CHAPTER 1

Introduction

1.1 Motivation

Mn (hydr)oxides occur in a wide variety of geological settings and often consist of a mixture of Mn^{III} and Mn^{IV}. In soils and sediments, $Mn^{III,IV}$ (hydr)oxides are among the strongest oxidants for the degradation of natural and synthetic organic compounds.

Because of the exceedingly large number of organic compounds found in aquatic environments, it is not feasible to study the reactions of every individual organic compound with $Mn^{III,IV}$ (hydr)oxides. An efficient approach is to develop structure-reactivity relationships for a small number of organic compounds with simple structures, which provides a basis for understanding pathways and rates for organic compounds with increasingly complex structures. As far as aromatic organic compounds are concerned, this approach has been applied for the oxidation of phenols[1], dihydroxybenzenes [2], anilines [3, 4] and, recently, more complex aromatic structures [5, 6]. Small oxygen-donor aliphatic compounds are of geological importance. Some of them have anthropogenic sources, used as industrial, pharmaceutical, and agricultural reagents. Reactions of these aliphatic organic compounds with $Mn^{III,IV}$ (hydr)oxides have been mostly focused on individual compounds [7-10] instead of a series of structurally related compounds. In this research, we aim to develop a deeper understanding of the molecular-level reaction mechanisms by investigating reactions of a wider range of structurally related small aliphatic organic compounds.

1.2 Oxygen-Donor Aliphatic Compounds

The oxygen donors of the aliphatic organic compounds employed in this study are from carboxylate, phosphonate, carbonyl, hydroxyl, or ester groups. A few compounds also possess nitrogen donor from the amine group. Inductive and resonance interactions among the functional groups just described will affect the ease of oxidation. Carboxylate and phosphonate groups are effective at coordinating metal ions in solution, facilitating adsorption *(11-13)*, and in some cases, assisting dissolution *(14, 15)*.

Some compounds are of considerable biogeochemical importance. Citric acid, oxalic acid, and malonic acid are biological chelating agents that are released by the roots of all vascular plants *(16-21)*; their concentrations near growing root tips may reach millimolar levels *(19, 22)*. Putative biogeochemical roles reflect their ability to complex metal ions. In homogeneous solutions, citric acid addition alleviates aluminum toxicity to biota by forming less toxic complexed species *(21, 23, 24)*. In heterogeneous systems, ligand-assisted dissolution by citrate yields dissolved metal ion-citrate complexes. This is undesirable in the case of toxic metal ions, but beneficial in the case of nutrient metal ions like iron *(14, 21)*. Ligand-assisted dissolution also solubilizes anionic mineral constituents. Hence, dissolution by citrate can release nutrient anions such as phosphate *(25-27)*. Release of the non-chelating agents pyruvic acid, lactic acid, glyoxylic acid, glycolic acid, and 2-hydroxyisobutyric acid by plant roots, bacteria, and fungi yields measurable concentrations in soil interstitial waters *(22, 28, 29)*.

A number of the compounds also have anthropogenic sources. For example, the herbicide glyphosate possesses three Lewis Base groups (amine, phosphonate, carboxylate) suitably placed for chelating Fe[III] *(30, 31)* and by inference other +III metal

ions. U.S. glyphosate use in 2001 was approx. 40 million kilograms *(32)*, more than any other agrochemical active ingredient. Fosamine is also a widely used herbicide *(33)*. Chelating agents used for hardness control (e.g. pyrophosphoric acid) and pharmaceuticals with chelating agent properties (e.g. antiviral compounds *(34, 35)* such as phosphonoformic acid and phosphonoacetic acid, and bone loss preventatives *(36)* such as the bis-diphosphonates fosamax and clodronate) are present in residential wastewaters, and can enter soils through the land application of biosolids and the use of septic tank/leachfield systems. β-diketone compounds have numerous practical applications both in industrial fields (e.g. used as fuel additives *(37)*) and medicinal fields (e.g. used in preparation of anticancer reagents *(38-41)*).
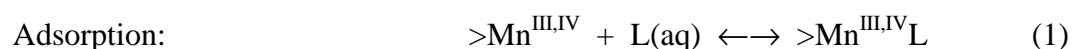
1.3 $Mn^{III,IV}$ (Hydr)oxides and Dissolved Mn^{III}

1.3.1 $Mn^{III,IV}$ (Hydr)oxides. The overall abundance of manganese in the earth's crust is only one-fiftieth that of iron *(42)*. $Mn^{III,IV}$ (hydr)oxides, like Fe^{III} (hydr)oxides, are much less soluble than (hydr)oxides in the +II oxidation state. Mn^{II} diffusing out of reducing zones and into O_2-containing zones becomes oxidized, causing localized accumulation of Mn^{III}- and Mn^{IV}-containing (hydr)oxide solids *(43, 44)*. Relative amounts of Mn^{III} and Mn^{IV} in such solids depend upon conditions present during their formation, and subsequent aging and chemical reaction. Natural samples invariably contain a mixture of the two oxidation states. $Mn^{III,IV}$ (hydr)oxides are stronger oxidants than Fe^{III} (hydr)oxides, which explains their importance as oxidants of inorganic species *(45, 46)* and organic compounds *(1, 2, 8, 9, 15, 47-50)*, including chelating agents *(8, 9, 15, 50)*.
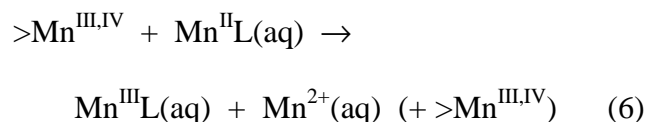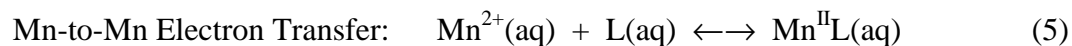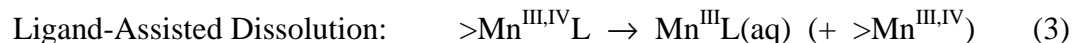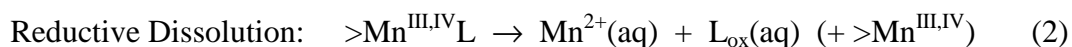
1.3.2 Dissolved Mn^{III}. In natural environments, the oxidation of dissolved Mn^{II}-chelate complexes and the ligand-assisted dissolution of Mn^{III}-containing solids serve as sources for dissolved Mn^{III}. Microbial-catalyzed Mn^{II} oxidation to Mn^{IV} via soluble or enzyme complexed Mn^{III} intermediates has been observed in diverse groups of bacteria and fungi *(51-54)*. Abiotic oxidation of Mn^{II}-NTMP(nitrilotrimethylenephosphonate) complexes by O_2 occurring via the formation of Mn^{III} intermediates has been proposed *(55)*. The release of dissolved Mn^{III} via ligand-assisted dissolution has been observed for reaction of pyrophosphate and citrate with a Mn^{III} dominant MnOOH(feitknechtite)/Mn_3O_4(hausmannite) mixture *(15)*.

There is much recent interest regarding the possible role of dissolved Mn^{III} complexes as powerful and reactive oxidants in surface waters, soils and sediments *(54, 56-58)*. The occurrence of dissolved Mn^{III} in soil interstitial waters, even in a transient existence, has important environmental implications. Dissolved Mn^{III} can cause the breakdown of anthropogenic chemicals, such as EDTA *(59)* and NTMP *(55)*. Dissolved Mn^{III} complexes generated by fungi are responsible for lignin degradation *(60)*. Dissolved Mn^{III} can affect biological functions. It is proposed that the high toxicity of dissolved Mn^{III} is related to its high oxidative reactivity *(61)*. Dissolved Mn^{III} competes with Fe^{III} for siderophore binding, with effects iron bioavailability *(62)*.

1.4 Mechanistic Foundation

Whenever an organic substrate is brought into contact with a Mn^{III,IV} (hydr)oxide phase, the following reaction pathways are potentially possible:

Adsorption: $\qquad$ >Mn^{III,IV} + L(aq) $\longleftrightarrow$ >Mn^{III,IV}L $\qquad$ (1)

Reductive Dissolution: $>Mn^{III,IV}L \rightarrow Mn^{2+}(aq) + L_{ox}(aq)$ $(+ >Mn^{III,IV})$ (2)

Ligand-Assisted Dissolution: $>Mn^{III,IV}L \rightarrow Mn^{III}L(aq)$ $(+ >Mn^{III,IV})$ (3)

Intramolecular Electron Transfer: $Mn^{III}L(aq) \rightarrow Mn^{2+}(aq) + L_{ox}(aq)$ (4)

Mn-to-Mn Electron Transfer: $Mn^{2+}(aq) + L(aq) \longleftrightarrow Mn^{II}L(aq)$ (5)

$$>Mn^{III,IV} + Mn^{II}L(aq) \rightarrow$$

$$Mn^{III}L(aq) + Mn^{2+}(aq) \ (+ >Mn^{III,IV}) \quad (6)$$

These pathway descriptions ignore proton levels and detailed species descriptions (e.g. 1:1 versus 1:2 complexes in solution). L denotes the organic substrate and L_{ox} denotes its oxidized product(s). $>Mn^{III,IV}$ denotes unoccupied surface sites, $>Mn^{III,IV}L$ denotes the organic substrate-surface site complex, and $Mn^{III}L(aq)$ denotes dissolved Mn^{III} complexes. Detachment of a surface-bound Mn atom may uncover new reactive sites (denoted in parentheses).

The energetics and kinetics of each pathway depend on adsorption, complexant, and reductant properties of the organic structures, the identity of the Mn (hydr)oxide surfaces, and the conditions of the environmental media (pH, major ion composition, and so on).

Adsorption, i.e. the formation of a precursor complex, is the first step to any surface chemical reaction *(63)*. The exact nature of this precursor complex is not at present known. Precursor complex formation may be outer-sphere or inner-sphere. Inner sphere complexes may be either monodentate or bidentate (coordination via one or both Lewis base groups). Bidentate complexes may be mononuclear (involving only one surface-bound $Mn^{III,IV}$ atom) or binuclear (organic substrate may bridge between

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neighboring $Mn^{III,IV}$ atoms). Two competitive parallel processes are possible subsequent to the adsorption step: reductive dissolution and ligand assisted dissolution.

In reductive dissolution, electron transfer from adsorbed organic substrate to surface-bound $Mn^{III,IV}$ atoms takes place, followed by release of Mn^{II} and oxidized organic substrate. Overall rates of $Mn^{II}(aq)$ production are proportional to the precursor complex formed during the adsorption step. A few points need to be made. Electron transfer may take place via an inner-sphere precursor complex, an outer-sphere precursor complex, or both, depending upon the identity of the reactants and prevalent conditions. The precursor complex may be a minor surface species, i.e., its stoichiometry and bonding arrangements may be different from the predominant form of the adsorbed organic substrate. As two reactions in series, either the adsorption step (Equation 1) or the electron transfer step (Equation 3) may be rate-limiting *(1)*. Regardless of which step is rate-limiting, Mn^{II} production and oxidized organic product (L_{ox}) production are proportional to the precursor complex concentration:

$$\frac{dMn^{II}(aq)}{dt} = w\frac{d[L_{ox}]}{dt} = k_R[>Mn^{III,IV}L] \tag{7}$$

w is a stoichiometric coefficient that accounts for reducing equivalents (per mole of organic substrate oxidized) and oxidizing equivalents (per mole of Mn reduced). A low extent of adsorption may be compensated for by a high rate of electron transfer within the adsorbed species.

In ligand-assisted dissolution, adsorbed chelating agents detach surface-bound Mn^{III} atoms, yielding Mn^{III}-chelating agent complexes in solution. Mn^{IV} has extremely low solubility and hence is not subject to ligand-assisted dissolution. It is believed that dissolution occurs via multidentate mononuclear surface complexes *(64, 65)*, where

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inner-sphere chelating agent adsorption polarizes metal ion-hydroxo/oxo bonds within the solid, causing them to break *(66)*. Ligand-assisted dissolution reactions are generally believed to be proportional to the extent of chelating agent adsorption *(67)*. Using $Mn^{III}(aq)$ to denote the total dissolved Mn^{III} concentration, we can write:

$$\frac{dMn^{III}(aq)}{dt} = k_L[>Mn^{III,IV}L] \tag{8}$$

Subsequent intramolecular electron transfer (Reaction 4) within the dissolved Mn^{III} complexes would ultimately yield the same products as reductive dissolution, i.e. Mn^{II} and oxidized organic substrate. Hence, if appreciable dissolved Mn^{III} is to be observed, rate constants for Reactions 1 and 2 must be large relative to rate constants for Reactions 3 and 4.

Reactions 5 and 6, if significant, will yield an autocatalytic time course plot, i.e. an S-shaped curve with induction period appearance with respect to parent compound loss and product formation. Godtfredsen and Stone *(68)* have monitored the production of dissolved Mn (presumed to be Mn^{II}) during reaction of citric acid with synthetic MnO_2(s, birnessite), and have observed an induction period that decreased in duration as the citrate concentration was increased. Autocatalysis occurs when the product of a reaction serves as a catalyst for the reaction.

1.5 Research Goals and Thesis Outline

The goal of this research is to learn how reductant, complexant, and adsorptive properties of aliphatic small organic compounds determine pathways and rates of reaction with Mn (hydr)oxides. Two synthetic Mn (hydr)oxides, MnO_2(birnessite), which contains both Mn^{III} and Mn^{IV}, and MnOOH(manganite), which consists solely of Mn^{III}, are selected for

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the study. Nearly three dozen aliphatic small organic compounds possessing oxygen-donor from carboxylate, phosphonate, carbonyl, hydroxyl, or ester functionalities in various combinations are selected for the study. Nitrogen-donor from amine functionalities are included in a few compounds. An inorganic compound, pyrophosphate, is also included in the study.

To fulfill our research goal, the following approaches are applied. *First,* provide an understanding of the connection between aliphatic organic compound structure and reactivity, by investigating a wider range of organic substrates than addressed in past studies. *Second*, analyze reaction products using capillary electrophoresis, which include monitoring dissolved Mn^{III} formation and organic oxidation products formation. *Third*, study how environmental factors, such as pH, oxide loading, organic concentration, and the presence of other metal ions and anions affect reaction rate. In doing so, we aim to improve our understanding of the molecular-level mechanisms for organic-Mn (hydr)oxide reactions. The structure-reactivity relationships developed for the organic compounds with simple structures should enable us to predict rates and pathways for organic compounds with increasingly complex structures.

Chapter 2 examines electron transfer, complex formation, and autocatalytic feedback for the citric acid-MnO_2 reaction. Citric acid oxidation products are identified, and the effects of pH and increasing citric acid concentrations are explored. Additive effects (Mn^{II}, Zn^{II}, orthophosphate, and pyrophosphate) help us draw connections between solution speciation, surface speciation, and reaction rates. Dissolved Mn^{III} concentrations during reaction are quantified. S-shaped plots for citric acid loss, Mn^{II} formation, and citric acid oxidation-product formation as a function of time indicate that

autocatalysis takes place. Some details regarding the molecular-level mechanism of the autocatalytic cycle are clarified, for the first time for a manganese-based dynamic redox system.

Chapter 3 is a study of possible pathways for reactions of thirteen organic compounds with two different Mn (hydr)oxides, MnO_2(birnessite) and MnOOH(manganite). Carboxylate and phosphonate groups are effective at coordinating metal ions in solution, facilitating adsorption *(11-13)*, and in some cases, assisting dissolution *(14, 15)*. Aldehyde oxygens, ketone oxygens, and amide nitrogens are exceedingly weak Lewis Bases, and hence contribute little to adsorption. As we shall see, inductive and resonance interactions among the above-mentioned functional groups affect the ease of oxidation.

Studies in Chapter 4 aim to understand and predict rates of electron transfer for reactions between organic compounds and MnO_2(birnessite) Organic compounds that of interest in this chapter possess a methylene group between the proximal carbonyl functions. The resonance afforded by proximal carbonyl functions is no longer possible, but keto-enol formation and the acidity of the methylene C-H bond become important considerations for electron transfer.

In Chapter 5, we address dissolved Mn^{III} arising from the ligand-assisted dissolution of Mn^{III}-containing solids. Attention is focused on a group of chelating agents most likely to resist oxidation by coordinated Mn^{III}. To develop chelating agent structure-reactivity relationships, eleven chelating agents are selected for this study. All of these chelating agents possess O donors from carboxylate and/or phosphonate (phosphate) groups. Four of the eleven also possess an N donor from an amine group.

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The issolution behavior of two Mn^{III}-containing solids, MnO$_2$(birnessite) versus MnOOH(manganite), is compared.

Chapter 6 summarizes important findings of this work, and provides the author's viewpoint on future directions pertaining to reactions between Mn^{III,IV} (hydr)oxides and organic substrates.

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