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ADSORPTION KINETICS OF PENTACHLOROETHANE BY IRON-BEARING SMECTITES

JAVIERA CERVINI-SILVA, JUN WU, JOSEPH W. STUCKI, AND RICHARD A. LARSON

Department of Natural Resources and Environmental Sciences, University of Illinois, Urbana, Illinois 61801 USA

Abstract—The oxidation state of structural Fe greatly alters surface chemistry, which may have a large influence on clay-organic interactions. The effect of structural-iron oxidation state on chlorinated hydrocarbons at the clay-water interface was examined. Pentachloroethane (5CA) was reacted with oxidized, reduced, and reoxidized forms of three different smectites: montmorillonite, ferruginous smectite, and nontronite in aqueous suspension under controlled-atmosphere conditions. Pentachloroethane was found to adsorb at different rates for the three smectites. A series of 5CA-adsorption rate constants in the presence of these clays showed a strong correlation with the Fe(II) content of the clay ($r^2 = 0.98$). The clay surface behaves as a Brønsted base and promotes 5CA dehydrochlorination. The adsorption kinetics at the clay-water interface were described by the formation of a precursor complex prior to 5CA dehydrochlorination.

Key Words—CMS Clay SWa-1, CMS Clay NG-1, Dehydrochlorination, Iron(II), Iron(III), Montmorillonite, Nontronite, Oxidation, Pentachloroethane, Reduction Reactions, Tetrachloroethene.

INTRODUCTION

The swelling nature of smectite clays permits H₂O and other molecules into the interlayer where numerous chemical processes may occur, including the transformation of organic compounds. The solute molecules experience short- and long-range interactions at the clay-water interface (Zhang *et al.*, 1990; Stucki and Tessier, 1991; Barriuso *et al.*, 1994; Xu, 1998) that may lead to the transformation of organic compounds (Cervini-Silva *et al.*, unpubl. data). The oxidation state of structural Fe in smectite clays is known to exert a profound influence on surface chemical properties of clays (Stucki, 1997), particularly as they relate to hydration (Stucki *et al.*, 1984; Gates *et al.*, 1993; Yan and Stucki, 1999), but evidence is emerging that these effects extend also to organic herbicides (Xu, 1998). Initial studies further indicate that the acid-base reactivity of smectites towards pentachloroethane (5CA) changes during the reduction of structural Fe (Cervini-Silva *et al.*, unpubl. data). The ubiquity of redox reactions in natural soils and sediments (owing to burial, submersion, wetting, drying, and other events), and the potential impact of changes in Fe oxidation state on the physical and chemical behavior of the surrounding material with respect to environmentally important processes, indicate that further investigation into the effects of redox on organic compounds in the clay-water interface is warranted.

The objective of this study was to investigate the fate of pentachloroethane in the presence of three Fe-bearing smectites, and to identify the extent of participation of structural Fe(II) in the adsorption and transformation of this compound. A kinetic model to explain the results is proposed.

MATERIALS

Chemicals used were pentachloroethane (5CA, 98%), tetrachloroethene (99%), trichloroethene (99%), pentane (high-purity) for trihalomethane (THM) analysis, sodium dithionite, sodium chloride, sodium carbonate, sodium bicarbonate, sodium chloride, and industrial ethanol. Samples used were montmorillonite from Upton, Wyoming [Upton; similar to API #25, Na_{0.82}(Si_{7.84}Al_{0.16})(Al_{3.10}Fe³⁺_{0.30}Mg_{0.66})O₂₀(OH)₄; Low, 1980], obtained from the American Colloid Company, Arlington Heights, Illinois (same sample used by Yan *et al.*, 1996a); and ferruginous smectite [SWa-1, Na_{0.87}(Si_{7.38}Al_{0.62})(Al_{1.08}Fe³⁺_{2.67}Fe²⁺_{0.01}Mg_{0.23})O₂₀(OH)₄; Manceau *et al.*, 2000] from Grant County, Washington, and nontronite [NG-1, Na_{0.70}(Si_{7.29}Fe³⁺_{0.63}Al_{0.08})(Al_{0.88}Fe³⁺_{3.08}Fe²⁺_{0.01}Mg_{0.06})O₂₀(OH)₄; Manceau *et al.*, 2000] from Hohen Hagen, Germany. The latter two were purchased from the Source Clays Repository of The Clay Minerals Society.

Prior to use, the <2- μ m particle-size fraction of each clay was saturated with Na⁺, dialyzed, and freeze-dried (Stucki *et al.*, 1984). Pentachloroethane was distilled before use (bp = 160°C); all other chemicals were used as received.

METHODS

Solution preparation of pentachloroethane

A 0.2 mM solution of 5CA was prepared in a 9:1 water-ethanol mixture. The solvent was purged with argon (99.9%) before and after adding 5CA. The solution was stirred for 30 min or until no emulsion was visibly detected. The concentration of 5CA was confirmed by gas chromatography with a standard curve.

Montmorillonite (Upton), ferruginous smectite (SWa-1), and nontronite (NG-1) clay-mineral suspen-

Table 1. Determination of Total Fe (Fe_T), Fe(II), and Fe(III) in smectites using the 1,10-phenanthroline method.

Smectite	Treatment ¹	g/100 g clay		
		Fe_T	Fe(II)	Fe(III)
Upton	U	2.5	0.23	2.27
	R		2.37	0.13
	RR		0.42	2.08
SWa-1	U	15.5	0.06	15.44
	R		15.14	0.36
	RR		0.14	15.36
NG-1	U	23.5	0.07	23.43
	R		22.32	1.18

¹ U, R, and RR refer to unaltered, reduced, and reduced-reoxidized treatments, respectively.

sions in the unaltered, reduced, and reduced-reoxidized forms were reacted with 5CA in aqueous solution (Solution A).

Clay preparation

Unaltered form. Thirty-mg portions of the respective freeze-dried clays were redispersed in 50-mL polycarbonate centrifuge tubes with 20 mL of NaCl (5 mM) by shaking gently overnight. This sample, with no reduction treatment, was designated the unaltered sample.

Reduced form. Suspensions of 20 mL of unaltered clay, prepared as described above, were combined with 10 mL of a citrate (0.8 M)-bicarbonate (0.3 M) buffer solution (pH = 8.4) (Stucki *et al.*, 1984), to which 100 mg of sodium dithionite were added. The mixture was heated for 4 h at 75°C under nitrogen flow. The suspension was centrifuged at 5000 revolutions per min in a Sorvall RC 5C plus centrifuge. The supernatant was discarded and replaced by a deoxygenated solution of sodium chloride (5 mM). This washing procedure was repeated three times. The final clay suspension contained 5 mg clay/mL (60 mg clay in 12 mL volume) and was at pH 7.3.

Reduced-reoxidized form. Aliquots of reduced-clay suspension with an initial concentration of 5 mg clay/mL were heated again at 75°C, except the purge gas was changed to oxygen for 72 h. After reoxidation, the clay was resuspended as described above.

Reduced [Fe(II)] and total Fe (Fe_T) were measured in each clay using a 1,10-phenanthroline-colorimetric method (Table 1) (Komadel and Stucki, 1988). The content of oxidized Fe [Fe(III)] was deduced by difference.

Clay reaction with pentachloroethane

Two mL of 5CA were combined with 2 mL of clay suspension (10 mg clay) in a 4.5-mL vessel. Each vessel (15 samples) was septum-sealed and then the headspace was saturated with high-purity argon with the aid of thin needles (#25). The final concentration of

Table 2. Stoichiometric ratio of total Fe (Fe_T), Fe(II), and Fe(III) and pentachloroethane in the reaction mixture.

Smectite	Treatment ¹	mole ratio ($\times 10^3$)		
		$Fe_T/5CA$	Fe(II)/5CA	Fe(III)/5CA
Upton	U	1.1	0.1	1.0
	R	1.1	1.06	0.058
	RR	1.1	0.19	0.93
SWa-1	U	7.0	0.027	6.9
	R	7.0	6.8	0.16
	RR	7.0	0.063	6.88
NG-1	U	0.1	0.031	1.0
	R	0.1	10	0.52

¹ U, R, and RR refer to unaltered, reduced, and reduced-reoxidized forms of the clay, respectively.

5CA was 0.1 mM; total clay content, 2.5 mg/mL; and NaCl concentration, 2.5 mM. In all experiments, structural Fe was in molar excess with respect of 5CA (Table 2). The vessels were placed horizontally in a wrist-action shaker, and removed every 30 min to collect samples.

Analysis

Aliquots of 0.1 mL of the reaction mixture were collected, filtered, diluted (1:100), and extracted 1:1 with pentane for trihalomethanes (THM) analysis. The samples were injected into a 3740 Varian gas chromatograph, equipped with an electron capture detector and a J & W Scientific column (DB5, 30 m \times 0.53 mm ID, and 3.0- μ m film thickness). A 25-min program was used with an initial temperature of 30°C (5 min), a final temperature of 140°C, and with a heating rate of 7°C/min.

Standard curves of pentachloroethane (retention time, RT = 15.7 min), tetrachloroethene (RT = 10.1), tetrachloroethane (RT = 13.5), and trichloroethene (RT = 6.1) were used for the identification and quantification of reactants and products.

RESULTS AND DISCUSSION

The concentration of 5CA decreased in the presence of the unaltered forms of NG-1, SWa-1, and Upton within the first hour and remained constant thereafter (Figures 1, 2, and 3). An adsorption rate constant, k_{obs} , for 5CA was calculated according to the integrated *pseudo* first-order rate equation

$$\ln \frac{[5CA]}{[5CA]_{initial}} = -k_{obs}t \quad (1)$$

and revealed that the rate of 5CA adsorption was proportional to the total Fe content of the smectite, *i.e.*, NG-1 > SWa-1 > Upton (Table 3). Concentration is represented by brackets.

The value of k_{obs} was also linearly related to the structural Fe(II) content of the smectite. For sample SWa-1 (Figure 4), the relationship was described by the linear equation:

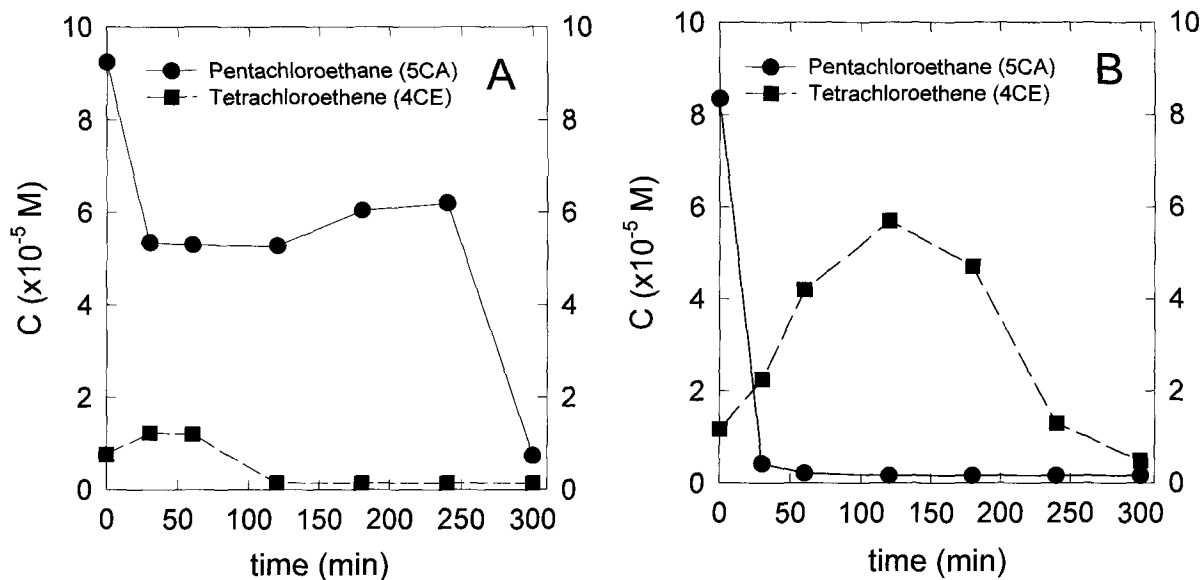


Figure 1. Reaction of pentachloroethane with NG-1 in the (A) unaltered and (B) reduced form.

$$k_{obs} = 0.0167[\text{Fe(II)}_c] + 0.157; r^2 = 0.99 \quad (2)$$

where k_{obs} is expressed in min^{-1} and $[\text{Fe(II)}_c]$ is the Fe(II) content of the clay-mineral structure expressed as mmole Fe(II)/g clay. Moreover, inclusion of unaltered, reduced, and reduced-reoxidized forms of all three smectites (Upton, NG-1, and SWa-1) yielded a similar linear relationship between k_{obs} and $[\text{Fe(II)}_c]$ (Figure 4):

$$k_{obs} = 0.0172[\text{Fe(II)}_c] + 0.154; r^2 = 0.93 \quad (3)$$

indicating that the adsorption of 5CA in the presence

of the three smectites in all oxidation states studied is described by the same function.

To understand the underlying factors that control 5CA reaction at smectite surfaces, consider the strong interaction between smectite basal surfaces and the surrounding H_2O molecules as reported by Yan *et al.* (1996b, 1996c). Using Fourier transform infrared (FTIR) spectroscopy, they confirmed that the stretching vibrations of the structural Si-O groups at the smectite basal surfaces are coupled to the bending vibrations, H-O-H, of interlayer- H_2O molecules. They

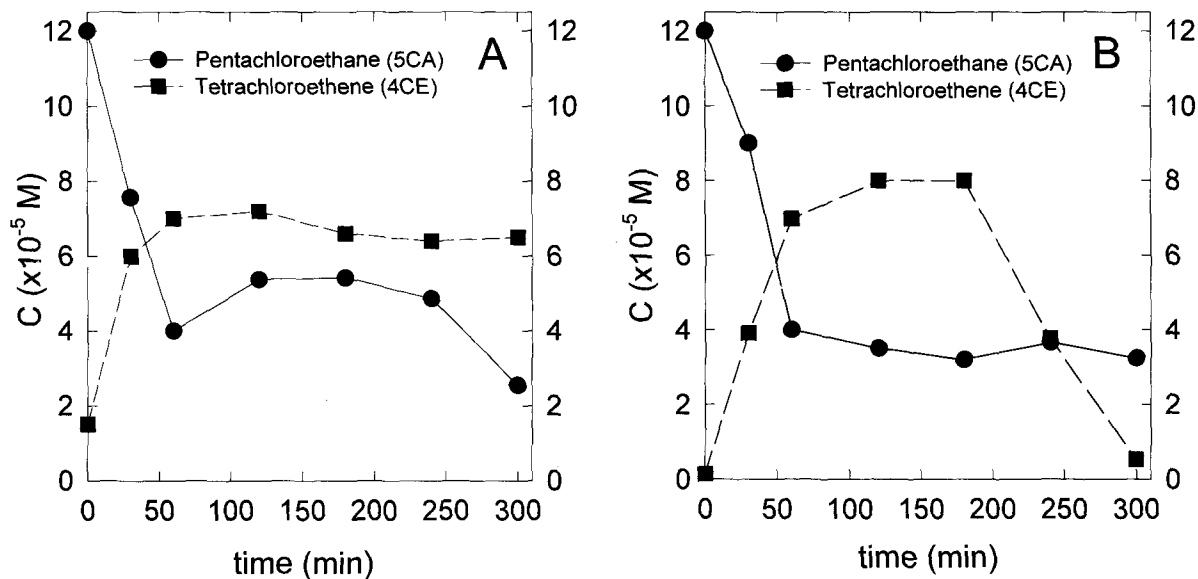


Figure 2. Reaction of pentachloroethane with SWa-1 in the (A) unaltered and (B) reduced form.

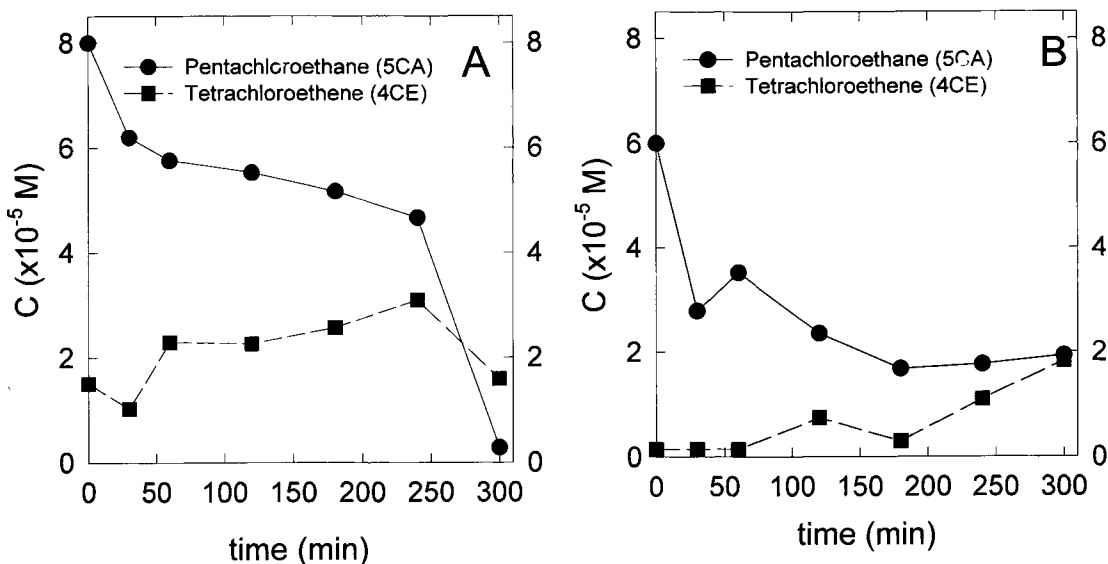


Figure 3. Reaction of pentachloroethane with Upton in the (A) unaltered and (B) reduced form.

further observed that this coupling prevails at different H_2O contents regardless of whether the exchangeable cation is Na^+ or Li^+ . Stucki and Yan (1999) recently observed that the Si-O and H-O-H coupling is also affected by the oxidation state of structural Fe in the smectite, confirming directly that changes in the valence state of octahedral Fe have a profound influence on the oxygen ions at the smectite basal surfaces, which in turn polarize the interlayer- H_2O molecules towards the Si-O basal groups. Such interactions are consistent with the hypothesis that the smectite-basal surface behaves as a Brønsted base relative to proton-donor species that may be present in the interlayer region.

The Brønsted basicity in smectites increases when structural Fe is reduced from Fe(III) to Fe(II). Experiments by FTIR show that near the clay surface, the

H-O-H bending vibrational frequency increases as the Fe(II) content in the clay increases, which is likely caused by a stronger clay-water interaction (Yan and Stucki, 1999). The reduction of structural Fe also increases the surface-charge density of the clay (Stucki, 1988; Stucki and Tessier, 1991; Gates *et al.*, 1993; Yan and Stucki, 1999), causing the Fe(II)-bearing smectites to acquire a strong nucleophilic character that facilitates the transformation of chlorinated alkanes. The high concentration of H_2O relative to that of 5CA, and the fact that smectite surfaces hydrate (Yan *et al.*,

Table 3. Iron(II) contents of and 5CA reaction rates with smectites Upton, SWa-1, and NG-1 in the unaltered (U), reduced (R), and reduced-reoxidized (RR) forms. k_{obs} is the 5CA adsorption-rate constant (min^{-1}); k_{ii} , the 4CE formation rate (min^{-1}); and $k_{obs} - k_{ii}$ (min^{-1}), the estimated lifetime of the precursor complex.

Smectite	Treatment	Fe(II) (mmol/g)	k_{obs} ($\times 10^{-2}$)	k_{ii} ($\times 10^{-3}$)	$k_{obs} - k_{ii}$ ($\times 10^{-2}$)
NG-1	U	0.012	1.93	75	1.9
SWa-1	RR	0.025	1.8	6.5	1.2
Upton	U	0.040	0.36	0.1	0.35
Upton	RR	0.075	2.2	3.8	1.8
SWa-1	U	0.108	1.4	5.8	0.87
Upton	R	0.424	3.1	9.3	2.2
SWa-1	R	0.852	3.3	27	0.6
SWa-1	R	1.370	3.8	1.8	3.7
SWa-1	R	2.720	6.1	4.9	5.7
NG-1	R	4.000	9.4	4.0	9.0

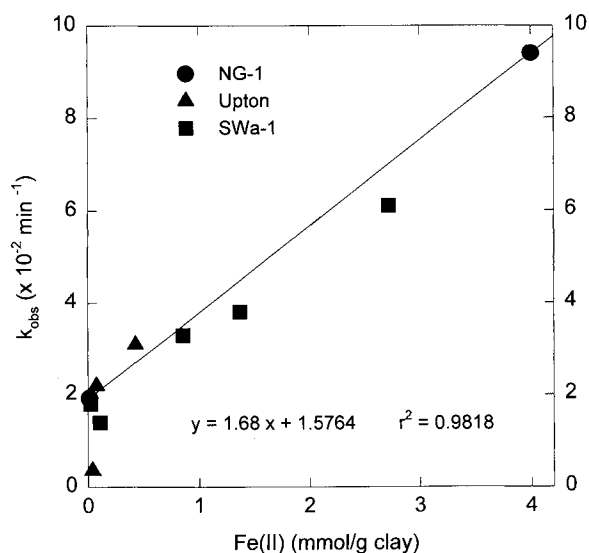


Figure 4. Reaction of pentachloroethane with NG-1, Upton, and SWa-1 at different reduction levels (adsorption-rate constant of pentachloroethane, k_{obs} (min^{-1}), as a function of Fe(II) content in the clay [mmol Fe(II)/g clay]).

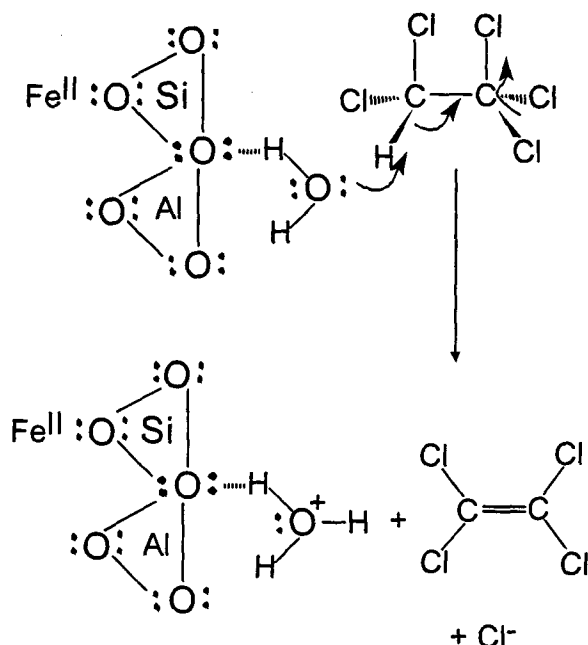


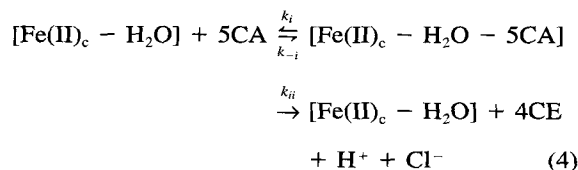
Figure 5. Proposed mechanism of reaction between smectite surface and pentachloroethane.

1996b, 1996c; Yan and Stucki, 1999), suggest that H₂O molecules mediate the hydrogen bridging and the long-range interactions between 5CA and the clay surface ("outer sphere complex"; Wilkins, 1991).

The formation of tetrachloroethene (4CE) is explained by the dehydrochlorination of 5CA (Roberts and Gschwend, 1991; Cervini-Silva *et al.*, unpubl. data). Dehydrochlorinations are α , β eliminations initiated by the abstraction of a proton by a strong base, followed by the release of chloride (Lowry and Richardson, 1987; Roberts and Gschwend, 1991; Larson and Weber, 1994). The presence of smectites accelerated the formation of 4CE when compared to neutral hydrolysis ($k_H = 1.31 \times 10^{-4} \text{ min}^{-1}$; Jeffers *et al.*, 1989; Larson and Weber, 1994). Figures 1, 2, and 3 show that the 5CA concentration decreased with unaltered clays within the first hour and remained constant afterwards. In contrast, the rate of adsorption of 5CA was much faster with the reduced form of the clays (Table 3). The maximum conversion of 5CA to 4CE was observed in the latter case, which supports the hypothesis that the clay surfaces behave as a base towards 5CA when adsorbed (Figure 5).

Kinetic model

A kinetic mechanism consistent with our results involves a two-step process: 1) rapid adsorption of 5CA at the hydrated surface forming an outer-sphere complex, followed by 2) 5CA dehydrochlorination to form 4CE:



where Fe(II)_c represents the smectite containing structural Fe(II), $[\text{Fe(II)}_c - \text{H}_2\text{O}]$ is the hydrated clay surface or clay-aquo complex, and $[\text{Fe(II)}_c - \text{H}_2\text{O} - 5\text{CA}]$ is a precursor complex that results from the binding of 5CA to the aquo complex. k_{-i} corresponds to the dissociation rate of the precursor complex; and k_{ii} corresponds to the loss of the precursor complex to the formation and desorption of 4CE.

From the model given in Equation (4), the complete rate-law expression is obviously more complex than that given in Equation (1). After applying the steady-state principle to the formation of the precursor complex (Thornton and Thornton, 1978; Stumm and Wieland, 1991; Stumm, 1992; Pilling and Seakins, 1995), the more complete rate-law expression is given by

$$\begin{aligned}
 -\frac{d[5\text{CA}]}{dt} &= \frac{d[\text{Fe(II)}_c - \text{H}_2\text{O} - 5\text{CA}]}{dt} \\
 &= k_i[\text{Fe(II)}_c - \text{H}_2\text{O}][5\text{CA}] \\
 &\quad - (k_{-i} + k_{ii})[\text{Fe(II)}_c - \text{H}_2\text{O} - 5\text{CA}] \quad (5)
 \end{aligned}$$

The observed rate constant from Equation (1) is related to Equation (5) by

$$k_{obs} = k_i[\text{Fe(II)}_c - \text{H}_2\text{O}] \quad (6)$$

giving

$$\begin{aligned}
 -\frac{d[5\text{CA}]}{dt} &= \frac{d[\text{Fe(II)}_c - \text{H}_2\text{O} - 5\text{CA}]}{dt} \\
 &= k_{obs}[5\text{CA}] - (k_{-i} + k_{ii}) \\
 &\quad \times [\text{Fe(II)}_c - \text{H}_2\text{O} - 5\text{CA}] \quad (7)
 \end{aligned}$$

The initial concentration of 5CA was low ($1 \times 10^{-4} \text{ M}$) compared to the Fe content and aquo complex of the clay (Table 2), and the amount of precursor complex was limited by the initial concentration of 5CA, so

$$[\text{Fe(II)}_c - \text{H}_2\text{O}] \leq [5\text{CA}] \quad (8)$$

In the steady state, the equality of Equation (8) can be substituted into the last term of Equation (7) as a first approximation.

Another simplification occurs if the loss rate for the precursor complex is much greater by the forward path than by the reverse path, *viz.*

$$k_{ii} \gg k_{-i} \quad (9)$$

which reduces Equation (7) to

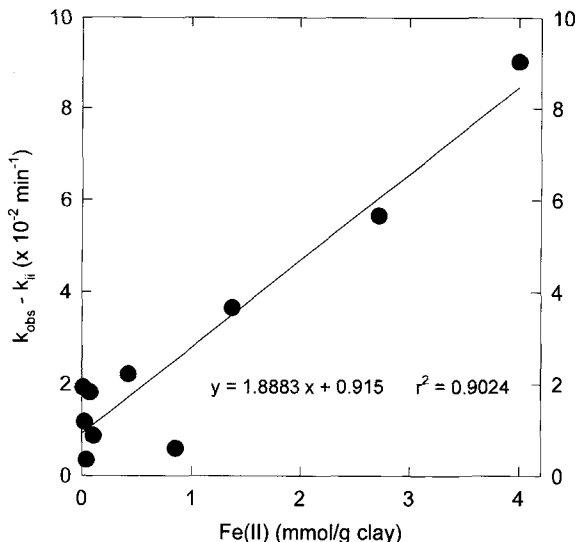


Figure 6. The reaction of pentachloroethane with NG-1, Upton, and SWa-1. Stability of the precursor complex, $k_{obs} - k_{ii}$ (min^{-1}), as a function of the Fe(II) content in the clay [mmol Fe(II)/g clay].

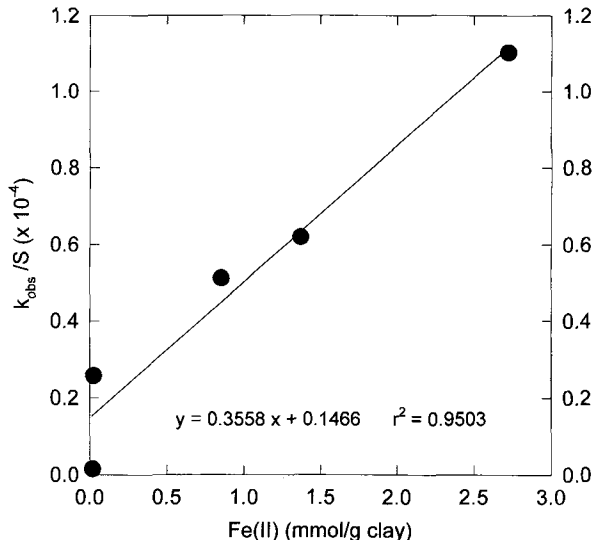


Figure 7. The adsorption-rate constant of pentachloroethane, k_{obs} (min^{-1}), as a function of the clay specific surface area, S (m^2/g clay), with SWa-1 at different reduction levels.

$$\frac{d[5\text{CA}]}{dt} = \frac{d[\text{Fe(II)}_c - \text{H}_2\text{O} - 5\text{CA}]}{dt} = [5\text{CA}](k_{obs} + k_{ii}) \quad (10)$$

The rate of 5CA dehydrochlorination depends on the amount of Fe(II) in the clay and is limited by the stability of the precursor complex [Equation (10)]. The lifetime of the precursor complex (τ ; Stumm, 1992), $\tau^{-1} = k_{obs} - k_{ii}$, varies depending on the clay (Tables 1, 2, and 3; Figure 6). Unaltered NG-1 and Upton show adsorption of 5CA and no formation of 4CE where $k_{obs} \gg k_{ii}$; whereas unaltered SWa-1 shows formation of 4CE and $k_{obs} > k_{ii}$. On the other hand, the trend in the reactivity of the reduced and reduced-reoxidized clays shows that the lifetime of the precursor complex decreases as the Fe(II) content in the clay increases. These results confirm that structural Fe(II) plays a major role in promoting the dehydrochlorination of 5CA.

Surface area

Lear and Stucki (1989) observed that the Fe(II) content in smectite SWa-1 modified the specific surface area (S), and concluded that Fe(II) promotes layer collapse, thereby decreasing the available surface area. The experimental results were described in terms of the Fe(II) content where $\text{Fe(II)}_c = \text{Fe(II)}_{\text{SWa-1}} < 0.37$ mmole/g clay ($r^2 = 0.96$):

$$S = -133[\text{Fe(II)}_c] + 715 \quad (11)$$

and where $\text{Fe(II)}_{\text{SWa-1}} > 0.37$ mmole/g clay ($r^2 = 0.95$):

$$S = -463[\text{Fe(II)}_c] + 685 \quad (12)$$

where S is expressed in m^2/g clay. The magnitude of the slope in Equation (11) [for small amounts of Fe(II) in the clay] is approximately three times that of Equation (12) [$\text{Fe(II)}_{\text{SWa-1}} > 0.37$ mmole/g clay]. This suggests that Fe(II) content initially has a strong effect on S , but the effect diminishes at greater levels of reduction [$\text{Fe(II)}_{\text{SWa-1}} > 0.37$ mmole/g clay]. These data may explain the non-linearity observed in Figures 4 and 5, where k_{obs} is described by a different function for $\text{Fe(II)}_{\text{SWa-1}} < 0.37$ than for $\text{Fe(II)}_{\text{SWa-1}} > 0.37$ mmole/g clay. The decrease in S coupled with the increase in k_{obs} (Figure 7) confirms that 5CA dehydrochlorination depends more strongly on the chemical activity of the surface than on the total surface area only.

Assuming complete clay hydration, the amount of $[\text{Fe(II)}_c - \text{H}_2\text{O}]$ formed is proportional to Fe(II)_c (Table 1), and the rate of 5CA dehydrochlorination in the presence of SWa-1 may then be rewritten in terms of $\text{Fe(II)}_{\text{SWa-1}}$ and S as:

$$-\frac{d[5\text{CA}]}{dt} \approx [\text{Fe(II)}_{\text{SWa-1}}](k_{obs} - k_{ii}) \approx (k_{obs} - k_{ii})/S \quad (13)$$

Combining Equations (10), (11), (12), and (13), the 5CA dehydrochlorination rate may be expressed for the particular case where $\text{Fe(II)}_{\text{SWa-1}} < 0.37$ mmole/g clay (Figure 7):

$$-\frac{d[5\text{CA}]}{dt} \approx (5 - 7.5 \times 10^{-3} S)(k_{obs} - k_{ii}) \quad (14)$$

and where $\text{Fe(II)}_{\text{SWa-1}} > 0.37$ mmole/g clay:

$$-\frac{d[5CA]}{dt} \approx (14.8 - 2.1 \times 10^{-2} S)(k_{obs} - k_{ii}) \quad (15)$$

CONCLUSIONS

The rate of 5CA adsorption on smectite strongly depends on the oxidation state and total amount of structural Fe in the clay. Clays containing higher amounts of Fe(II) promoted pentachloroethane adsorption. The reduction of structural Fe(II) increases the surface charge of the clay, imparting greater Brønsted-base character to the clay surface. The result is a greater adsorption rate constant of 5CA.

The adsorption kinetics of 5CA at the clay-water interface consists of the formation of a precursor complex while adsorbed, followed by 5CA dehydrochlorination and 4CE desorption. The stability of the precursor complex, $(k_{obs} - k_{ii})$, is proportional to the Fe(II) content in the clay. These results are interpreted to mean that Fe(II) is a strong nucleophilic agent, and plays an important role in the mobility of halogenated alkanes in soils.

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E-mail of corresponding author: jstucki@uiuc.edu
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Ms. 303; A.E. George F. Vance)