, chloride ion and hydrogen gas were produced in the reaction; protons were consumed. Process kinetics were dependent on solution pH, surface area of the elemental metal, carbon tetrachloride concentration, buffer selection and solvent composition (volume fraction 2-propanol). Reaction rate was first-order with respect to carbon tetrachloride at concentrations less than 7.5 mM. This class of reactions offers promise as a means for initiating the destruction of heavily halogenated organic compounds.

1. Introduction

The widespread industrial and agricultural use of halogenated aliphatic compounds as solvents, degreasing agents, pesticides, and fumigants has led to the contamination of many ground water systems. There are strong environmental and economic incentives for improving existing methods of remediation and/or developing new treatment technologies for these wastes. Heavily halogenated aliphatics are particularly resistant to remediation strategies based on aerobic, microbial transformations [1]. One approach is to dehalogenate or partially dehalogenate organic halides under reducing conditions to yield intermediates that are more amenable to subsequent aerobic treatment.

A number of investigators have observed patterns in the reductive transformation of halogenated aliphatic compounds in mixed bacterial cultures [2] and cell-free reactors containing reductant, bacterially derived electron carriers (vitamin B₁₂ and hemein), and the halogenated targets [3, 4]. It is generally agreed that the feasibility

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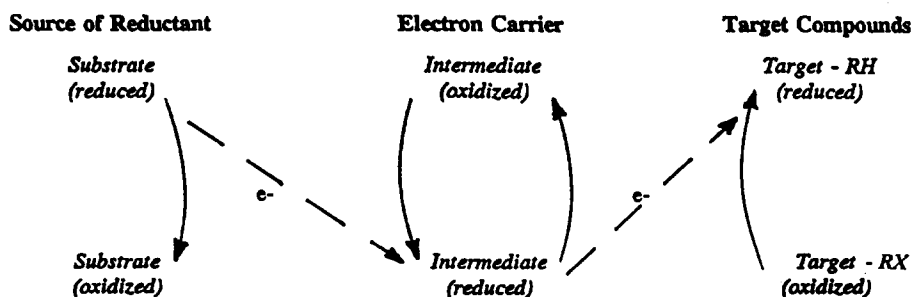


Fig. 1. Generalized elements of catalyzed systems for the reductive: Dehalogenation of halogenated organic compounds (after Schwarzenbach et al. [9]).

and rates of such reactions are governed by reaction energetics (overall free-energy change and/or carbon-halogen bond strength of the target) and what Bouwer and Wright [2] called the electron acceptor condition – the availability of competitive electron acceptors such as molecular oxygen and nitrate. Biochemical catalytic mechanisms remain, in general, somewhat speculative and may be diverse.

Zero-valence metals such as iron and zinc were identified as agents for abiotic dehalogenation reactions by Sweeney and Fischer [5], who used granular zinc to enhance the degradation of pesticides. Reynolds et al. [6] found that a variety of polyhalogenated aliphatic compounds were transformed to unidentified products in the presence of stainless steel, elemental aluminum or galvanized steel. In each case, the reaction proceeded after a noticeable lag period that may have been required for the elimination of molecular oxygen. Gillham et al. [7] further explored the chemistry and limitations of zero-valence metals as agents for the reductive transformation of halogenated methanes, ethanes, and ethenes. The minimum reactive system consisted of only the metal, distilled water and the target. Although half lives varied considerably in an Fe-mediated system, rates were generally faster for heavily halogenated targets (e.g., 13.6 h for trichloroethene vs. 106 h for vinyl chloride under similar conditions). Rates of reaction were many times faster than those representing abiotic transformations under natural conditions [1]. A porous, Fe-containing cut-off wall in the path of a contaminant plume decreased TCE concentrations by an order of magnitude or more [7]. Gillham and O'Hannesin [8] described column tests in which first-order transformation kinetics for the reduction of TCE were observed.

The elements of catalyzed systems for the reductive dehalogenation of halogenated organic compounds (Fig. 1) consist of a reductant, one or more electron-carrying or hydrogen-carrying intermediates, and the halogenated target [9]. In the systems described here, the reductant is elemental iron or zinc, elemental hydrogen is a suspected intermediate or electron carrier, and the target compound is bromoform or carbon tetrachloride. Results suggest that the reductive dehalogenation of halomethanes by elemental metals is mediated by hydrogen at the metal surface. When overall transformation rates were reaction limited, rate dependence on solution pH, mass of metal, and target concentration was apparent. Cosolvent effects were observed in the zinc

Table 1

Metals used in screening experiments (5 ml liquid (H₂O/2-propanol) volume in 10 ml hypovials, 0.07 g metal or metal oxide, 34 mM bromoform)

| Metal | E_{H}° (V) (vs. SHE) ^a | Manufacturer | Size/form |
|--------------------------------|---|--------------|----------------------|
| Zinc | – 0.7628 | Fisher | < 600 μm |
| Iron | – 0.409 | Aldrich | < 600 μm |
| Tin | – 0.1364 | Fisher | Shot pellets |
| Aluminum | – 1.706 (0.1 f NaOH) | Baker | 2.36–0.85 mm |
| Al ₂ O ₃ | NA | Fisher | 75–180 μm |
| SiO ₂ | NA | DuPont | Chips |

^a R.C. Weast and M.J. Astle, CRC Handbook of Chemistry and Physics, 61st edn.

system. Rates were not strictly a function of transformation thermodynamics. The mechanism for dehalogenation is apparently more complex than has been reported previously.

2. Methods and materials

Screening experiments were conducted in 10 ml glass hypovials with a 50/50 ratio of liquid and headspace volumes. Liquid contents generally consisted of a 50/50 v/v mixture of deionized water (Milli-Q) and 2-propanol (reagent grade, Mallinckrodt), although 2-propanol was sometimes omitted. Zero-valence metals (Zn, Al, Sn, Fe) and metal oxides (Al₂O₃ and SiO₂) were suspended individually in the solvent (Table 1) before reactors were crimp sealed with Teflon-coated septa. The contents were purged with high purity argon (US Airweld) for 15–30 min prior to introduction of halogenated target. Bromoform (Aldrich) was injected through the septum to produce a liquid-phase concentration of 34 mM. After 1 hour, a 20 μl gas sample was withdrawn from the reactor headspace for analysis of dibromomethane (DBM), acetone and methane. Controls were developed in a similar manner without metal or metal oxide addition. Reactor contents were shaken throughout the 1 h reaction period. Independent variables for the hypovial screening experiments included solvent concentration, halogenated target, and metal identity and oxidation state.

Bench-scale experiments were also conducted in well-mixed, heterogeneous suspensions consisting of solvent, metal and halogenated target (carbon tetrachloride) under an argon atmosphere. A more regular form of elemental iron was obtained for these experiments (heterogeneous spheroids with an effective diameter of about 5 μm). These could be maintained in suspension with a minimum of stirring energy. Surface area measurements reported later pertain to this source. Suspended mass of Fe(0) or Zn(0) was generally 0.42 g per 180 ml of liquid, but varied modestly among experiments. Precise masses are reported with the respective experimental results. Solution pH was stabilized using a pH stat (Brinkman 665 Dosimat and 615 Impulsomat) or 0.1 M acetate buffer. In the standard experimental procedure, metal and solvent

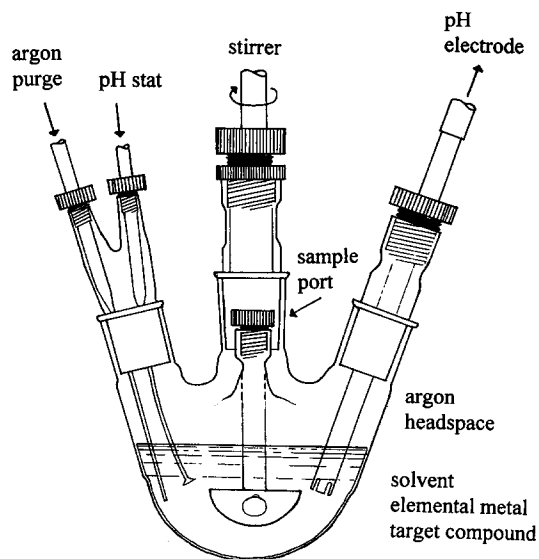


Fig. 2. Bench-scale reactor used for reductive dehalogenation experiments: Liquid phase contained elemental metal (iron or zinc), solvent and target compound. The pH was maintained with a pH stat. Reactor was stirred continuously to suspend the metal. Contents were purged with argon to remove oxygen prior to introduction of halogenated target.

(180 ml of H_2O or 50/50 v/v H_2O /2-propanol) were measured into a 360 ml round-bottom flask (Fig. 2). The reactor was purged with argon for 30 min prior to metal addition and for an additional 30 min thereafter. Liquid contents were stirred continuously at a rate that was sufficient to maintain the metal in suspension. Upon completion of purging, carbon tetrachloride was introduced into the liquid phase at concentrations from 0.5 to 7.5 mM to initiate the reaction. Headspace and liquid phase were sampled at 5–30 min intervals in order to establish rates of target disappearance and product formation. Volatile components were analyzed via gas chromatography using either FID (50 °C, DB1 capillary column) for 20 μl headspace samples, or ECD (50 °C, DB624 capillary column) when 20 μl headspace samples were extracted into pentane (Baxter, THM analysis grade). Chloride ion was measured using ion chromatography (Dionex QIC) or an ion-selective electrode (Orion). The presence of $\text{H}_2(\text{g})$ was detected via gas chromatography (TCD, 50 °C, Carboxen 1000 60/80 mesh packed column). Fe(II) or Zn(II) was measured using colorimetric procedures based on orthophenanthroline [10] or zincon methods [11] respectively.

3. Results and discussion

The results of screening experiments (not shown) indicated that rates of reductive dehalogenation of carbon tetrachloride and bromoform by zero-valence metals are

pH-sensitive. Protons were first liberated (rapidly, over a period no longer than several minutes) and then consumed in the remainder of these reactions. Kinetics were also sensitive to solvent composition (2-propanol concentration). In a reaction mixture consisting of 50/50 v/v H₂O/2-propanol plus powdered Fe(0) and bromoform, the primary products were dibromomethane, acetone, Fe(II), Br⁻, and H₂(g). All the zero-valence metals tested reduced bromoform to dibromomethane to some extent, although Fe(0) and Zn(0) were decidedly more active than Sn(0) and Al(0) (Fig. 3). Results are not strictly comparable because solid-phase, mass-specific surface areas were not measured. Reductive dehalogenation was not observed in systems that contained metal oxides. The superiority of Fe(0) over Zn(0) as an agent for the reductive dehalogenation of bromoform suggests that process kinetics are not purely a function of reaction thermodynamics (Table 1, Fig. 3).

Bench-scale experiments indicated that the rate of transformation of CCl₄ was first order in carbon tetrachloride over the range [CCl₄] < 7.5 mM (liquid-phase concentration). At the end of the experiment, CCl₄ lost was approximately equal to CHCl₃ formed (Fig. 4), suggesting that the rate of chloroform dehalogenation is considerably lower than that of CCl₄, at least in the presence of a significant carbon tetrachloride residual. The oxidation of 2-propanol to acetone suggests that hydroxyl radicals may be produced under these conditions. Fe(II) production (Fig. 4) was not stoichiometrically related to any single reactant or product, presumably because H₂(g) formation and 2-propanol oxidation contributed to the overall (reactor) redox balance. Typically, more Fe(II) was produced than CCl₄ consumed, presumably because iron oxidation was responsible for proton reduction (hydrogen formation) as well as CCl₄ reduction. It was not possible to establish an electron balance based on experimental results because H₂(g) formation was not quantified. Based on the observed product distribution it is expected that, on a molar basis, ferrous iron and acetone were equal to the chloroform and molecular hydrogen formed.

Experiments with Zn(0) clearly showed that reaction rate was proportional to the mass of zinc provided (Fig. 5), or more likely the surface area of the suspended metal. Electron micrographs of the metal particles (elemental iron and zinc; not shown) indicated that the iron particles were essentially spherical although somewhat heterogeneous in size. The effective diameter was estimated at 5 μm. Zn(0) particles, on the other hand, were irregular flakes, with an effective particle size on the order of 500 μm. BET surface area measurements (Pacific Sorption Service, Chico, CA) indicated that the specific surface areas of these metals were approximately equal (Zn(0), 0.47 m²/g; Fe(0), 0.41 m²/g), presumably due to the higher porosity of the zinc.

The sensitivity of the pseudo-first-order rate constant for the reduction of CCl₄ by Zn(0) (in water) to pH variation is illustrated in Fig. 6. The rate of CCl₄ disappearance dropped 10-fold in response to an increase in pH from 3.5 to 5.5. This is in marked contrast to the results of Matheson and Tratnyek [12] who observed only a 5-fold decrease in rate from pH 5.0 to 10.0. Differences in the observed pH dependence in these studies may have arisen from differences in respective pH range or from the obliteration of pH dependence due to mass-transport limitations in the earlier study.

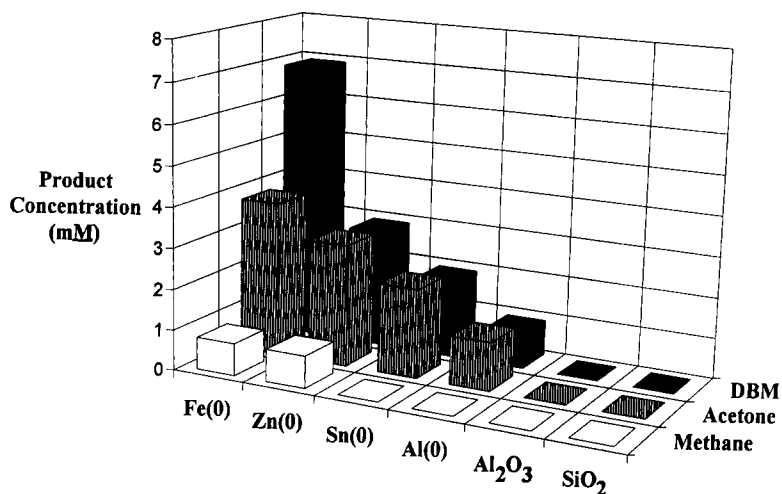


Fig. 3. Reductive dehalogenation using different metals and metal oxides: Product distribution in hypovials used for dehalogenation screening experiments. Starting compound was bromoform, which was reduced to dibromomethane (DBM) and methane. Acetone was produced from 2-propanol. Differences in the specific surface areas of the metals screened prevent direct comparison of rates.

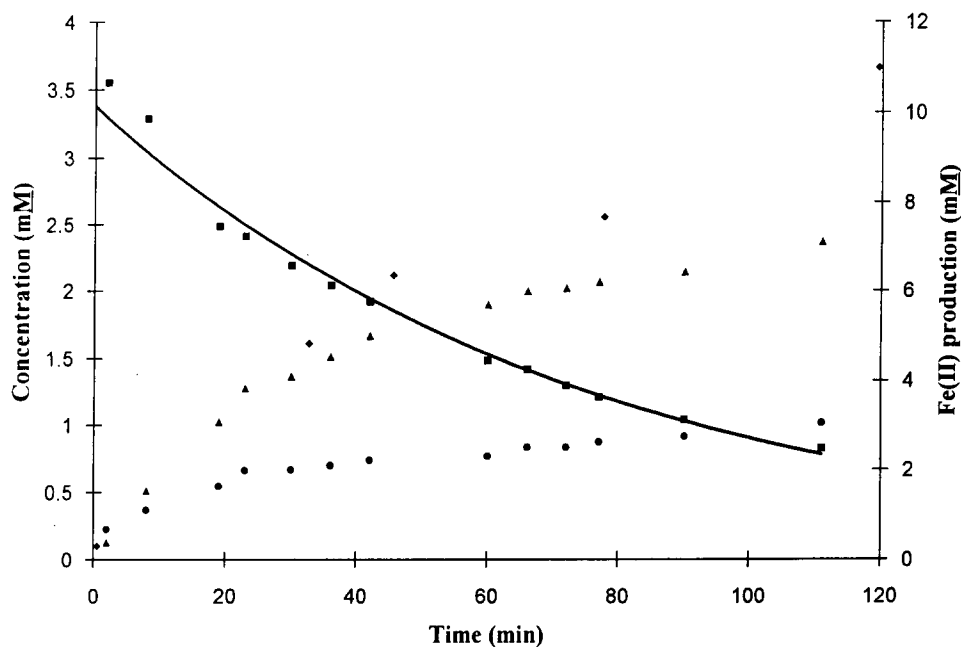


Fig. 4. Carbon tetrachloride dehalogenation using zero-valence iron: CT (■) degradation, chloroform (▲), acetone (●), and iron (◆) production in an experimental system initially containing 2.9 mM CT in a 50/50 H₂O/2-propanol cosolvent mixture with 0.42 g Fe(0) provided as 5 μm diameter particles. The liquid-phase was buffered at 5.8 with 0.1 M acetate. Solid line represents the first-order best fit of CT data ($k = 0.03 \text{ min}^{-1}$). (Note: $\Delta \text{CT} \cong -\Delta \text{CF}$ throughout the course of the experiment.)

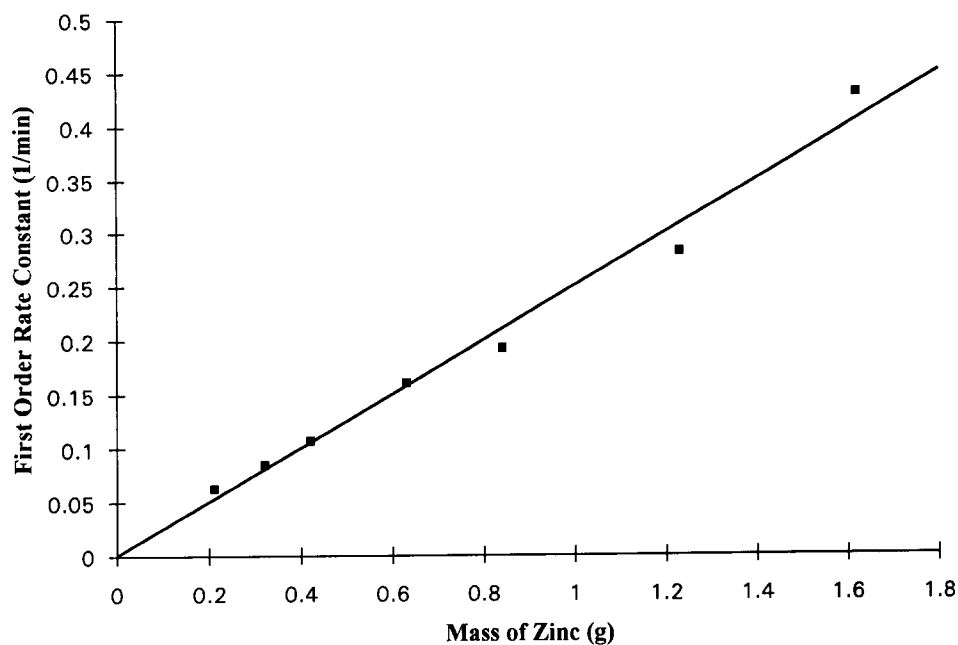


Fig. 5. Dependence of reaction rate constant on Zn(0) surface area: Rate of dehalogenation is directly proportional to zinc mass and surface area. Reacting system consisted of 0.65 mM CT in H₂O with varying masses of Zn(0). The liquid-phase was buffered at 4.8 with 0.1 M acetate.

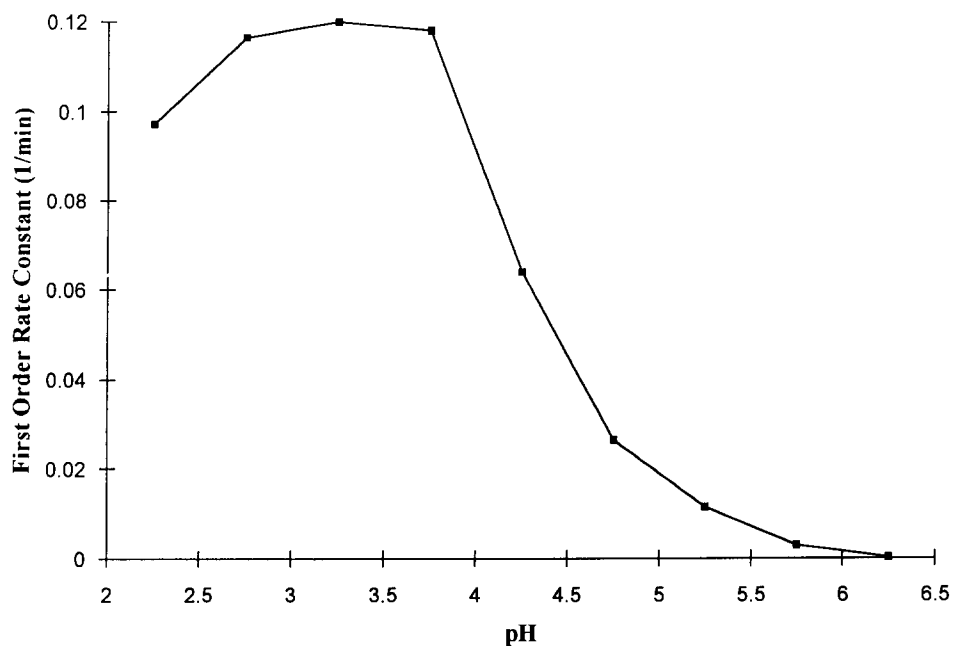


Fig. 6. Dependence of reaction rate constant on bulk solvent pH: The reacting system consisted of 0.65 mM CT in H₂O with 0.45 g Zn(0). The pH was maintained with a pH stat.

CCl_4 transformation rates proved to be sensitive to stirring or shear rate in the $\text{Fe}(0)$, but not the $\text{Zn}(0)$, system (Figs. 7 and 8). Because transformation rates were significantly greater in the $\text{Fe}(0)$ system, even at the slower stirring rate, the overall rate of reaction may have been mass transfer limited in the experiments involving elemental iron, and reaction-limited in the zinc experiments. Results suggest that pH and surface-area effects in the zinc system were independent of mass transfer kinetics and may be used to establish elements of a reaction mechanism.

A convincing mechanism for the reductive dehalogenation of haloorganics by zero-valence metals has not yet been proposed. Matheson and Tratnyek [12] maintained that dehalogenation was not mediated by $\text{H}_2(\text{g})$ or $\text{Fe}(\text{II})$ in the bulk aqueous-phase solution, suggesting that observed reactions take place at the metal surface. Direct transfer of electrons from the metal to the halogenated target is a possibility, and the reduction of H^+ at the surface would account for $\text{H}_2(\text{g})$ generation. While satisfying in its simplicity, such a mechanism does not account for either the observed dependence of reaction rate on the bulk solution pH or solvent effects. Instead, it is suggested that the overall dehalogenation reaction consists of a series of steps, at least one of which involves proton reduction at the metal surface. That is, hydrogen may play the role of intermediate in electron transfer at the surface of the metal.

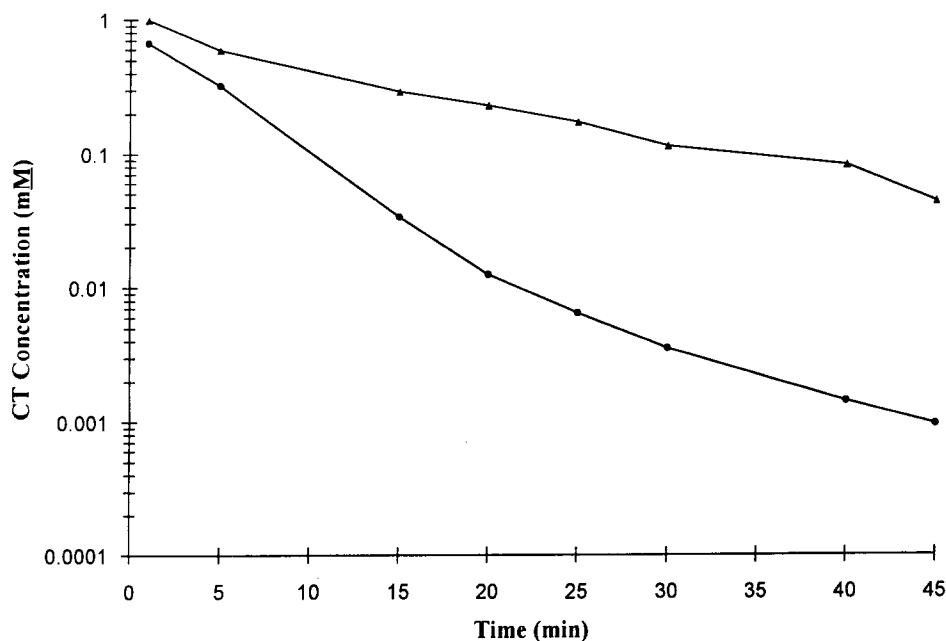


Fig. 7. Dependence of reaction rate constant on mixing intensity, iron system: High stir (●) rate was 600 rpm, and low stir rate (▲) was 300 rpm. The reacting system consisted of 0.65 mM CT in H_2O with 0.42 g $\text{Fe}(0)$, and pH held at 4.7 with a pH stat.

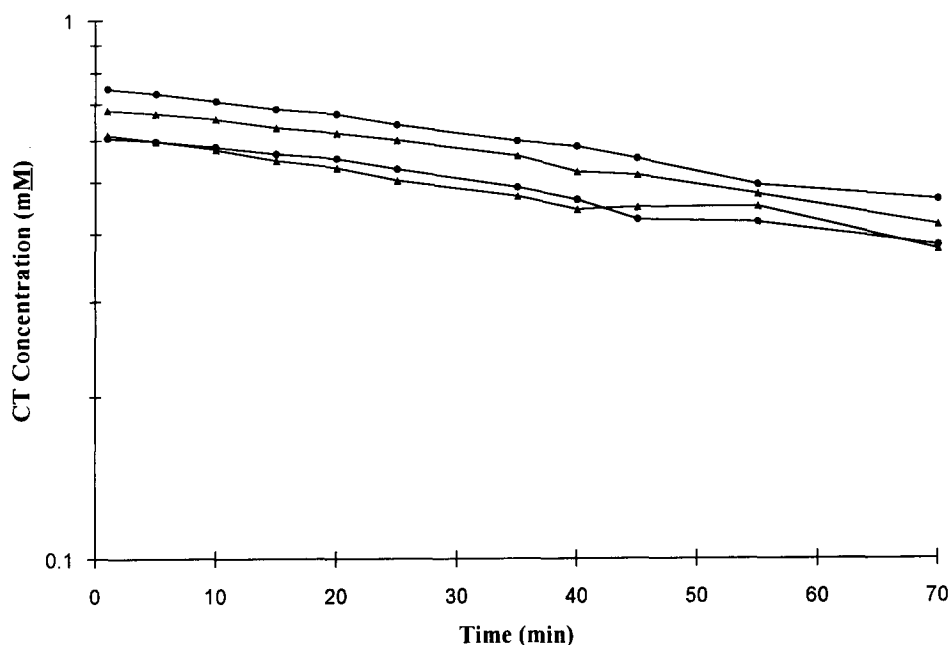


Fig. 8. Dependence of reaction rate constant on mixing intensity, zinc system: High stir rate (●) was 600 rpm and low stir rate (▲) was 300 rpm. The reacting system consisted of 0.65 mM CT in H₂O with 0.45 g Zn(0), and pH held at 4.7 with a pH stat.

Because the reductive dehalogenation of CCl₄ has been observed in a variety of catalytic settings, it is possible to provide only a crude comparison of reaction rates in highly dissimilar systems (Table 2). From the table, it is readily apparent that chemical analogs offer great kinetic advantages relative to bacterially catalyzed systems for the hydrogenolysis of CCl₄.

Despite unresolved mechanistic complexities, the use of elemental metals for reductive dehalogenation reactions has the potential for initiating the transformation of persistent, hazardous organic compounds such as TCE, carbon tetrachloride and chloroform. One could envision such reactions, for example, at the start of a two-stage process designed to mineralize such heavily halogenated solvents. After removing some or all of the halogen groups, residuals could be oxidized to CO₂. There is ample evidence to suggest that partially or fully dehalogenated solvents are much better substrates for oxidative transformations, including those that are biochemically catalyzed in ground waters [1].

Acknowledgements

Support for this research was provided by NIEHS Superfund Basic Research Program.

Table 2
Maximal rates of CCl₄ transformation in representative catalytic systems

| System | Experimental conditions ^a | Rate (mM/h) | References |
|---|---|--|--------------------------|
| B ₁₂ modified Ag electrode, electrolysis cell | – 1.45 V ^b [CT] ₀ = 4.0 mM 25 × 21 mm electrode 200 ml cathode liquid volume pH = 6.85 | 0.09 | Santo [13] |
| Fe(0) | [CT] ₀ = 5.1 mM Acetate buffer = 0.1 M Fe(0), 5 μm diameter spheres, 0.84 g in 180 ml liquid 50/50 v/v H ₂ O/2-propanol pH = 5.7 | 3.0 | Arnold et al. [14] |
| <i>S. putrefaciens</i> 200 | A ₆₀₀ = 1.5 (cell density) [CT] ₀ = 20 mM substrate = 18 mM lactate | 3 × 10 ⁻⁴ | Picardal [15] |
| Glucose fermenting <i>E. coli</i> K-12 | 53 mg/l total protein substrate = 5.6 mM glucose CT ₀ = 456 nmol in 250 ml bottle (150 ml liquid volume) pH = 7.0 | 1.3 × 10 ⁻⁶ | Criddle et al. [16] |
| Ag electrode, electrolysis cell | – 0.71 V vs. SHE CT ₀ = 20 μmol in 354 ml cathodic cell (170 ml liquid volume) pH = 7.0 | 1.5 × 10 ⁻² | Criddle and McCarty [17] |
| Ti(III)-citrate and cofactor (cofactors = vitamin B ₁₂ , coenzyme F ₄₃₀ , or hematin) | 27 mM Ti(III)-citrate CT ₀ = 2.2 μmol total mass 10 ml reactor, 1 ml liquid volume pH = 8.2 | 16 (vitamin B ₁₂) 22 (coenzyme F ₄₃₀) 0.52 (hematin) | Gantzer and Wackett [18] |

^a Note that experimental conditions are not uniform. Rates are provided as a basis for broad comparison only.

^b Relative to Ag/AgCl reference electrode.

References

- [1] T.M. Vogel, C.S. Criddle and P.L. McCarty, Transformations of halogenated aliphatic compounds, Environ. Sci. Technol., 21 (1987) 722.
- [2] E.J. Bouwer and J.P. Wright, Transformations of trace halogenated aliphatics in anoxic biofilm columns, J. Contam. Hydrol., 2 (1988) 155.
- [3] C.A. Schanke and L.P. Wackett, Environmental reductive elimination reactions of polychlorinated ethanes mimicked by transition-metal coenzymes, Environ. Sci. Technol., 26 (1992) 830.
- [4] U.E. Krone, R.K. Thauer, H.P.C. Hogenkamp and K. Steinbach, Reductive formation of carbon monoxide from CCl₄ and Freons 11, 12, and 13 catalyzed by corrinoids, Biochemistry, 30 (1991) 2713.

- [5] K.H. Sweeney and J.R. Fischer, Reductive degradation of halogenated pesticides. US Patent No. 3,640,821, 8 February 1972.
- [6] G.W. Reynolds, J.T. Hoff and R.W. Gillham, Sampling bias caused by materials used to monitor halocarbons in groundwater, *Environ. Sci. Technol.*, 24 (1990) 135.
- [7] R.W. Gillham, S.F. O'Hannesin and W.S. Orth, Metal-enhanced abiotic degradation of halogenated aliphatics; laboratory tests and field trails, Paper presented at the 1993 HazMat Conference, Chicago, IL, 9–11 March 1993.
- [8] S.F. O'Hannesin, M.S. Thesis, University of Waterloo, Ontario, 1993.
- [9] R. Schwarzenbach, R. Stierli, K. Lanz and J. Zeyer, Quinone and iron porphyrin mediated reduction of nitroaromatic compounds in homogeneous aqueous solution, *Environ. Sci. Technol.*, 24 (1990) 1566.
- [10] A.A. Schilt, Analytical Applications of 1,10-Phenanthroline and Related Compounds, Int. Ser. Monogr. Anal. Chem., Vol. 32, Pergamon Press, London, 1969.
- [11] R.M. Rush and J.H. Yoe, *Anal. Chem.*, 26 (1954) 1345.
- [12] L.J. Matheson and P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron metal, *Environ. Sci. Technol.*, in press.
- [13] G.A. Santo, Reductive dehalogenation using a chemically modified electrode, Masters Thesis, Civil Engineering Department, University of Arizona, 1993.
- [14] R.G. Arnold, T.L. Bishop, R.J. Kuhler, E.A. Betterton and K.D. Warren, Dehalogenation of chlorinated organics by zero-valence metals, in: Proc. Pacific Basin Conf. on Hazardous Waste, Honolulu and Hawaii, 1993.
- [15] F. Picardal, Mechanisms of bacterially catalyzed reductive dehalogenation, Ph.D. Dissertation, Civil Engineering Department, University of Arizona, 1992.
- [16] C.S. Criddle, J.T. DeWitt and P.L. McCarty, Reductive dehalogenation of carbon tetrachloride by *Escherichia coli* K-12, *Appl. Environ. Microbiol.*, 56 (1990) 3247.
- [17] C.S. Criddle and P.L. McCarty, Electrolytic model system for reductive dehalogenation in aqueous environments, *Environ. Sci. Technol.*, 25 (1991) 973.
- [18] C.J. Gantzer and L.P. Wackett, Reductive dechlorination catalyzed by bacterial transition-metal coenzymes, *Environ. Sci. Technol.*, 25 (1991) 715.