

B-6 The Reductive Dehalogenation of Carbon Tetrachloride in the Presence of FeS/FeS₂ as Affected by Hydrophobic Sites.

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1. Introduction

The fate of hydrophobic contaminants, such as HACs, is highly dependent on sorptive behavior. Sorption can affect directly or indirectly in pollutant degradation by reducing mobility of contaminants and/or catalyzing their transformations. Since HACs are typically bound to solids and/or trapped in a solid matrix in groundwater environments, both the water and the soil/sediment matrix must be considered for studying HACs chemical transformation. However most of the transformation reactions have been studied without considering the catalytic role of the solid surface. Among transformation reactions, reductive dehalogenation and reductive elimination are the least studied. Thermodynamic calculations indicate that Fe(II) and S(-II) (mainly exist as Fe²⁺ and HS⁻), which are abundant species in anoxic ground water, can be the reducing agents for the reductive dehalogenation of some HACs. Although thermodynamic calculations indicate that reductive dehalogenations are feasible, these reactions have been showed to proceed very slowly because hydrated ferrous and sulfide ions have limited opportunities to react with the nonpolar(or hydrophobic) organics in the aqueous phase due to their immisible moities in the homogeneous phase. The sorption of uncharged organic chemicals to the solid surface is dominated by hydrophobic interactions. Therefore, it can be expected that the reductive dehalogenation of HACs will be very effective at the surface of hydrophobic solids containing those reducing agents such as Fe²⁺ and HS⁻. FeS and FeS₂ known as the most abundant solid in the anoxic environments carries the surface hydrophobicity and is composed of ferrous iron and sulfide. However, no study has been reported on the correlation between dechlorination rates and hydrophobicity of mineral surface in the reductive dehalogenation of HACs. Our experiments showed that heterogeneous reduction of HACs studied with FeS/FeS₂ were greatly enhanced as compared to those with heterogeneous reactions with ferrous iron-containing clays and homogeneous reactions containing aqueous ferrous iron and sulfide without solid.

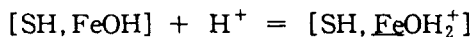
Therefore, when investigating reductive transformation of HACs, it is thus imperative to study the surface chemical behavior of FeS and FeS₂. In order for apolar HACs to accept electrons from Fe(II) or S(-II), they need to contact each other. This interaction can, however, happen on the unwet (hydrophobic) surface of FeS₂ and FeS by the hydrophobic adsorption of HACs onto the FeS/FeS₂ surface and the subsequent electron transfer reaction. The sorption of uncharged organic chemicals to the solid surface is dominated by hydrophobic interactions. The overall process of the surface reaction can be described by the following steps : sorption of the organic compound to a reactive or unreactive site, formation of an alkyl radical, transfer of a second electron, decomposition into products, and desorption of the products. Because (1) FeS and FeS₂, itself, can be a substrate to react with HACs, and (2) FeS and FeS₂ can carry Fe²⁺ and HS⁻ on its surface. These ions are the potential determining ions (PDIs) of FeS/FeS₂ and can react with HACs to undergo reductive dehalogenation. In this study, Carbon tetrachloride as HACs will be investigated. It is thus important to develop a rate law describing degradation reactions of halogenated organics by FeS and FeS₂

This information will reveal the rate-limiting step which controls reductive dehalogenation of toxic HACs. The outcome of these studies may lead to the development of new (ground) water remediation or treatment processes.

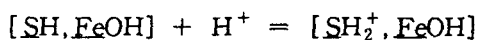
2. RATIONALE

Determination of the total hydroxyl (or hydrated) sites

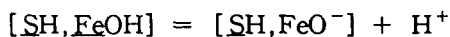
The surface of FeS/FeS₂ is neither totally hydrophobic nor hydrophilic. The hydrophilic surface undergoes the hydrolysis reaction and forms the surface hydroxyls. This reaction is pH dependent.



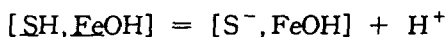
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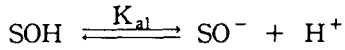


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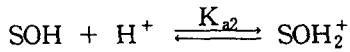


This behavior is similar to the surface hydroxyls of oxides in aqueous phase. Actually, it is impossible to difference the hydrated FeOH and SH surface

functional groups. For the sake of simplicity, the surface hydroxyl group, SOH , is used in the following discussion. The apparent surface hydrolysis reaction are



$$K_{a1}^{\text{int}} = \frac{\{\text{SO}^-\} \cdot \{\text{H}^+\}}{\{\text{SOH}\}}$$



$$K_{a2}^{\text{int}} = \frac{\{\text{SOH}_2^+\}}{\{\text{SOH}\} \cdot \{\text{H}^+\}}$$

Where $\{ \}$ designates the surface concentration of the species. The total number of surface hydroxyls sites, N_s , is therefore the sum of these three hydroxyl groups:

$$N_s = \{\text{SOH}_2^+\} + \{\text{SOH}\} + \{\text{SO}^-\}$$

The surface concentration of protons $\{\text{H}^+\}$ is related to its bulk phase quantity, $[\text{H}^+]$, by the Boltzmann equation.

$$\{\text{H}^+\} = [\text{H}^+] \exp(-F\psi_0/RT)$$

where F , ψ_0 , R , T are the Faraday constant, surface potential, gas constant, and absolute temperature, respectively. In the absence of specific adsorption, the surface potential can be calculated from the Gouy-Chapman theory of the electrical double layer:

$$\psi_0 = 2RT/ZF \sinh^{-1} \left\{ \sqrt{\pi / 2RT \epsilon I} \right\} \sigma_0$$

where Z is the valence of the electrolyte and ϵ is dielectric constant. The surface charge, σ_0 , is obtained from zeta potential data. At $\text{pH} < \text{pH}_{zpc}$ the surface is positively charged, therefore,

$$N_s = \{\text{SOH}_2^+\} + \{\text{SOH}\}$$

Likewise, at $\text{pH} > \text{pH}_{zpc}$ the surface is negatively charged, i.e.,

$$N_s = \{\text{SOH}\} + \{\text{SO}^-\}$$

The terms $\{SOH_2^+\}$ and $\{SOH\}$ are determined from zeta potential data, i.e.,

$$\{SOH_2^+\} = \sigma_+/S$$

and

$$\{SO^-\} = \sigma_-/S$$

where S is a conversion factor for charge to surface concentration. By substituting the above equations and with further mathematical manipulation, one has the following equations.

For $pH > pH_{ZPC}$ (- charge)

$$K_{al}^{int} = \frac{[SO^-] \cdot [H^+]}{[SOH]} = \frac{\frac{\sigma_-}{S} \cdot [H^+]}{\frac{Ns - \sigma_-}{S}}$$

$$K_{al}^{int} \cdot (Ns - \sigma_-) = \sigma_- \cdot [H^+]$$

$$[H^+] = \frac{K_{al}^{int} \cdot Ns - K_{al}^{int} \cdot \sigma_-}{\sigma_-}$$

$$[H^+] = K_{al}^{int} \cdot Ns \cdot \frac{1}{\sigma_-} - K_{al}^{int}$$

For $pH < pH_{ZPC}$ (+ charge)

$$K_{a2}^{int} = \frac{[SOH_2^+]}{[SOH] \cdot [H^+]} = \frac{\frac{\sigma_+}{S}}{\frac{Ns - \sigma_+}{S} \cdot [H^+]}$$

$$K_{a2}^{int} \cdot (Ns - \sigma_+) \cdot [H^+] = \sigma_+$$

$$[H^+] = \frac{\sigma_+}{K_{a2}^{int} \cdot (Ns - \sigma_+)}$$

$$\frac{1}{[H^+]} = \frac{K_{a2}^{int} \cdot (Ns - \sigma_+)}{\sigma_+} = \frac{K_{a2}^{int} \cdot Ns - K_{a2}^{int} \cdot \sigma_+}{\sigma_+}$$

$$\frac{1}{[H^+]} = K_{a2}^{int} \cdot Ns \cdot \frac{1}{\sigma_+} - K_{a2}^{int}$$

A plot of $1/[H^+]$ versus $1/\sigma_+$ for the positive surface and of $\{H^+\}$ versus $1/\sigma_-$ for the negative surface will yield intercepts and slopes allowing the determination of the total number of surface sites, Ns

The surface potential can thus be determined by the zeta potential data. Along with the specific surface area of FeS and FeS₂ determined by the BET method,

approximate concentrations of unwet and wet sites can be determined. These data associated with hydrophilic sites are listed in Table 1. Table 1 indicates that FeS₂ has much hydrophilic sites than FeS mineral, in contrast to the specific surface area of each minerals. From this results, we will assume that hydrophobic sites of FeS play a much role in dechlorination of CT than that of FeS₂.

Table 1. The data associated with hydrophilic sites for each minerals

parameters	FeS	FeS ₂
Ns	1.537 sites/nm ²	3.245 sites/nm ²
[SOH]	0.0000014045 moles/L	0.0000020477 moles/L
Asp	0.55 m ² /g	0.38 m ² /g
K _{a1} ^{int}	6.07 × 10 ⁻⁷	5 × 10 ⁻⁸
pK _{a1} ^{int}	6.2168	7.301
K _{a2} ^{int}	1.633 × 10 ⁻⁸	3.178 × 10 ⁻¹⁰
pK _{a2} ^{int}	7.787	9.4979
pH _{zpc}	7.0	8.4