

# Theoretical and Experimental Studies of the Dechlorination Mechanism of Carbon Tetrachloride on a Vivianite Ferrous Phosphate Surface: Supporting Information

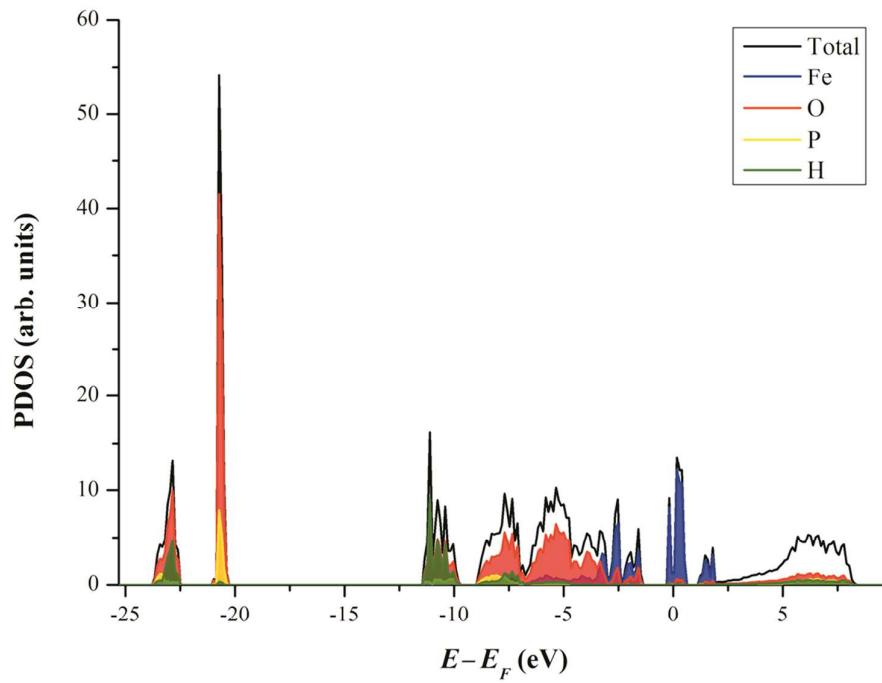
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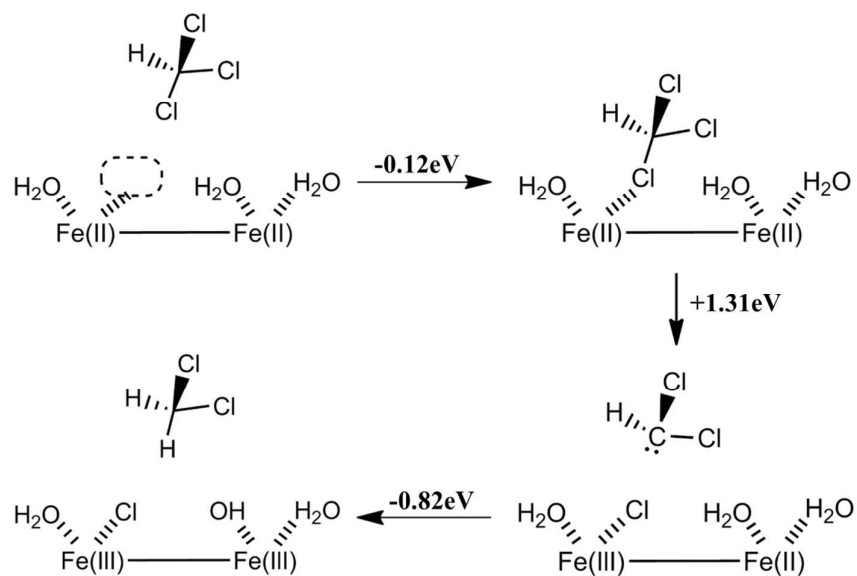
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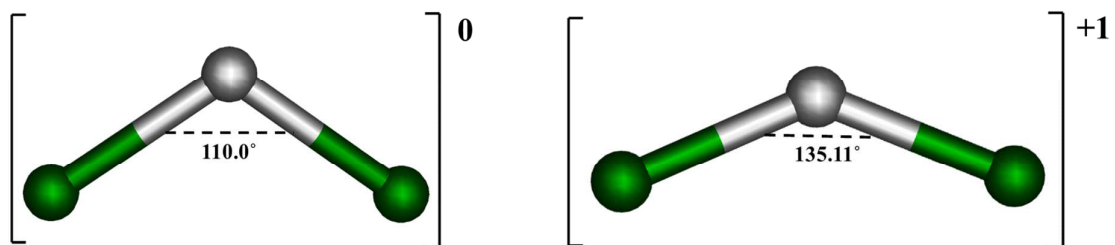
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**Figure S1.** The partial density of states for vivianite structure. The main character of the electronic structure near Fermi energy was detected from Fe 3d states with negligible contribution by phosphate groups.



**Figure S2.** The second dissociative electron transfer (diss-ET) step of chloroform (HCCl<sub>3</sub>) to form dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). Unlike the diss-ET step of CCl<sub>4</sub>, diss-ET of HCCl<sub>3</sub> is an endothermic process requiring 1.31 eV, which can be attributed to the lower reduction potential of HCCl<sub>3</sub> than that of CCl<sub>4</sub> (0.560 V vs. 0.675 V). Thus, HCCl<sub>3</sub> was observed as a major product from the experiment without the formation of CH<sub>2</sub>Cl<sub>2</sub> or further reduced species such as methyl chloride (CH<sub>3</sub>Cl) and methane (CH<sub>4</sub>).



**Figure S3.** Cl-C-Cl angles of free  $\bullet\text{CCl}_2$  ( $110.0^\circ$ ) and  $\text{CCl}_2^+$  ( $135.11^\circ$ ) computed using density functional theory (DFT). The Cl-C-Cl angle of the surface adsorbed dichlorocarbene ( $:\text{CCl}_2^*$ ) is comparable to that of free  $\bullet\text{CCl}_2$  ( $109.6^\circ$  vs.  $110.0^\circ$ ), indicating that  $:\text{CCl}_2^*$  is nearly neutral.

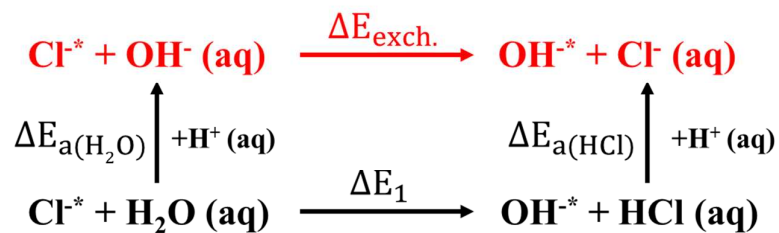
**Table S1.** The observed pseudo-first-order rate constants ( $k_{\text{obs}}$ ), remaining amounts of  $\text{CCl}_4$ , and product recoveries ( $\text{HCCl}_3$ , formate, methane and chloride) at different pH values (pH 3, 5, 7, 9, and 11).

	$\text{CCl}_4$	$\text{HCCl}_3$	Formate	Methane	$\text{Cl}^-$
pH 3					
$k_{\text{obs}}$ ( $\text{d}^{-1}$ )	$1.163 \times 10^{-2}$	$7.545 \times 10^{-2}$	$1.006 \times 10^{-6}$	$2.699 \times 10^{-8}$	$1.590 \times 10^{-6}$
$R^2$	0.836	0.931	0.682	1.000	0.594
$\text{CCl}_4$ remaining and product recovery (mM)	0.033	0.028	0.003	$5.864 \times 10^{-10}$	0.147
pH 5					
$k_{\text{obs}}$ ( $\text{d}^{-1}$ )	$4.055 \times 10^{-2}$	$6.939 \times 10^{-2}$	$2.148 \times 10^{-2}$	$3.168 \times 10^{-7}$	$1.543 \times 10^{-2}$
$R^2$	0.874	0.954	0.915	1.000	0.948
$\text{CCl}_4$ remaining and product recovery (mM)	0.033	0.028	0.003	$5.864 \times 10^{-10}$	0.147
pH 7					
$k_{\text{obs}}$ ( $\text{d}^{-1}$ )	$6.511 \times 10^{-2}$	$3.537 \times 10^{-2}$	$1.403 \times 10^{-6}$	4.827	$1.099 \times 10^{-1}$
$R^2$	0.972	0.978	0.819	0.006	0.849
$\text{CCl}_4$ remaining and product recovery (mM)	0.010	0.051	0.016	$1.062 \times 10^{-10}$	0.200
pH 9					
$k_{\text{obs}}$ ( $\text{d}^{-1}$ )	$6.931 \times 10^{-2}$	$4.134 \times 10^{-1}$	$1.410 \times 10^{-6}$	$5.098 \times 10^{-6}$	$1.420 \times 10^{-1}$
$R^2$	0.986	0.843	0.821	1.000	0.940
$\text{CCl}_4$ remaining and product recovery (mM)	0.000	0.054	0.021	$3.902 \times 10^{-11}$	0.217

pH 11

$k_{\text{obs}}$ ( $\text{d}^{-1}$ )	$1.742 \times 10^{-1}$	$5.449 \times 10^{-1}$	$9.167 \times 10^{-2}$	$4.347 \times 10^{-6}$	$1.494 \times 10^{-1}$
$R^2$	0.980	0.807	0.942	1.000	0.967
$\text{CCl}_4$ remaining and product recovery (mM)	0.000	0.056	0.026	$3.178 \times 10^{-11}$	0.243

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**Scheme S1.** To calculate the energy change required for the exchange of  $\text{Cl}^*$  on the vivianite surface with  $\text{OH}^-$  in the solution phase (red), we considered the above thermodynamic cycle (black). Following the cycle,  $\Delta E_{\text{exch.}} = \Delta E_1 - \Delta E_{\text{a}(\text{H}_2\text{O})} + \Delta E_{\text{a}(\text{HCl})}$ , where  $\Delta E_1$  is computed using density functional theory (DFT) calculations.  $\Delta E_{\text{a}}$  is calculated using the experimental acid dissociation constant ( $K_{\text{a}}$ ) obtained from the relation  $\Delta E_{\text{a}} = -RT \ln K_{\text{a}}$ , resulting in  $\Delta E_{\text{a}(\text{H}_2\text{O})} = 0.93 \text{ eV}$  and  $\Delta E_{\text{a}(\text{HCl})} = -0.47 \text{ eV}$ .