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Reductive Dechlorination of Carbon Tetrachloride Using Iron(II) Iron(III) Hydroxide Sulfate (Green Rust)

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The reductive dechlorination of CCl_4 and $CHCl_3$ in the presence of the synthetic sulfate form of green rust (GR_{SO_4}), $Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4yH_2O$, at pH ∼ 8 and room temperature was investigated. Reduction of CCl_4 produces $CHCl_3$ and C_2Cl_6 as main chloroaliphatic products, while GR_{SO_4} is oxidized to magnetite (Fe_3O_4). The formation of C_2Cl_6 indicates a coupling reaction between trichloromethyl radicals in the suspension. Chloroform was much less susceptible than CCl_4 to reductive dechlorination by GR_{SO_4} showing reduction rates approximately 100 times less than for reduction of CCl_4. The transformation of CCl_4 by GR_{SO_4} can be described by pseudo-first-order reaction kinetics with respect to formation of chloride. At room temperature the rate expression is given as: $d[Cl^-]/dt \cong -d[CCl_4]/dt = r\cdot k_{obs}[Fe(II)]_{GR}$, where k_{obs} is in the range $(0.47 \times 10^{-5})-(2.18 \times 10^{-5})$ s^{-1} for CCl_4 concentrations above its aqueous solubility. This narrow range may be due to the constant CCl_4(aq) concentration owing to buffering of the CCl_4(aq) concentration by free phase CCl_4(l) thereby indicating that the reaction takes place in solution. Experiments with initial CCl_4 concentrations below its aqueous solubility support this theory. The reaction kinetics are compared with similar reactions where iron(0) is used as reductant of CCl_4. The first-order rate constants for transformation of CCl_4 with zerovalent iron and GR_{SO_4}, respectively, are found to be in the same range. Thus, GRs formed during corrosion of iron(0) under nonacid conditions may considerably contribute to the total reduction of CCl_4 measured in iron(0) systems.

Introduction

Layered iron(II) iron(III) hydroxides with anionic interlayers and the general composition $[Fe^{II}_{(6-x)}Fe^{III}_{x}(OH)_{12}]^{x+}[(A)_{x/n}\cdot yH_2O]^{x-}$ ($x = 0.9-4.2$; A is an *n*-valent anion, e.g., CO_3^{2-}, Cl^-, and SO_4^{2-}; and *y* denotes the varying amount of interlayer water) are known as green rusts (GRs) due to their bluish-green colors. They can be found as corrosion products of iron metal or as precipitates in anaerobic soils and sediments (*1, 2*). They are easily synthesized in the laboratory by partial oxidation of iron(II) or by reactions between iron(II) and iron(III) in solid or solution phases (*3−5*). Green rusts are potentially strong sorbents due to their interlayer which holds and exchanges anions and polar noncharged molecules. Green rusts can also act as strong reductants. Unfortunately, precise data for the free energy of formation of GRs do not exist. However, from available estimates of free energies of formation of the sulfate-interlayered GR (GR_{SO_4}) (*4, 7*), the standard redox potentials of magnetite reduction to GR_{SO_4} are calculated to be in the range −0.29 to 0.23 V for eq 1 (Table 1). Reduction of goethite (α-FeOOH) to GR_{SO_4} shows higher reduction potentials, but in comparison with other iron(II)-containing reductants, GR_{SO_4} represents a strong reductant under standard conditions (Table 1).

Green rust reduces nitrate to ammonium in an apparent first-order reaction; magnetite is formed as the iron oxide product (*8*). The rate of reaction appears to depend on the exposed surface area of GR_{SO_4} particles, and high reaction rates can be obtained when there is ready access to the interlayer (*9*). The ready reduction of nitrate makes it likely that GR_{SO_4} may also facilitate the reduction of reducible organic substances such as nitrosubstituted aromatics and chloroaliphatics. This is supported by the fact that several chloroaliphatics, among others carbon tetrachloride, are stronger electron acceptors than nitrate (*10*). Both groups of organic compounds have been observed to become reduced in natural or synthetic mixed iron(II)−iron(III) systems but without GR_{SO_4} being identified as the actual reductant yet (*11−13*). The missing identification could be due to rapid aerial oxidation of GR_{SO_4} during sampling. According to the region of stability of GRs in pe−pH diagrams, GRs will always occur as intermediate phases in the formation of iron oxides during oxidation of iron(II) in neutral and weakly alkaline solutions (*6, 14*). Hazardous halogenated aliphatics released from industrial, commercial, and agricultural sources are prevalent groundwater contaminants. Due to the potential toxicity and carcinogenicity of chlorinated aliphatics, knowledge about their transformation potential is important in evaluating their environmental fate. Reductive dechlorination of chlorinated aliphatics may proceed both through microbial reactions (*15−19*) and through abiotic reduction, e.g., by use of iron(0) (*20−25*). Furthermore, structural iron(II) in sheet silicates has been shown to be a faster reductant of CCl_4 than iron(II) in solution indicating that the thermodynamical favorable reduction of CCl_4 by GRs may not be kinetically hindered (*26*).

In the present investigation the stoichiometry and kinetics of CCl_4 and $CHCl_3$ abiotic reduction by synthetic GR_{SO_4} have been studied in order to clarify whether GRs might contribute to reduction of chlorinated aliphatics.

Experimental Section

Materials and Methods. The sulfate form of GR_{SO_4} was synthesized by air oxidation of iron(II) sulfate solutions at a constant pH of 7.00 according to the given procedures (*27*). To enable later chloride measurement a double-junction electrode with saturated solutions of KCl and K_2SO_4 as inner and outer electrolytes, respectively, was used for pH measurement during synthesis (Methrom 6.0219.120 (PF)). The GR_{SO_4} was washed with Ar-bubbled glass distilled water and separated on a glass filter funnel, redispersed in 200-mL Ar-bubbled glass distilled water in a 300-mL storage flask, and transferred to 4 × 120-mL serum bottles. The GR_{SO_4} was transferred with Ar pressure through a Teflon tube directly from the storage flask to the sealed Ar-flushed septum bottles. Teflon-coated rubber septa were kept in place with aluminum crimp seals. Washing, separation, and redispersion of GR_{SO_4} were conducted in an Ar-flushed glovebox.

Pure CCl_4 and $CHCl_3$ were added to the GR_{SO_4} suspensions in variable amounts (25 μL−1 mL). At room temperature approximately 25 μL of CCl_4 is soluble in 50 mL water (*28*). Hence, the concentration of CCl_4 in solution was in excess

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TABLE 1. Redox Reactions of Fe(II)-Containing Reductants at 25 °C and 1 atm[a]

reduction half-reaction	$\Delta_r G°$ ($kJ \cdot mol^{-1}$)	E^0_H (V)
(1) $2Fe_3O_4(s) + 2e^- + SO_4^{2-}(aq) + 4H^+(aq) + 7H_2O(l) \rightleftharpoons Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 \cdot 3H_2O(s)$	55.36	−0.287
(2) $6\alpha\text{-}FeOOH(s) + 4e^- + SO_4^{2-}(aq) + 6H^+(aq) + 3H_2O(l) \rightleftharpoons Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4 \cdot 3H_2O(s)$	9.92	−0.026
(3) $\alpha\text{-}FeOOH(s) + e^- + H^+(aq) \rightleftharpoons Fe(OH)_2(s)$	2.40	−0.025
(4) $2\alpha\text{-}FeOOH(s) + 2e^- + H_4SiO_4(aq) + 2H^+(aq) \rightleftharpoons Fe_2SiO4(s) + 4H_2O(l)$	16.55	0.086
(5) $3\alpha\text{-}FeOOH(s) + e^- + H^+(aq) \rightleftharpoons Fe_3O_4(s) + 2H_2O(l)$	−23.46	0.243
(6) $\alpha\text{-}FeOOH(s) + e^- + 3H^+(aq) \rightleftharpoons Fe^{2+}(aq) + 2H_2O(l)$	−64.56	0.669

[a] Data for free energies of formation taken from (*4, 43–45*).

of $Fe(II)_{GR}$ in the majority of the reaction mixtures even though the evaporation of CCl_4 to headspace was ignored. This surplus maintains the initial concentration of $CCl_4(aq)$ throughout the reaction as $CCl_4(aq)$ consumed in the reaction with GR_{SO_4} is replaced with CCl_4 transferring from the pure liquid phase into solution. The sealed septum bottles were placed on a shaking table (125 strokes·min^{-1}) at room temperature.

At different time intervals 1 mL of unfiltered and 3 mL of 0.22-μm Millipore filtered samples were withdrawn from the reaction mixture using a 5-mL Ar-flushed polyethylene syringe; 1 mL of the filtrate was transferred directly to the reagent used for iron(II) determination ($Fe(II)_{sol}$) while the remaining 2-mL filtrate was transferred to a polyethylene test tube for chloride determination. The unfiltered samples were treated for at least 30 min with 20 mL of 0.1 M HCl before filtration through a 0.22-μm Millipore filter to remove the insoluble iron oxide products. This treatment selectively dissolves the GR_{SO_4}, and thus the concentration of iron(II) in the filtrate provides an estimate of iron(II) in GR_{SO_4} plus solution ($Fe(II)_{GR+sol}$) (*8*). An estimate of iron(II) in GR_{SO_4} can be calculated as the difference: $[Fe(II)_{GR}] = [Fe(II)_{GR+sol}] - [Fe(II)_{sol}]$. All handling and sampling of the GR_{SO_4} and $FeSO_4(aq)$ solutions were carried out under a 99.9995% Ar atmosphere. Determination of pH before and after each experiment was made in an Ar-flushed glovebox. During reaction between GR_{SO_4} and CCl_4 or $CHCl_3$, the pH was allowed to change freely.

All chemicals were p.a. quality or better. All plastic ware and glassware were washed with 1.2 M HCl and 4.8 M HNO_3, respectively, after machine washing and rinsed with triple-deionized water. Glass-distilled water was used in all reagents.

Analyses. Identification of chlorinated aliphatics in headspace was done by GC−MS using a system consisting of an HP5890 Series II gas chromatograph directly coupled to a JEOL JMS-AX505W mass spectrometer. An HP-1 column (25 m × 0.2 mm, 0.33-μm film thickness) preceded by a Chrompack 1.5-m retention gap of medium polarity was used. The head pressure was 70 kPa, and helium was used as carrier gas. The oven temperature program was as follows: 25 °C for 5 min, 25−200 °C at 10 °C/min, 200 °C for 5 min; 100-μL headspace sample was injected with the injector in split mode and at 150 °C. The ion source was run in EI mode at 240 °C, 70 eV ionization energy. Identifications were done using the built-in search facilities and NBS library.

Iron(II) was determined using a modified phenanthroline method (*29*). All solutions mixed with 1,10-phenanthroline were kept in the dark until measurement to avoid photochemical redox reactions. No interference from CCl_4 was found in the determination of iron(II) in solution. Chloride was determined using a $Hg(SCN)_2$ colorimetric method and flow injection analysis (*30*). X-ray diffraction (XRD) was used to test identity, purity, and crystallinity of the starting GR_{SO_4} and solid end products. Samples for XRD were collected on 0.22 -μm Millipore filters and preserved against oxidation by admixing glycerol (*31*). Examination by XRD was carried out using a Philips PW 1710 goniometer and iron-filtered Co Kα radiation (40 kV, 40 mA). Glycerol smears were scanned between 6° and 80° 2θ with a scan speed of 1° 2θ/min using divergence, scatter, and receiving slits of 1°, 1°, and 0.2 mm, respectively.

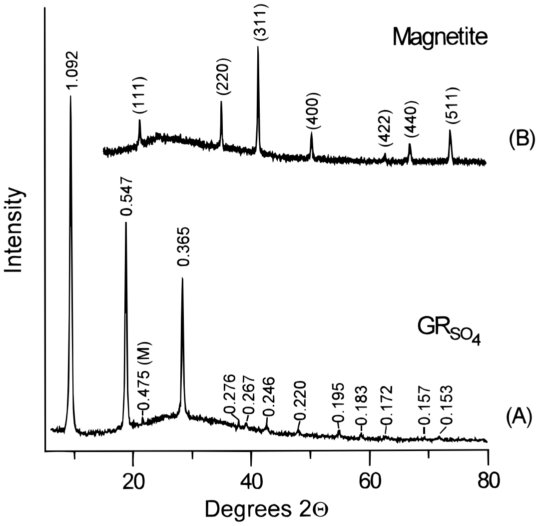

FIGURE 1. X-ray diffractograms of solids at the start (A) and the end (B) of reaction between GR_{SO_4} and CCl_4. Indices refer to a cubic cell for magnetite; *d* spacings in nm. Humps are due to glycerol preservation. M refers to magnetite.

Results and Discussion

Stoichiometry. The integrity of the septum-seal system with regard to maintaining anaerobic conditions inside the septum bottle was determined by measuring the change in concentrations of $Fe(II)_{GR}$ and $Fe(II)_{sol}$ with time in samples from a pure GR_{SO_4} suspension without addition of oxidants kept in sealed septum bottles. No oxidation of iron(II) in GR or in solution could be detected during a period of 63 days.

Hydrolysis of CCl_4 in water and the reactivity of CCl_4 toward iron(II) in solution were examined by following the change in concentrations of $Fe(II)_{GR}$, $Fe(II)_{sol}$, and chloride during the reaction between aqueous iron(II) and CCl_4. The experiment showed very limited reaction between aqueous iron(II) and CCl_4 (Table 2, control 1). Hence CCl_4 reduction by iron(II) in solution can be considered negligible within the time span of these experiments. Production of chloride in control experiments containing only water and CCl_4 in sealed Ar-flushed septum bottles showed that hydrolysis of CCl_4 in water was nondetectable within 2−3 days.

X-ray diffraction of the synthetic GR_{SO_4} values gave identical traces as in previous studies (*4*), and the GR_{SO_4} values were found to be pure and well-crystalline (mean crystal thickness along the *c*-axis determined from the width of the (003) peak at half-height corrected for instrumental broadening was 37.3 ± 5.8 nm) (Figure 1). Chemical analysis of the GR_{SO_4} gave an Fe(II):Fe(III) ratio of approximately 2:1, in agreement with literature (*27*). The only solid iron oxide product was magnetite ($Fe^{III}_2Fe^{II}O_4$) (Figure 1), and all GR_{SO_4} was consumed during reaction in excess of CCl_4. Gas

TABLE 2. Reaction Parameters and Kinetics of CCl_4 Reduction by GR_{SO_4}

experiment	$[CH_xCl_{4-x}]_{init}$[a] (mM)	$[Fe(II)]_{GR,init}$[b] (mM)	$(d[Cl^-]/dt)_{init}$[c] ($M \cdot s^{-1}$) × 10^{-8}	k_{obs}[d] (s^{-1}) × 10^{-5}	r^2 [d]
control 1[e]	251	0	na[f]	na[f]	na[f]
control 2[g]	124	23.11	0.010	0.0003	0.911
GR17 Hg2[h]	69.0	4.65	2.43	1.90	0.9868
GR17 Hg3[h]	70.9	3.98	2.50	2.18	0.9628
GR18 Hg6[h]	129	7.98	1.64	0.47	0.9924
GR18 Hg9[h]	264	7.98	2.20	0.88	0.9751
GR20 Hg1[h]	20.7	7.94	2.46	1.45	0.9788
GR20 Hg2[h]	20.7	7.83	2.03	1.13	0.9867
GR20 Hg5[h]	62.1	7.96	1.97	0.67	0.9965
GR20 Hg6[h]	62.1	7.51	2.01	0.72	0.9975
GR30 Hg2[h]	73.5	7.33	2.41	1.10	0.9761
GR30 Hg3[h]	73.5	7.57	2.26	0.98	0.9830
GR19 Hg1[i]	5.18	25.15	0.94	0.27	0.9949
GR19 Hg2[i]	10.36	26.21	1.43	0.31	0.9980
GR19 Hg3[i]	15.54	24.96	1.75	0.28	0.9960
GR19 Hg4[i]	20.73	24.26	1.94	0.39	0.9881

[a] Initial concentration of CH_xCl_{4-x} in GR suspension. [b] Initial concentration of Fe(II) in GR_{SO_4}. [c] Initial rate of Cl^- formation. [d] Pseudo-first-order rate constant determined by nonlinear regression of rate data with r^2 the coefficient of regression. [e] 18 mM $FeSO_4$(aq) solution; $[CCl_4]_{init}$. [f] Not applicable. [g] $[CHCl_3]_{init}$. [h] $[CCl_4]_{init}$ above the aqueous solubility of CCl_4. [i] $[CCl_4]_{init}$ below and slightly above the aqueous solubility of CCl_4.

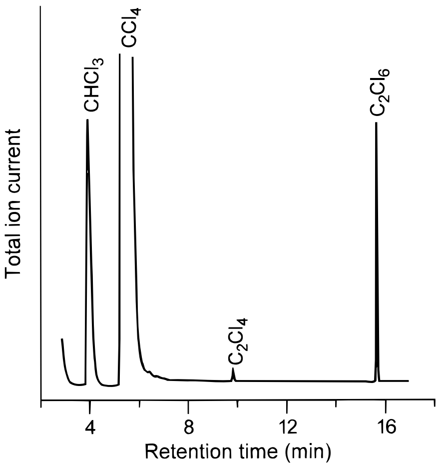

FIGURE 2. Gas chromatographic headspace analysis of dechlorination products from the reaction between CCl_4 and GR_{SO_4}. Retention times were 3.53 min ($CHCl_3$), 5.4 min (CCl_4), 9.83 min (C_2Cl_4), and 15.67 min (C_2Cl_6), respectively.

chromatographic (GC−MS) analyses of chlorinated aliphatics in the headspace above the reaction mixture at the end of reaction clearly showed the production of $CHCl_3$ (t_R 3.93 min) as the major product and C_2Cl_6 (t_R 15.67 min) as the minor product (Figure 2). Trace amounts of C_2Cl_4 (t_R 9.83 min) were also present. Other chlorinated reaction products were not detected. Formation of nonchlorinated reaction products such as formic acid or carbon dioxide cannot be excluded, but these compounds were not detected in headspace samples at the end of reaction. With the two products, $CHCl_3$ and C_2Cl_6, the stoichiometry of the reactions may tentatively be given as

$$Fe^{II}{}_4Fe^{III}{}_2(OH)_{12}SO_4 + CCl_4 \rightleftharpoons 2Fe_3O_4 + CHCl_3 + Cl^- + SO_4{}^{2-} + 3H^+ + 4H_2O \quad (2)$$

$$Fe^{II}{}_4Fe^{III}{}_2(OH)_{12}SO_4 + 2CCl_4 \rightleftharpoons 2Fe_3O_4 + C_2Cl_6 + 2Cl^- + SO_4{}^{2-} + 4H^+ + 4H_2O \quad (3)$$

Thus 1 mol of chloride is produced per 4 mol of $Fe(II)_{GR}$ consumed in eq 2, whereas this ratio is 1:2 in eq 3. It should be noted that only half of the Fe(II) in GR_{SO_4} is oxidized to Fe(III) in magnetite.

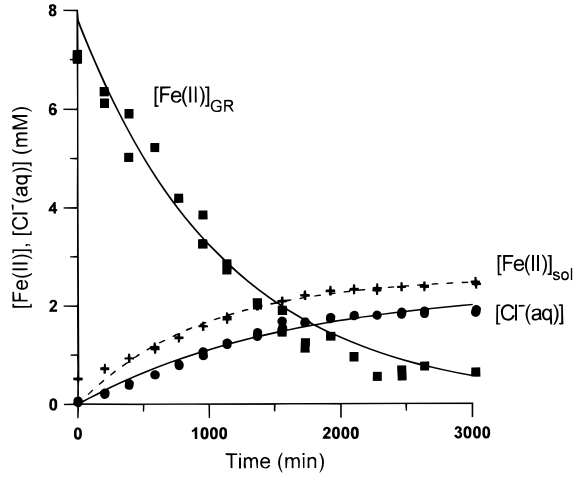

FIGURE 3. Change in concentrations of $Fe(II)_{GR}$, $Fe(II)_{sol}$, and chloride during the reaction between GR_{SO_4} and CCl_4. Solid lines represent first-order fits derived by nonlinear regression. The broken line is included as a guide to the eye.

An example of the change in concentrations of $Fe(II)_{GR}$, $Fe(II)_{sol}$, and Cl^- during the reaction between GR_{SO_4} and CCl_4 is shown in Figure 3. Initial and final pH in this experiment were ~8 and ~6.5, respectively. The increase in $Fe(II)_{sol}$ with time is attributed to dissolution of GR_{SO_4} as pH decreases (cf. eqs 2 and 3). At completion of reaction with respect to GR, the ratio between formation of Cl^- and total consumption of $Fe(II)_{GR}$ equals 0.28 ± 0.06 on average of several experiments. However, as a result of the production of protons, the total consumption of $Fe(II)_{GR}$ is due to both dissolution of $Fe(II)_{GR}$ and reduction of CCl_4 by $Fe(II)_{GR}$. Consequently, the consumption of $Fe(II)_{GR}$ due to reduction of CCl_4 can be estimated as $[Fe^{II}(GR)]_{reduction} = \Delta[Fe^{II}(GR)]_{total\ consumption} - \Delta[Fe^{II}(sol)]_{formation}$. The ratio, r, between the amount of produced Cl^- and the amount of $Fe(II)_{GR}$ used for reduction of CCl_4 is the true stoichiometric ratio and equals 0.41 ± 0.13 on average of several experiments. This value indicates that $CHCl_3$ cannot be the only chlorinated aliphatic produced and that both reactions (eqs 2 and 3) and possibly other reactions are taking place.

Kinetics. Both the consumption of $Fe(II)_{GR}$ and the production of chloride have successfully been fitted by first-order expressions (eqs 4 and 5), respectively (Figure 3)

TABLE 3. First-order Rate Constants and Initial Rates for Reductive Dechlorination of CCl_4 with Iron(0) or GR_{SO_4}

experimental conditions ^{a}	k_1 (s^{-1})^b	initial rate ($M \cdot s^{-1}$)	ref
5.0 g of Fe^0 7.2 μM CCl_4	4.9×10^{-4}	$3.5 \times 10^{-9\,c}$	25
1.00 g of Fe^0 100−200 μM CCl_4 15 °C; unbuffered pH = 8	$(7.5 \times 10^{-4}) \pm (5.0. \times 10^{-5})$	$(7.0 \times 10^{-8})-(1.6 \times 10^{-7})^c$	20
1.0 g of Fe^0 1.5−5.5 μM CCl_4 28 ± 3 °C	$(8.1 \times 10^{-5}) \pm (2.5 \times 10^{-6})$	$(1.2 \times 10^{-10})-(4.6 \times 10^{-10)c}$	22
10.0 g of Fe^0 1.5−5.5 μM CCl_4 28 ± 3 °C	$(4.8 \times 10^{-4}) \pm (2.2 \times 10^{-5})$	$(6.9 \times 10^{-10})-(2.8 \times 10^{-9)c}$	22
2.9 mM CCl_4 acetate buffer = 0.1 M 0.42 g of Fe^0 in 180 mL of liquid 50/50 (v/v) H_2O/2-propanol pH = 5.8	5.0×10^{-4}	$1.5 \times 10^{-6\,c}$	23
4−8 mM $[Fe(II)]_{GR}$ 20.7−264 mM CCl_4 pH = 8; 25 °C	$(0.47 \times 10^{-5})-(2.18 \times 10^{-5})$	$(1.9 \times 10^{-8})-(1.7 \times 10^{-7})^d$	this investigation

[a] Note that experimental conditions are not uniform. Rates are provided as a basis for broad comparison only. [b] Calculated from $[CCl_4(aq)] = [CCl_4(aq)]_{max} \cdot e^{-kt}$. [c] Initial rate = $-d[CCl_4]/dt = k_1 \cdot [CCl_4]_{init}$; excess Fe^0. [d] Initial rate = $d[Cl^-]/dt = k_{obs} \cdot [Fe(II)]_{GR,init}$; excess CCl_4.

$$[Fe(II)]_{GR} = [Fe(II)]_{GR,init} e^{-kt} \tag{4}$$

$$[Cl^-(aq)] = [Cl^-(aq)]_{max}(1 - e^{-kt}) \tag{5}$$

The observed rate constants (k_{obs}) derived from the chloride production curves for different initial concentrations of $Fe(II)_{GR}$ and CCl_4 are listed in Table 2. For constant pH the rate law may be given by

$$\frac{d[Cl^-]}{dt} = r \cdot k[Fe(II)]_{GR}[CCl_4(aq)]^z \tag{6}$$

where t is time, z is the reaction order with respect to CCl_4, and k is the rate constant.

As the initial concentration of CCl_4 oxidizing equivalents was much in excess of the initial concentration of $Fe(II)_{GR}$ and due to buffering of $CCl_4(aq)$ concentration by free phase $CCl_4(l)$, $[CCl_4(aq)]$ is considered constant during the whole reaction, and conditions used for derivation of pseudo-first-order rate constants and the following relation apply

$$-\frac{d[CCl_4]}{dt} = \frac{d[Cl^-]}{dt} = -r \cdot \frac{d[Fe(II)]_{GR}}{dt} = -r \cdot k_{obs}[Fe(II)]_{GR} \tag{7}$$

where $k_{obs} = k[CCl_4(aq)]^z$. Experiments with various initial concentrations of $Fe(II)_{GR}$ and CCl_4 always in large excess gave k_{obs} in the range $(0.47 \times 10^{-5})-(2.18 \times 10^{-5})$ s^{-1} (Table 2). This range is narrow which may be attributed to the constant $CCl_4(aq)$ concentration owing to buffering of the $CCl_4(aq)$ concentration by free phase $CCl_4(l)$ thereby indicating that the reaction takes place between $CCl_4(aq)$ and GR_{SO_4}. Experiments with initial CCl_4 concentrations below aqueous solubility support this theory as the initial rate of chloride formation increases as a function of the initial CCl_4 concentration until a level is reached (Table 2, GR19).

The initial rates of chloride formation obtained in this study are compared with initial rates of CCl_4 disappearance for similar reactions where iron(0) is used as the reductant (Table 3). Note that k_1 in Table 3 has been calculated from the disappearance rate constant of CCl_4, whereas k_{obs} in Table 2 is the chloride formation rate constant (eq 5). It is only possible to provide a rough comparison of rate constants from different data fits and dissimilar systems, as the full rate laws for both systems have not been established and different initial concentrations of CCl_4 and reactive surface areas of iron reactants have been applied. However, reduction of CCl_4 appears to be in the same order of magnitude for systems containing either iron(0) or iron(II) in GRs. Hitherto, the role of GRs for reduction of CCl_4 when iron(0) comprises the initial reductant has not been recognized. However, GRs form as intermediate corrosion products of cast iron (*1, 32−36*) and thus also should form where iron(0) is used for remediation. Green rusts are also expected to form in nonacid hydromorphic soils, sediments, and landfills which often contain substantial amounts of iron. In all these environments GRs may actively participate in the reduction of CCl_4.

Experiments with the same initial concentrations of $CHCl_3$ and CCl_4 showed a much slower formation of chloride during reaction between GR_{SO_4} and $CHCl_3$ compared with the formation of chloride during reduction of CCl_4. For example, 2.15 mM chloride was formed within 52 h of reaction between GR_{SO_4} and CCl_4 whereas only 0.37 mM chloride was formed within 36 days in the reaction between GR_{SO_4} and $CHCl_3$ (Table 2, control 2). This agrees with the fact that high degrees of substrate halogenation favor rapid reduction (*10*). Therefore GR_{SO_4} is assumed not to reduce appreciable amounts of $CHCl_3$ produced during the reduction of CCl_4. Investigation of the reactivity of GR_{SO_4}'s toward C_2Cl_6 was not performed. Products formed in reductive dechlorination of CCl_4 with iron(0) as the reductant were mainly $CHCl_3$ (*20, 23, 25*) and CH_2Cl_2 from further reduction of $CHCl_3$ (*20, 25*). No further dechlorinated products such as CH_3Cl or CH_4 or coupling products such as C_2Cl_6 have been identified (*20*). Conversion to $CHCl_3$ typically accounted for at least 50% of the CCl_4 lost, and the subsequent much slower reductive dechlorination of $CHCl_3$ leading to the appearance of CH_2Cl_2 occurred only in the presence of negligible CCl_4 residuals (*20, 22, 23*).

Most researchers agree that the first step of CCl_4 transformation is the one-electron reduction of CCl_4 to give a trichloromethyl radical and a chloride ion (eq 8) (*37, 38*)

$$CCl_4 + e^- \rightleftharpoons CCl_3^{\bullet} + Cl^- \tag{8}$$

Presumably C_2Cl_6 is formed by a coupling reaction dimerization between two trichloromethyl radicals (eq 9) (*39, 40*)

$$2CCl_3^{\bullet} \rightleftharpoons C_2Cl_6 \tag{9}$$

Although evidence for the formation of the trichloromethyl radical is largely indirect (*39*) and other reports of the identification of the trichloromethyl radical have proven controversial (*38*), a one-electron reduction as the initial step in the transformation of CCl_4 is strongly favored.

The reaction mechanism between a highly nonpolar compound such as CCl_4 and a polar layered mineral such as GR_{SO_4} is not completely understood. Reactive sites located at the GR mineral surface probably initiate the reaction. Interestingly, the rate of CCl_4 reduction observed here is close to the rates of nitrate reduction by GR_{SO_4} (*8*). It was found that nitrate reacted only at outer GR_{SO_4} particle surfaces, whereas much higher reduction rates could be obtained when nitrate had access to interlayer positions (*9*). Carbon tetrachloride probably cannot penetrate the GR interlayer, as reduction rates then would be much higher. Increasing the reactive surface area by decreasing particle sizes or opening up the GR interlayers by amphiphilic molecules should greatly enhance the rate of reduction.

Abiotic transformations are generally much slower than biotic reactions, but they can still be significant within the time scales commonly associated with groundwater movement (*10*). Hence, GRs should be considered possible important reductants of CCl_4 in nonacid and iron(II)-rich subsoils or aquifers where microbial activity is limited. It is shown here that reductive dechlorination of CCl_4 can proceed at appreciable rates in abiotic systems in the presence of GRs. Remediating contaminated groundwater with zerovalent metals has been proposed by several researchers (*20, 22, 25, 41, 42*). In situ abiotic degradation of chlorinated contaminants involves burying scrap iron fillings in the ground thereby creating a permeable reaction wall crossing the path of the contaminant plume. Injection and dispersion of synthetic GR suspensions into subsurfaces should be even easier thus suggesting a useful and cheap in situ method of remediating nonacid subsoils and groundwaters contaminated by chlorinated aliphatics as well as nitrate and probably other pollutants.

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