

CHAPTER 6

Summary and Conclusions

6.1 Important Findings of This Thesis.

In the introduction of this thesis, different pathways have been proposed for reactions between organic compounds and Mn (hydr)oxides. We have found that rates and pathways depend on: (i) reductant, complexant, and adsorptive properties of organic compounds; (ii) experimental conditions such as pH, organic compound concentration, oxide loading, and in the presence of metal ions or certain anions; (iii) the characteristics of Mn (hydr)oxides selected in this research, MnO₂(birnessite) and MnOOH(manganite). We will here summarize our findings for each chapter.

Chapter 2: MnO₂ oxidizes citrate to 3-ketoglutarate and acetoacetate. Plots of citrate loss as a function of time, and plots of dissolved Mn^{II} and citrate oxidation product formation, all yield S-shaped curves, indicating autocatalysis. Increasing the citrate concentration decreases the induction period. The maximum rate (r_{\max}) along the reaction coordinate follows a Langmuir-Hinshelwood dependence on citrate concentration. Increases in pH decrease r_{\max} and increase the induction time. Adding Mn^{II}, Zn^{II}, orthophosphate, or pyrophosphate at the outset of reaction decreases r_{\max} . Mn^{II} addition eliminates the induction period, while orthophosphate and pyrophosphate addition increase the induction period. Our findings indicate that two parallel processes are responsible. The first, relatively slow process involves the oxidation of free citrate by surface Mn^{III,IV}, yielding Mn^{II} and citrate oxidation products. The second process, which

is subject to strong positive feedback, involves concerted reaction of Mn^{II} and citrate with surface $\text{Mn}^{\text{III,IV}}$, yielding citrate oxidation products and two equivalents of Mn^{II} .

Chapter 3: This study examines reaction of a synthetic MnO_2 (birnessite), which contains both Mn^{III} and Mn^{IV} , and a synthetic MnOOH (manganite), which consists solely of Mn^{III} , with phosphonoformic acid, oxalic acid, glyoxylic acid, and ten other structurally-related organic compounds. Significant concentrations of dissolved Mn^{III} were detected in the phosphonoformic acid reactions with MnOOH , indicating that ligand-assisted dissolution took place. Mn^{II} is the predominant dissolved Mn species in the phosphonoformic acid reactions with MnO_2 , in the reactions for any other combination of organic substrate and Mn (hydr)oxide, suggesting a redox reaction dominated. Rates of the redox reaction depended on several factors. *First*, the reductant, adsorptive, and complexant properties of the organic compounds: glyoxylic acid, phosphonoformic acid and oxalic acid are more conducive to oxidation than the other organic compounds. The overall reactivity among thirteen organic compounds change over several orders of magnitude. *Second*, rates for glyoxylic acid, phosphonoformic acid and oxalic acid decrease with increasing pH. *Third*, the surface-area corrected rates indicate that MnOOH and MnO_2 can yield dramatically different rates with some compounds, but not with other compounds. With MnO_2 , the range of reactivity is nearly 20-times greater than that of MnOOH .

Chapter 4: This study examines rates and pathways for redox reactions between a synthetic MnO_2 (birnessite) and thirteen organics, including eight β -diketones, two β -ketocarboxylic acids, and three β -dicarboxylic acids. With β -diketones, high reactivity generally corresponds to high enol content, which is contributed by the presence of labile

α -H atom(s). With β -dicarboxylic acids, malonic acid and dimethylmalonic acid are much more reactive than dimethylmalonic acid, indicating that a α -H is required for higher reactivity. Malonic acid oxidation via the conversion of a α -H into a α -OH to yield tartronic acid has been proposed based upon product analysis. For acetylacetone, acetoacetic acid, and malonic acid, the effect of pH on reactivity correlates well with the pH dependence of adsorption.

Chapter 5: This study examines Mn^{III} solubilization from a synthetic MnO_2 (birnessite), which contains one-fifth of Mn^{III} , and a synthetic MnOOH (manganite), which contains solely Mn^{III} , by two groups of chelating agents in large excess with respect to oxide concentration in circum-neutral solutions, using the measurement of total dissolved Mn ($\text{Mn}_{\text{T}}(\text{aq})$) and Mn^{III} ($\text{Mn}^{\text{III}}(\text{aq})$). For reaction of the two oxides with inorganic pyrophosphate (PP) and five related phosphonate- and carboxylate-containing chelating agents, MP, EDP, and PPA do not cause discernable dissolution. PP, MDP and PAA yield $\text{Mn}^{\text{III}}(\text{aq})$ as the predominant $\text{Mn}_{\text{T}}(\text{aq})$ species, regardless of pH, chelating agent concentration and oxide loading, although at different rates and to a different extent. Since PP, MDP and PAA are not oxidized by Mn^{III} within timescales of each dissolution experiment, $\text{Mn}^{\text{III}}(\text{aq})$ production arises from ligand-assisted dissolution. The typical dissolution profile exhibits an initial fast dissolution and later dissolution slows down over time. Comparing PP and MDP, PAA solubilizes Mn^{III} to a significantly lesser extent. For reaction of MnOOH with four aminophosphonate- and aminocarboxylate-containing ligands, IDMP causes primarily ligand-assisted dissolution; PMG causes both ligand-assisted dissolution and reductive dissolution; MIDA causes reductive dissolution only; IDA does not contribute to dissolution.

6.2 Future Research

Despite the fact that this study answers many questions pertaining to reactions between $\text{Mn}^{\text{III,IV}}$ (hydr)oxides and small oxygen-donor aliphatic compounds, several questions remain unanswered, and inspire additional research that is of particular interest.

6.2.1 LogK Values for $\text{Mn}^{\text{III}}\text{H}_x\text{L}_n(\text{aq})$. Ligand-assisted dissolution of Mn^{III} -containing (hydr)oxide surface may be limited by thermodynamic or kinetic constraints. In Chapter 5, PP-, MDP-, and PAA-assisted MnO_2 (and MnOOH) dissolution exhibits non-linear dissolution kinetics, in which the increase of $\text{Mn}^{\text{III}}(\text{aq})$ levels out over time. Are these leveling out $\text{Mn}^{\text{III}}(\text{aq})$ concentrations true plateaus under thermodynamic control? PP, MDP and PAA exhibit different leveling out $\text{Mn}^{\text{III}}(\text{aq})$ concentrations. Is this because PP, MDP and PAA have different thermodynamic capability of solubilizing Mn^{III} ? To answer these questions, the logK values of Mn^{III} complexes in aqueous solution ($\text{Mn}^{\text{III}}\text{H}_x\text{L}_n(\text{aq})$) need to be known. To date, the logK values of $\text{Mn}^{\text{III}}\text{H}_x\text{L}_n(\text{aq})$ have only been reported for very few chelating agents in the CRITICAL database (1). Even with these few chelating agents, the reported Mn^{III} speciation and the corresponding logK values are determined under highly acidic conditions ($\text{pH} < 1.0$), which cannot be applied to the circum-neutral pH range of natural waters. As a result, it is important to determine reliable logK values of $\text{Mn}^{\text{III}}\text{H}_x\text{L}_n(\text{aq})$ in the circum-neutral pH range.

6.2.2 Degradation of Dissolved Mn^{III} Complexes. Intramolecular electron transfer within dissolved Mn^{III} complexes is an important sink for dissolved Mn^{III} . Degradation of dissolved Mn^{III} complexes has been mostly focusing on a few carboxylate-based chelating agents, such as oxalate (2, 3), citrate and EDTA (4).

Phosphonate-based chelating agents are widely used as industrial, pharmaceutical and agricultural reagents and hence released into aquatic environments (5-7). Results from this thesis reveal that they are more efficient to promote Mn^{III} solubilization than their carboxylate analogs. Degradation of dissolved Mn^{III} complexes with phosphonate-based chelating agents, such as Mn^{III}-phosphonofornate complexes, however, has never been studied. More related research is worth doing in the future.

6.2.3 Reactions with Other Mn^{III,IV}-Containing Phases. Findings reported in Chapter 3 and 5 demonstrate that the characteristics of Mn (hydr)oxides (MnOOH versus MnO₂) play an important role in rates and pathways for reactions with organic substrates. Findings reported by Weaver and Hochella (8) illustrate the similarities and differences in Cr³⁺(aq) sorption and oxidation by seven different Mn (hydr)oxides. In natural aquatic environments, Mn (hydr)oxides are a group of minerals that exhibit diverse structures and multivalent (+II, +III, +IV) phases (9). More than thirty Mn (hydr)oxide minerals have been found (9). An examination of organic substrate reactivity with other Mn (hydr)oxides will expand our understanding of reactions in Mn-containing soils and sediments.

6.3 Literature Cited

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