

Changes in metal oxidation state and speciation can have significant health and ecotoxicological consequences. A few examples are provided below:

- i)** Mining and industrial activities have contaminated soils and sediments throughout the world, including Baltimore Harbor. Reactions of molecular oxygen (O_2) with sparingly soluble $Cr^{III}(OH)_3(s)$ may generate the far more soluble and transportable chromate ion ($HCr^{VI}O_4^-$, $Cr^{VI}O_4^{2-}$).
- ii)** Combustion of gasoline containing the anti-knocking agent MMT (methylcyclopentadienyl manganese(I) tricarbonyl) forms a fine aerosol consisting of $Mn^{III,IV}$ (hydr)oxide solids. When inhaled, biofluids convert the oxidized manganese to soluble Mn^{II} . Within the nose, subsequent translocation of Mn^{II} along olfactory neurons leads to elevated manganese in a region of the brain called the olfactory bulb (1). A Parkinson's-like condition termed manganism can result.
- iii)** Water supply plants maintain a disinfectant residual to ensure the deactivation of pathogenic bacteria. Recently it has been discovered that switching from free chlorine ($HOCl^0, OCl^-$) to chloramine residuals raises dissolved lead concentrations (2). Higher lead levels in drinking water, in turn, may elicit adverse neurological effects, especially in children. Lytle and Schock (3) have determined that free chlorine is capable of oxidizing $Pb^{2+}(aq)$ to $Pb^{IV}O_2(s)$, but that chloramines cannot. The re-reduction of $Pb^{IV}O_2(s)$ to $Pb^{2+}(aq)$ by dissolved organic compounds in drinking water must also be contended with.

Substantive understanding of these environmentally significant redox reactions begins with carefully and creative experimentation. Governing concepts for addressing metal-to-metal electron transfer were in fact developed from experiments performed with simple metal ion species in aqueous solution (4). Examples **i-iii** pose new challenges, most notably mineral surface-bound metal reactants and products. With a few notable exceptions (e.g. Ref. 5,6), environmental chemists have sought primarily phenomenological information, i.e. rate constants and equilibrium constraints.

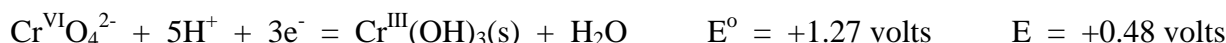
We seek to develop models to predict reaction rates and speciation profiles of redox-active metals. Our reasons are entirely practical. Metal speciation in surface waters, soils, sediments, and biofluids and accompanying toxicity profiles are often quite complex, given the diversity of dissolved inorganic (e.g. hydroxide ion, carbonate, phosphate, silicate, borate), dissolved organic (e.g. carboxylate, hydroxyl, amine, mercapto), and particulate-bound Lewis Bases that can engage in coordination reactions. Even in the laboratory, it is often necessary to consider contributions to reaction from a number of different reactant species (7). We need to be able to alert regulators to scenarios where problematic metal species may be generated, and the ability to steer engineers and decision-makers away from technologies and management practices that lead to adverse environmental consequences.

Prof. Stone has more than 25 years experience investigating pathways and rates of reactions in water and at mineral/water interfaces. His laboratory has made significant advances in employing capillary electrophoresis to discern oxidation states and modes of metal ion coordination in aqueous media (8). Prof. Roth is experienced in applying reaction rate theories and isotope fractionation techniques in mechanistic inorganic chemistry (9). The Dreyfus Fellow, mentored by these PIs, will benefit from the facilities, instrumentation, and scholarly climate of both research groups. As the mainstay for collaboration, the Dreyfus Fellow will be in a unique position to advance environmental science, by interfacing with Chemistry, Environmental Science, and Environmental Engineering communities. This is the basis for building a productive and successful academic career.

The structure and properties of the transition state are key elements to consider in building successful quantitative models for electron transfer. Speciation information, i.e. stoichiometric relationships between metal ion and ligand, protonation level, and mode of coordination, helps us set the stage for

elucidating the rate-limiting step. For substitution-labile metal ions, conventional spectroscopic techniques will be used to evaluate the thermodynamic properties necessary to calculate the equilibrium concentrations of reactants prior to electron transfer (10). For substitution-inert metal ions, capillary electrophoresis can distinguish among candidate species at μM levels. With $\text{Co}^{\text{III}}(\text{IDA})_3^-$, we can distinguish between the *u-fac*-, *mer*-, and *s-fac*-diastereomers, and with $(\text{Co}^{\text{III}})_2(\text{NTA})_2$, we can distinguish between $(\mu\text{-OH})$ - and $(\mu\text{-OH})_2$ -bridged species (8). In isotope experiments, we envision replacing one atom within the transition state (e.g. ^{16}O) with a heavier one (^{18}O) thus effecting changes in vibrational structure. Measured isotope effects then provide clues regarding electron transfer mechanisms. Illustrative research areas open to the Dreyfus Fellow include:

i) Cr^{III} Oxidations by Molecular Oxygen (O_2) and Other Oxidants - Reduction potentials (E) have been calculated at pH 7.0, using 0.21 atm $\text{O}_2(\text{g})$ and 10 μM $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$:



Two pathways potentially exist for the oxidation of $\text{Cr}^{\text{III}}(\text{OH})_3(\text{s})$ by O_2 . In an outer-sphere mechanism, the reactants interact only through very weak electronic coupling in the transition state; the reactions are governed by the reduction potentials of the separated reactants. In an inner-sphere mechanism, electron transfer occurs at the same time a new bond is formed between the reactants; the reactions are driven by the strength of the incipient bond between the oxidized metal ion (Cr^{IV}) and reduced dioxygen ($\text{O}_2^{\bullet-}$ or O_2^{2-}) products. For both outer-sphere and inner-sphere mechanisms, establishing the thermodynamics of the primary electron transfer event is the key to assessing the rate of electron transfer. While this has been met with modest success in solution, its predictive potential has not been established for heterogeneous processes at mineral/water interfaces, where electron transfer may be coupled to metal ion solubilization (11,12).

The complexity of this problem may be somewhat simplified by considering that the net oxidation of $\text{Cr}^{\text{III}}(\text{OH})_3(\text{s})$ to $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ by O_2 yields a ΔG° equal to $0.92 \text{ kcal mol}^{-1}$, on the basis of reported redox potentials (see above). The initial electron transfer step is quite endoergic, however, with ΔG° equal to $+32.3 \text{ kcal mol}^{-1}$. Thus, reaction will not occur at an appreciable rate ($> 10^{-11} \text{ M}^{-1}\text{s}^{-1}$) by an outer sphere mechanism. If we ignore for the moment the intrinsic contribution, referred to as the reorganization energy, then we can calculate that a strong bond between the oxidized and reduced products, worth upwards of 30 kcal mol^{-1} , would be necessary for electron transfer via an inner-sphere mechanism (13).

What do we know about the reorganization energy? For outer-sphere electron transfer to O_2 treated adiabatically (14), the reorganization energy for the self-exchange reaction is quite large, e.g. 60 kcal mol^{-1} ; this is due largely to outer-sphere solvation changes (45 kcal mol^{-1}) as well as changes in O-O bonding (15 kcal mol^{-1}). Thus, in the context of Marcus' Electron Transfer Cross Relation (15), any outer-sphere electron transfer process involving O_2 or $\text{O}_2^{\bullet-}$ will have an intrinsic barrier of at least 30 kcal mol^{-1} from O_2 plus an additional contribution from the metal. Inner sphere processes have smaller apparent reorganization energies due to strong electronic coupling effects. While this smaller reorganization energy, combined with additional driving force coming from bond formation, is likely to result in greater rates, a predictive formalism for describing these processes has not yet been established (16).

Laboratory experiments to date have indicated that the direct oxidation of $\text{Cr}^{\text{III}}(\text{OH})_3(\text{s})$ by O_2 under conditions found in surface waters, soils, and sediments, is imperceptibly slow (17). Ligand-assisted dissolution of $\text{Cr}^{\text{III}}(\text{OH})_3(\text{s})$ by the synthetic chelating agents IDA, NTA, TMDTA, EDTA, and CDTA, and by the naturally-occurring chelating agent citrate has recently been demonstrated (18). Whether or not the resulting Cr^{III} -chelating agent complexes in solution are oxidized by O_2 has not yet been explored. Model building will involve consideration of the strengths that may facilitate inner-sphere electron transfer, e.g. those involving Cr^{IV} (19,20).

ii) Reactions of Manganese (Hydr)oxides by Organic Reductants - Polysaccharide-based mucus lines much of the respiratory tract and gastrointestinal tract, a last barrier to inhaled and ingested particulate matter. Plants, fungi, and many bacteria also maintain a layer of polysaccharide-rich exopolymer that mediates reactions with soil particulate matter. Manganese (hydr)oxides are strong sorbents for contaminant metal ions such as cobalt, nickel, and lead (21). Whenever the reduction of manganese (hydr)oxides to $Mn^{2+}(aq)$ takes place, associated contaminant metal ions are also released. At trace levels, dissolved manganese is a nutrient. At moderate to high concentrations, the facile nature of manganese oxidation/reduction reactions makes it an undesirable catalyst for autoxidation and free radical generation. The ability to quantitatively predict rates of manganese (hydr)oxide reduction would boost our understanding of its health effects and the role it plays in the environments.

Naturally-occurring and anthropogenic (e.g. from MMT combustion) manganese (hydr)oxides invariably contain multiple oxidation states of manganese. Mn^{III} possesses a d^4 configuration which yields Jahn-Teller distortion from pure octahedral geometry. Ligand exchange reactions of Mn^{III} in aqueous solution are known to be fast relative to those of other +III metal ions. Mn^{IV} possesses a higher charge and smaller radius, and its d^3 configuration yields high crystal field stabilization energy, $6/5\Delta_o$. Ligand exchange reactions of Mn^{IV} should therefore be exceptionally slow.

In a recent publication (22), we compared rates of reductive dissolution of a $MnOOH$ (manganite) preparation consisting solely of Mn^{III} , with those of a MnO_2 (birnessite) preparation consisting of 22 % Mn^{III} and 78 % Mn^{IV} . Once differences in surface area loadings are accounted for, oxalic acid, pyruvic acid, and 2,3-butanedione reduced both phases at comparable rates. Glyoxylic acid reduced MnO_2 (birnessite) more rapidly, while oxamic acid, lactic acid, and dimethyl oxalate reduced $MnOOH$ (manganite) more rapidly. We have recently included a MnO_2 (pyrolusite) phase consisting of 98 % Mn^{IV} (23) in our investigations.

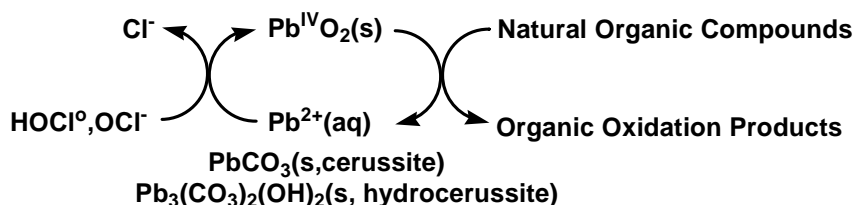
Overall rates of reductive dissolution reflect three reactions in series: (a) adsorption of the organic reductant; (b) electron transfer; and (c) release of $Mn^{2+}(aq)$ and oxidized organic into the surrounding medium. The only way to isolate the electron transfer step is to independently account for precursor and successor adsorption/desorption reactions. While Mn^{II} adsorption/desorption is readily accounted for (24) we have only recently developed the ability to quantify extents of organic compound adsorption on manganese (hydr)oxides, e.g. with the alkene carboxylic acids crotonic acid, 3-pentenoic acid, fumaric acid, and itaconic acid. Using this approach, we are opening the way towards distinguishing reactions of Mn^{III} and Mn^{IV} on a much more quantitative level.

iii) Oxidation and Reduction Reactions Influencing Lead Speciation - Reduction potentials (E) have been calculated for pH 7.0, 1.0 mM Cl^- , 0.21 atm $O_2(g)$, and 10 μM for other solutes:

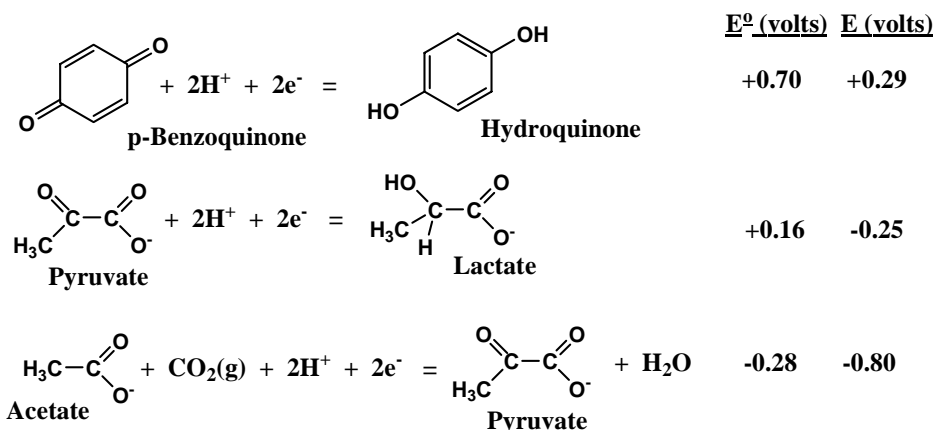


While $Pb^{2+}(aq)$ oxidation by O_2 under the conditions selected is nearly equiergic, ΔG for oxidation by both hypochlorous acid and monochloramine is strongly favorable. What's needed is energetic information about the initial electron transfer step. Lead in the +III oxidation state has been observed during the Pb^{II}/Pb^{IV} interconversion (25), but its' properties and speciation are poorly characterized. In addition, information regarding the immediate products of hypochlorous acid and monochloramine reduction are needed.

Drinking water contains both an oxidant residual and dissolved natural organic compounds, which serve as reductants. Concurrent Pb^{2+} oxidation and $Pb^{IV}O_2(s)$ reduction is likely:



As the half-reactions below indicate, many of the moieties found within natural organic matter yield favorable ΔG for the reduction of $\text{Pb}^{\text{IV}}\text{O}_2(\text{s})$. To build quantitative models for predicting reaction rates, we again return to the initial electron transfer step and the nature of the transition state.



$\text{Pb}^{\text{IV}}\text{O}_2(\text{s})$ as an oxidant provides an interesting comparison with the $\text{Mn}^{\text{III,IV}}$ (hydr)oxides discussed earlier. Extents of organic reductant adsorption and selectivities for particular Lewis Base groups and structures are likely to be different. Adsorption is a bond formation process. Whether adsorption can serve as the basis for an energetically favorable inner sphere electron transfer process is an interesting point of discussion. Pb^{IV} reduction involves a 6s orbital, while Mn^{III} and Mn^{IV} reductions involve 3d orbitals.

All of the research projects address prominent issues in the environmental sciences, as well as fundamental principles in the oxidation/reduction chemistry of mineral/water interfaces. To what extent does attachment of a metal reactant at a mineral/water interface influence the outcome of a reaction? Are inner-sphere reactions of mineral surfaces with molecular oxygen invariably favored over the outer-sphere processes? These are but two of the many avenues of research that the Dreyfus Fellow can pursue to make a major impact on environmental oxidation chemistry at the outset of his or her academic career.

References

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