Supporting Information

Effects of zwitterionic buffers on sorption of ferrous iron at goethite and its oxidation by CCl_4

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Additional information is available for the Material and Method section. Figures represent the chemical structures of several zwitterionic and cationic organic buffers (Figure S1), sorption isotherms of MOPS and HEPES (Figure S2), **effect of zwitterionic organic buffers on the oxidation of Fe(II) (Figure S3),** schematic reaction pathway of the reductive dehalogenation of CCl_4 by Fe(II) (Figure S4), and ATR-FTIR spectra of MOPS, HEPES and Fe(II) in aqueous solution (Figure S5).

10 Pages, 5 Figures

Material and Methods

Goethite. The iron mineral goethite (α-FeOOH) was purchased from Lanxess Germany GmbH as Bayferrox 920 Z. The storage was dry and cool as received under lab atmosphere. The goethite was characterized determining specific surface area (BET measurement), purity (X-ray diffraction), crystal morphology and particle size (scanning electron microscopy), total organic carbon and point of zero charge pH_{pzc} (1). The specific surface area was investigated by N_2 adsorption with a Gemini 2375 Surface Area Analyzer. The BET surface was 9.2 m^2/g using the multi point BET measurement. X-ray diffraction (μ-XRD, Bruker-D8 with GADDS) showed that the sample did not contain impurities. Furthermore the crystal form and the particle size were determined by scanning electron microscopy (LEO 1550 VP) after sputter deposition on a thin gold layer and showed pure needle shaped crystals. The particle size ranged between 0.6 and 0.9 μm in length. The TOC (total organic carbon) content was with 0.01% near the detection limit (Horiba P100 with TOC Boat Sampler, detection limit 0.006%). The point of zero charge (pH_{pzc}) was determined with 6.5 ± 0.4 by acid/base titration (1). All properties of goethite were in the expected range but in case of the pH_{pzc} at the lower end of previously reported values (2, 3).

Glove Box Conditions. All preparation steps that involved Fe(II) were conducted in a glove box (Unilab with an Unilab PLC control panel, Braun, Garching, Germany) to maintain strictly anoxic conditions ($O_2 < 1$ ppm). These working steps were conducted under a nitrogen atmosphere and the oxygen content was continuously measured with an oxygen sensitive sensor. The sensor was catalyzed after distinct time intervals to ensure sufficient oxygen measurement in the glove box. The dissolved Fe(II) was found to be stable in the atmosphere of the glove box (no decrease of the concentration over time).

Fe(II) Stock Solution. The preparation of the iron stock solution was performed by adding 3.63 g (0.065 mmol) metal iron (Fe(0)) to 100 mL of a 1 M HCl solution in a serum bottle (4). The 1 M HCl solution was made anoxic before the experiments by bubbling nitrogen through a rubber stopper in the solution for 30 min (gas outlet for pressure release). The suspension was heated up to 80°C while gently stirring. After 2 hours no more hydrogen evolution was observed. The suspension was filtered within the glove box with a 0.2 µm PTFE filter to remove any residual metal iron. The exact content of Fe(II) was determined photometrically (562 nm) by the ferrozine assay (5).

Analyses of CCl_4, $CHCl_3$ and C_2Cl_4 were performed on a TraceGC 2000 (ThermoFinnigan, Milano, Italy) gas chromatograph coupled to a TraceDSQ single quadrupole mass spectrometric detector (ThermoFinnigan, Austin, TX, US) was used. The injection was performed with a headspace method using a 2.5 mL gastight syringe (CTC-CombiPAL autosampler) and a split ratio of 1:50. For separation of the compounds an Rtx-VMS capillary column (60 m × 0.32 mm I.D., 1.8 µm film thickness, Restek Corp., Bellefonte, PA, US) was installed. The temperature of the column was initially hold at 40 °C for 4 min, heated up to 100 °C with a rate of 7 °C/min and maintained at 150 °C for another 5 min. For the mass spectrometer the electron impact ionization mode (EI) at 70 eV, a source temperature of 220 °C and transfer line temperature of 250 °C were applied. The scan mode was a full scan (m/z = 50 – 300). To avoid carry over, a gentle nitrogen stream was used to clean the syringe for 5 min after each injection. Data acquisition and processing were carried out using Xcalibur Data System Version 1.3 (ThermoFinnigan, Austin, TX, US).

Analyses of CO were performed on a Varian CP-3800 gas chromatography coupled to a thermal conductivity detector (TCD) (Varian Deutschland GmbH, Darmstadt, Germany). The injection was performed manually with a 200 µL gas tight syringe, an injector temperature of 150 °C and a split ratio of 1:2. The temperature of the column (Alltech, Mole-Sieve 30 m x 0.53 mm ID) was initially hold at 60 °C for 3 min, heated up to 200 °C with a rate of 75 °C/min and maintained at 200 °C for another 3 min. Helium was used as carrier gas with a flow rate of 5 mL/min. For the TCD a filament temperature of 185 °C and a negative polarity were applied. Data acquisition and processing were carried out using Chromeleon Version 6.11.

ATR-FTIR measurements were performed on a Bruker Vertex 80v equipped with an gas tight diamond multiple reflection ATR flow through cell.

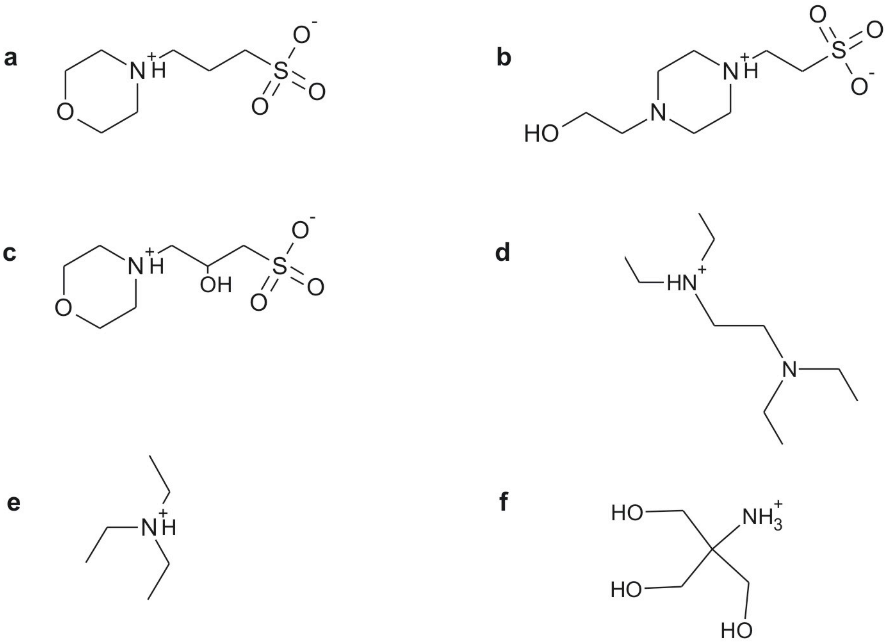

FIGURE S1: Chemical structure of *zwitterionic (a-c) and cationic (d-f)* organic buffers; (a) MOPS (3-morpholinopropane-1-sulfonic acid), (b) HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid), (c) MOPSO (3-(N-Morpholino)-2-hydroxypropanesulfonic acid), (d) TEEN (N,N,N',N'-tetraethylethylenediamine), (e) TEA (triethylammonium), (f) TRIS (tris(hydroxymethyl)aminomethane)

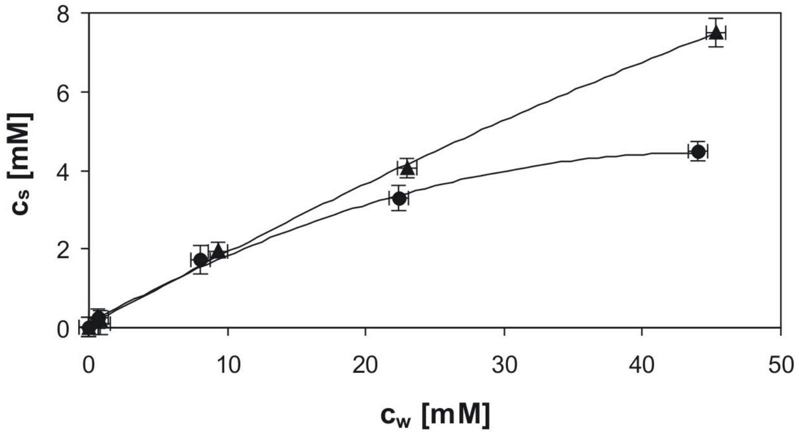

FIGURE S2: Sorption isotherm of (▲) MOPS and (●) HEPES on goethite/Fe(II) surface at pH 7 after 24 hours of shaking, an aqueous Fe(II) concentration of 1mM and 50 m^2/L goethite (n = 4 ± 1 SD).

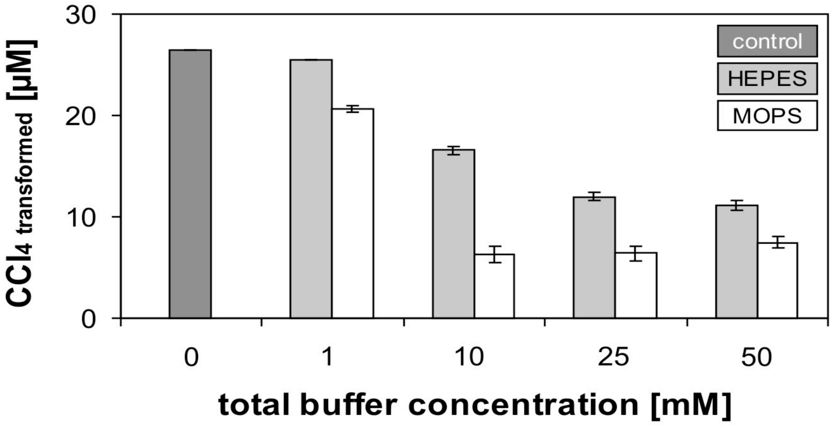

FIGURE S3: Effect of zwitterionic organic buffers on the oxidation of Fe(II) at goethite at pH 7 shown as transformation of CCl_4 (C_0 = 30 µM) after 100 h; without buffers (control; dark grey), with HEPES (light grey), MOPS (white) (n = 4 ± 1 SD).

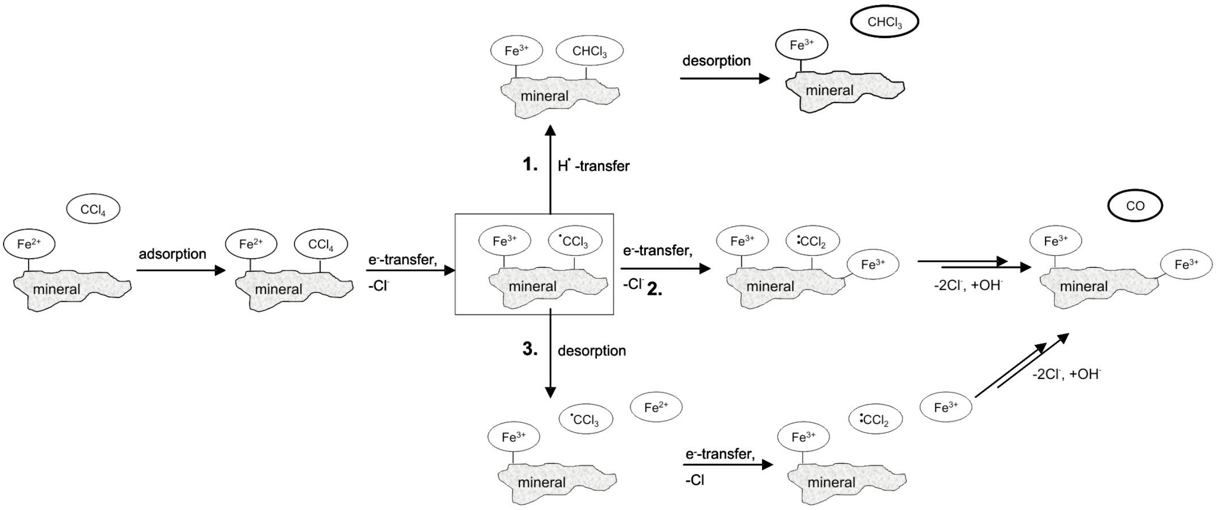

FIGURE S4: schematic reaction pathway of the oxidation of Fe(II) and transformation of CCl_4: after reductive dehalogenation of CCl_4 to a $\cdot CCl_3$ radical (shown in the middle of the figure) on the mineral surface three pathways are possible: 1. transfer of a hydrogen radical or 2. further dehalogenation and hydrolysis or 3. desorption and following e-transfer in the suspension; modified from Elsner et al. (6).

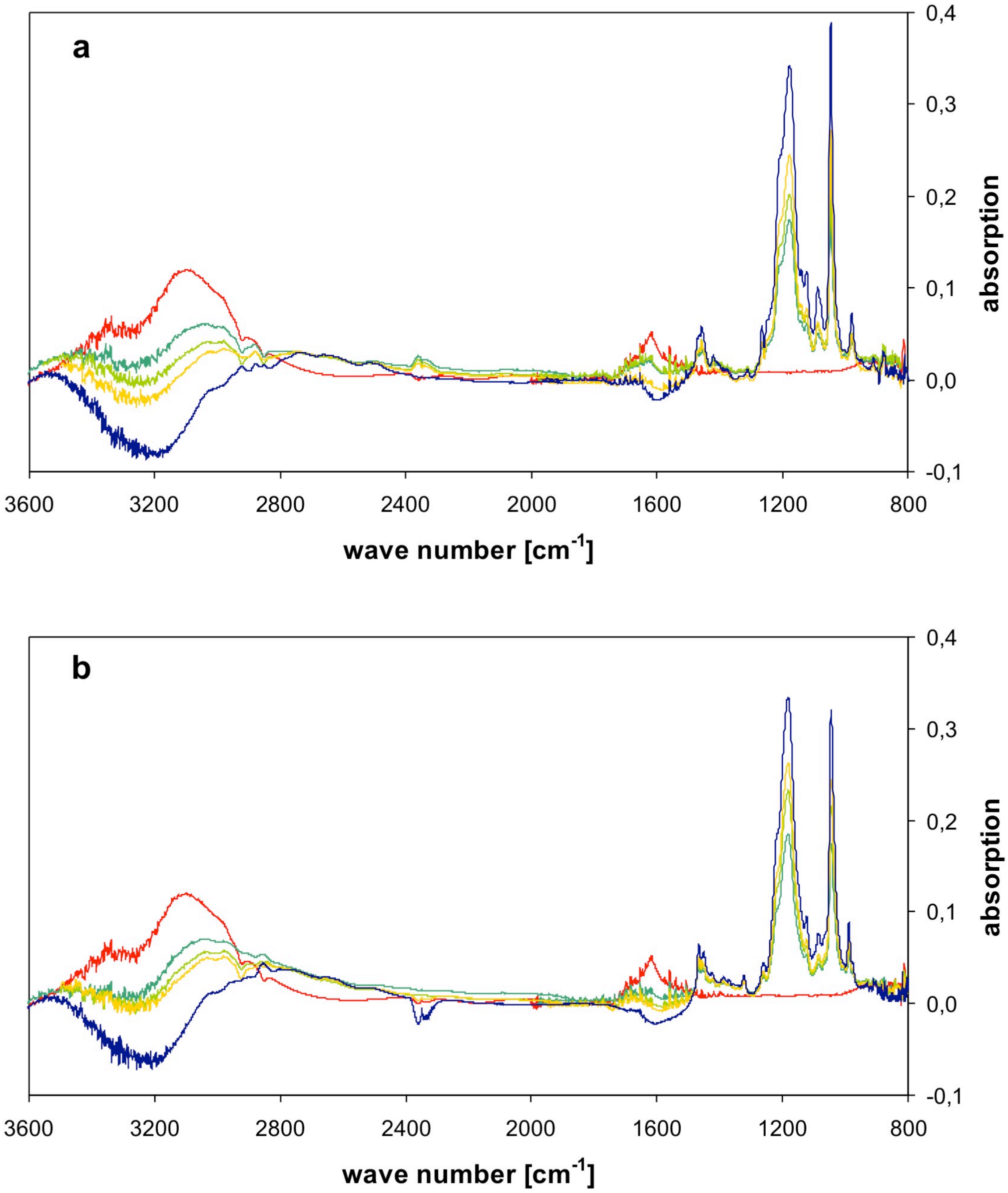

Figure S5: ATR-FTIR spectra of (**a**) MOPS (blue), complexes between Fe and MOPS: 1:1 (green), 1:2 (light green) and 1:3 (yellow) and Fe(II) (red); (**b**) HEPES (blue), complexes between Fe and HEPES: 1:1 (green), 1:2 (light green) and 1:3 (yellow) and Fe(II) (red). Relevant parts of the spectra are located between 2820 and 2760 cm^{-1} for N-CH$_2$ stretching and between 1300 and 1000 cm^{-1} for CN stretching. These spectra were extracted after subtracting the water background signal.

References

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