

# Manganese(II) Oxidation and Mn(IV) Reduction in the Environment—Two One-Electron Transfer Steps Versus a Single Two-Electron Step

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The chemistry of electron transfer processes are reviewed using a knowledge of orbital properties and available experimental data.  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  oxidation with  $\text{O}_2$  are discussed and compared.  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  oxidation by  $\text{O}_2$  occurs via an inner sphere process after complexation with inorganic (e.g.;  $\text{OH}^-$ , increase pH) or organic ligands that replace water; whereas  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  at circumneutral pH occurs via an outer sphere mechanism. An outer sphere electron transfer process is symmetry forbidden for  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  based on analysis of the frontier molecular orbitals of the reactants. At higher pH, an inner-sphere process is also available for  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  oxidation as hydroxide and organic ligands replace water and bind Fe(II). The bonding of  $\text{O}_2$  to  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  in the precursor complex results in faster electron transfer for the inner sphere process than occurs in the outer-sphere process which occurs at lower pH. The bonding between the reactants in an inner sphere process is likely “end on” bonding for  $\text{O}_2$  to the metal with a bent M-O-O bond angle. Side-on bonding for  $\text{O}_2$  to the metal is possible and could lead to two-electron transfers from Mn(II) compounds but requires stabilization of the Mn-O<sub>2</sub> bonding with organic ligands such as porphyrins. This would occur as an oxidative addition type reaction where the Mn(II) would give up two electrons to two different orbitals of  $\text{O}_2$  and increase its local coordination environment. For two-electron transfers during Mn(II) compound oxidation, multinuclear Mn complexes are required. One-electron transfers are more likely to occur during the oxidation of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  by  $\text{O}_2$  and the reduction of  $\text{MnO}_2$  than two-electron transfers. Both soluble and solid phase Mn(III) species form as intermediates or stable species. From a microbiological viewpoint, Mn(III) compounds are ideal reagents as Mn(III) can act as an electron acceptor forming soluble  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  or as an electron donor forming insoluble  $\text{MnO}_2$ . One-electron transfers are predicted based on the different spatial characteristics of the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals. The  $d_{z^2}$  orbital has electron density on all three Cartesian coordinate axes (primarily the z axis) but the  $d_{x^2-y^2}$  orbital has electron density only in the xy plane. Adding or losing two electrons simultaneously is not as likely a process but possible.

However, O atom transfer can readily account for a two-electron transfer in  $\text{MnO}_2$  reduction. Better knowledge of the structures of Mn intermediates and of the types of reductant appears to be key for describing whether two one-electron transfer steps or a single two-electron step may be operative during  $\text{MnO}_2$  reduction.

**Keywords** aqueous manganese (III), manganese(II) oxidation, manganese(III), Mn(IV) reduction, one-electron transfer, two-electron transfer

## INTRODUCTION

The oxidation of aqueous  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  has received much attention over the years and is the subject of considerable interest in environmental chemistry and microbiology (Stumm and Morgan 1996; Morgan 2005). In this paper, I review the different reactivity of aqueous  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  by  $\text{O}_2$  using an analysis of their molecular orbitals; in particular, the metal d orbitals which accept or donate electrons during oxidation and reduction. Both metal ions and  $\text{O}_2$  are formally Lewis acids as they both accept electrons; metals accept two electrons from each ligand binding to them whereas  $\text{O}_2$  accepts electrons during redox processes. This chemical behavior suggests that reactivity may be slow if inner-sphere processes are important. As shown below,  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  oxidation can occur via outer-sphere processes, whereas  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  oxidation must occur via inner-sphere processes. For both of these metal oxidation reactions to be facile, it is necessary to enhance the metal ion's ability to lose an electron (become a reducing agent or a “base”). This can be accomplished with the appropriate ligating atoms. Aqueous  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  are both labile cations with  $d^6$  ( $t_{2g}^4 e_g^2$ ) and  $d^5$  ( $t_{2g}^3 e_g^2$ ) electron configurations, respectively. This lability allows for easy interchange of ligands. Also, five- and six-coordinate geometries for these metals are favored over the four-coordinate (tetrahedral) geometry in order to enhance metal basicity (and metal reducing power) and to stabilize the higher oxidation state which results on oxidation of these metals.  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  can only undergo a one-electron loss to Fe(III) species but  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  can undergo either one-electron or two-electron loss to Mn(III) and Mn(IV) species, respectively. Mn(III) solid (oxy)hydroxide phases are well known during the

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chemical oxidation of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  (e.g., Murray et al. 1985). A question arises whether Mn(III) can be soluble in environmental processes as is known in purely chemical processes (e.g., Cotton et al. 1999) and, if so, is it stable or does it disproportionate.

The oxidation of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  occurs above pH 1 (Stumm and Morgan 1996)—the reaction is slow at acid pH and faster at neutral and basic pH. However, the oxidation of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  is exceedingly slow or nonexistent until pH > 9 (Diem and Stumm 1984; Stumm and Morgan 1996). A key feature of these reactions is the effect that  $\text{OH}^-$  and other O atom ligands have on enhancing metal basicity or metal reducing power and on stabilizing the higher oxidation states of the metals formed during the oxidation. However, the pathways for the iron and manganese reactions are discretely different from each other, which can be shown from an analysis of their frontier molecular orbitals.

## RESULTS AND DISCUSSION

### $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ Oxidation—A Frontier Molecular Orbital Analysis

Background material for this work can be found in a variety of inorganic chemistry textbooks (e.g., Pearson 1976; Shriver et al. 1994; Cotton et al. 1999) and papers (e.g., Luther, 1987, 1990) but the essentials are provided throughout the discussion.

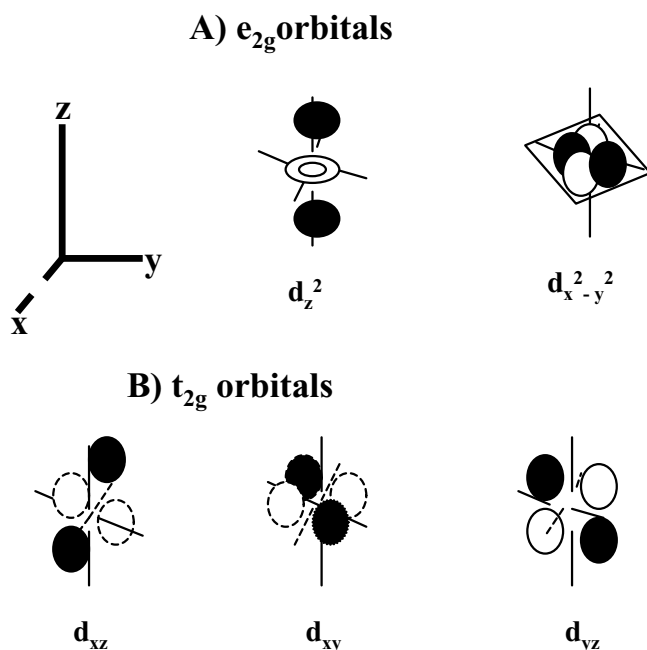


FIG. 1. The shapes of the d orbitals. The  $e_g$  orbitals (A) in octahedral symmetry have  $\sigma$  bonding and antibonding character because they have electron density on the bond axes (the Cartesian axes). The  $t_{2g}$  orbitals (B) in octahedral symmetry have  $\pi$  character because they have electron density in between the bond axes (the Cartesian axes). The color of the orbital lobes indicate + (black) or - (white) character for the original wavefunction. Lobes of similar sign (color) can overlap to have bonding or to have electron transfer.

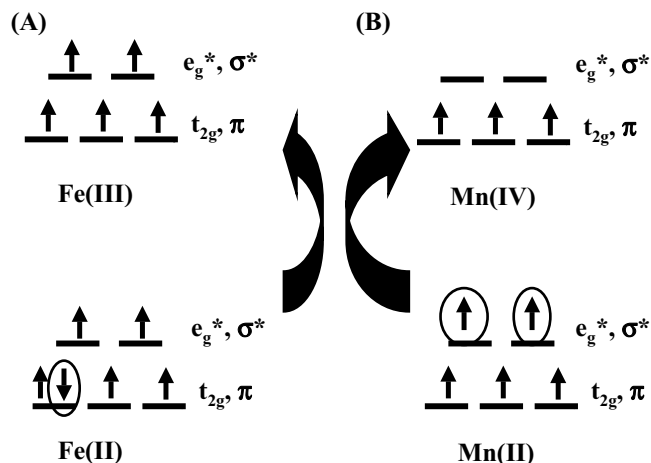


FIG. 2. Orbital energy diagrams for the Fe(II, III) (A) and Mn(III, IV) (B) oxidation states in octahedral geometry. Large arrows indicate the loss of electrons (circled) in each set.

Figure 1 shows the metal d orbitals (hydrogen-like for simplicity) and Figure 2 shows their electron occupancy for octahedral  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  ( $d^6 - 6$  d electrons),  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  ( $d^5 - 5$  d electrons) and for octahedral compounds of Fe(III) and Mn(IV). The 5 d orbitals split into a set of  $t_{2g}$  orbitals from the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals which have pi ( $\pi$ ) character and a set of  $e_g^*$  orbitals from the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals which have sigma ( $\sigma$ ) character. The \* indicates antibonding orbitals. Formally the  $t_{2g}$  orbitals have nonbonding character in octahedral geometry. But, with ligating atoms that have extra lone pairs of electrons such as oxygen ( $\pi$  donor ligands), the  $t_{2g}$  orbitals can accept electrons. With ligands that have empty orbitals such as dioxygen, olefins and organic S and P compounds ( $\pi$  acceptor ligands), the empty orbitals can accept electron density from the  $t_{2g}$  orbitals. In other geometries, the d orbitals split into different energy configurations and have different bonding characteristics.

The circles and arrows in Figure 2 indicate that loss of an electron from  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  comes from a  $t_{2g}$  orbital whereas loss of electrons from  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  come from  $e_g^*$  orbitals. Because the  $t_{2g}$  and  $e_g^*$  orbitals have different symmetry, the mechanisms for electron loss for  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  should be different. In addition, the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals occupy different regions of space. The  $d_{z^2}$  orbital has electron density on all three Cartesian coordinate axes (primarily the z axis) but the  $d_{x^2-y^2}$  orbital has electron density only in the xy plane. Thus, losing two electrons simultaneously for  $\text{Mn}^{2+}$  is not expected.

### $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ and $\text{O}_2$

Figure 3 (right side) shows that the highest occupied molecular orbitals (HOMO or electron donor orbitals) and lowest unoccupied molecular orbitals (LUMO or electron acceptor orbitals) for  $\text{O}_2$  are the same orbitals as these are singly occupied molecular orbitals (SOMO). Thus  $\text{O}_2$  cannot accept two electrons into the same molecular orbital as this is a violation of the

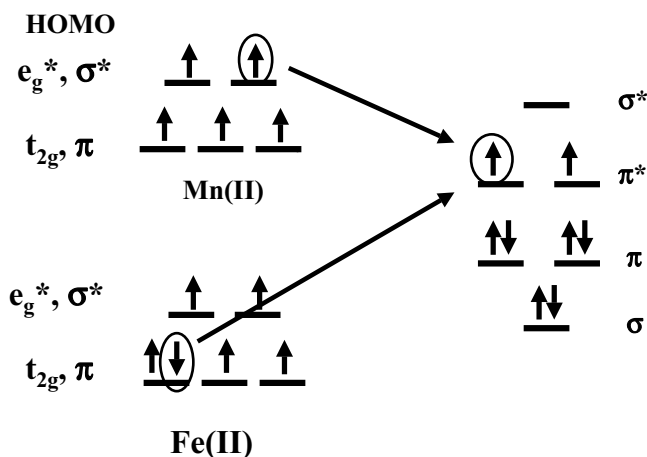


FIG. 3. Orbital energy diagrams showing the loss of electrons from  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  to  $\text{O}_2$  (right orbital diagram). Note the  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  orbital has the same symmetry ( $\pi$ ) as  $\text{O}_2$  whereas  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  has a mismatch. The  $\text{O}_2$  singly occupied molecular orbitals have an energy of  $-0.44$  eV and are a good electron acceptor.

Pauli Exclusion Principle. This orbital population for  $\text{O}_2$  also makes  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  oxidation as a two-electron transfer process difficult. For both  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  oxidation, an electron must be lost and be transferred to the  $\pi^*$  orbital(s) of  $\text{O}_2$ . For outer-sphere electron transfer processes where the reactants do not form bonds, electron transfer is symmetry allowed when

both reactant orbitals are of the same type (Pearson 1976; Shriver et al. 1994) as is the case for the HOMO of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and the LUMO of  $\text{O}_2$  (both are  $\pi$  symmetry). Because the HOMO of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  is  $\sigma$  symmetry, an outer sphere reaction process with  $\text{O}_2$  is symmetry forbidden. Figure 4 shows a schematic diagram for the reaction of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  with  $\text{O}_2$ . The top portion of the figure shows the orbitals of one O atom from water or hydroxide ion (on the left) binding directly to  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  but the dashed line indicates that there is no bond formed between  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and  $\text{O}_2$ . However, the  $d_{xy}$  orbital of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  and the  $\pi_y^*$  orbital of  $\text{O}_2$  are properly aligned in space for electron transfer and oxidation of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ .

This simple orbital picture fits the pH data that is described in Stumm and Morgan (1996). The rate law for  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  oxidation by  $\text{O}_2$  is in equation 1 and is consistent with an

$$\frac{-d[\text{Fe(II)}]}{dt} = k[\text{Fe(II)}][\text{OH}^-]^2 p\text{O}_2 \quad [1]$$

outer sphere electron process. As pH increases so does oxidation and the amount of hydroxide bound to  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ . When hydroxide ion, a  $\pi$  donor ligand, is bound to  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  instead of water, there is more electron donation through the  $p_y$  (and  $p_x$ ) like orbital of hydroxide ion to the  $d_{xy}$  (and  $d_{yz}$ ) orbital of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  because of the excess negative charge. This facilitates the loss of an electron from  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  to  $\text{O}_2$ . In essence the  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  is made to act more as a base by hydroxide ion. The

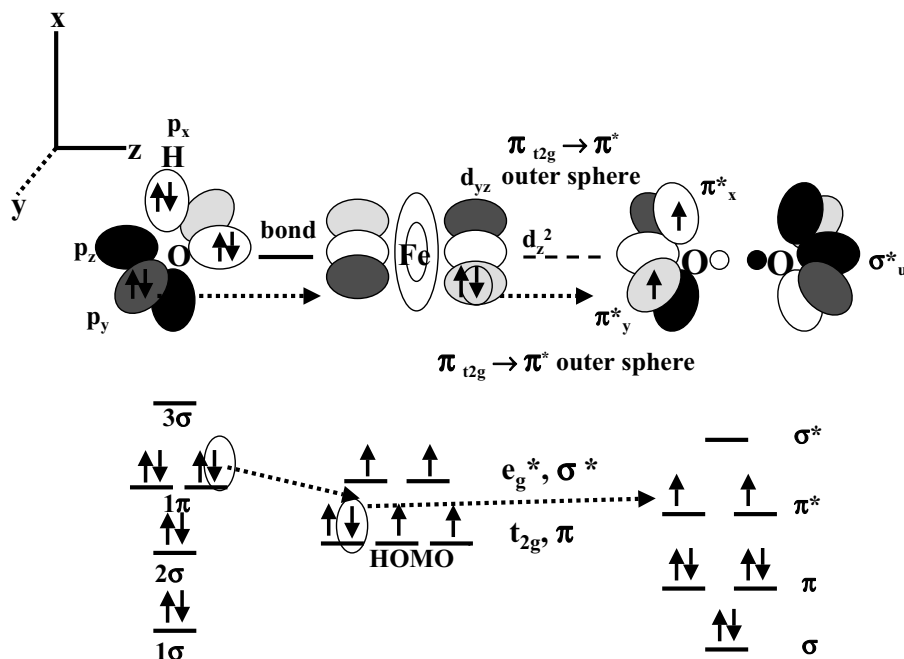


FIG. 4. Molecular orbital diagram (top) demonstrates the electron transfer process during the metal centered oxidation of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  by  $\text{O}_2$ . O atoms from ligands (on left) push electron density from the  $p_x$  and  $p_y$  orbitals to the  $d_{xz}$  and  $d_{yz}$  orbitals of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  to stabilize the higher oxidation state that results. One of the  $d_{xz}$  and  $d_{yz}$  orbitals of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  in turn donates an electron to the  $\pi_x^*$  or  $\pi_y^*$  orbital of  $\text{O}_2$ . Bottom part of the figure shows the orbital energy diagrams of each species. Note that Cartesian coordinate axes are drawn differently from Figure 1. Black and white lobes are in the  $xz$  plane and gray scale lobes are in the  $yz$  planes.

higher the pH is, the more likely the oxidation will occur. However, inner sphere processes are also likely at higher pH (Luther 1990). These are described below for  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  with  $\text{O}_2$ .

### $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ and $\text{O}_2$

The electron transfer from  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  to  $\text{O}_2$  cannot occur by an outer-sphere process for two major reasons. First, the transfer of electrons from Mn  $e_g^*(\sigma)$  to  $\text{O}_2\pi^*$  is a poor symmetry mix because  $\pi$  to  $\pi$  as well as  $\sigma$  to  $\sigma$  transfers are favored for outer-sphere mechanisms but not  $\pi$  to  $\sigma$  or  $\sigma$  to  $\pi$ . Second, the  $t_{2g}(\pi)$  to  $\pi^*$ -electron transfer is energetically unfeasible because the  $t_{2g}$  orbital is not the HOMO orbital of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ . Thus, the case for  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  oxidation is more complex as  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  must lose electrons from the  $e_g^*$  orbitals which are on the bond axis. Figure 5 shows a schematic diagram for the reaction of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  with  $\text{O}_2$ . The top portion of the figure shows the orbitals of one O atom from water or hydroxide ion (on the left) binding directly to  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  but there must be an angular bond (bent Mn-O-O or "end on" attachment by  $\text{O}_2$ ) formed between an  $e_g^*$  orbital of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  and a  $\pi^*$  orbital of  $\text{O}_2$ . As this bond forms there is a formal electron transfer from the  $\text{Mn}^{2+}$  to  $\text{O}_2$  and this transfer can be considered to be the formation of  $\text{Mn}^{3+}$  and the superoxide ion,  $\text{O}_2^-$ . Hydroxide ion binding to Mn helps to stabilize the higher oxidation states of Mn along both the  $\sigma$  and  $\pi$  systems. The angular bonding between  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$

and  $\text{O}_2$  would be analogous to the bonding of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  to  $\text{O}_2$  in hemoglobin (Shriver et al. 1994). Recent ab initio calculations also show that an outer sphere mechanism is not available for this reaction (Rosso and Morgan 2002) in accordance with a linear free energy analysis of metal oxidation rates by Wehrli (1990).

As in the case of  $\text{Fe}^{2+}$ , increasing the pH increases the rate of oxidation as more hydroxide ion binds to  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ . The rate law for  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  oxidation is given in equation 2. This rate law indicates that the formation of manganese oxide solid phases

$$\frac{-d[\text{Mn(II)}]}{dt} = k_0[\text{Mn(II)}] + k_1[\text{Mn(II)}][\text{MnO}_2] \quad [2]$$

(e.g.;  $\text{MnO}_2$ ) enhances the oxidation and thus the process is autocatalytic as  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  adsorbs to and complexes with solid phases. The process is also enhanced by bacteria and organic chelates with carboxyl and hydroxyl functional groups. The initial steps in the electron transfer process can be represented simply by equations 3 and 4.

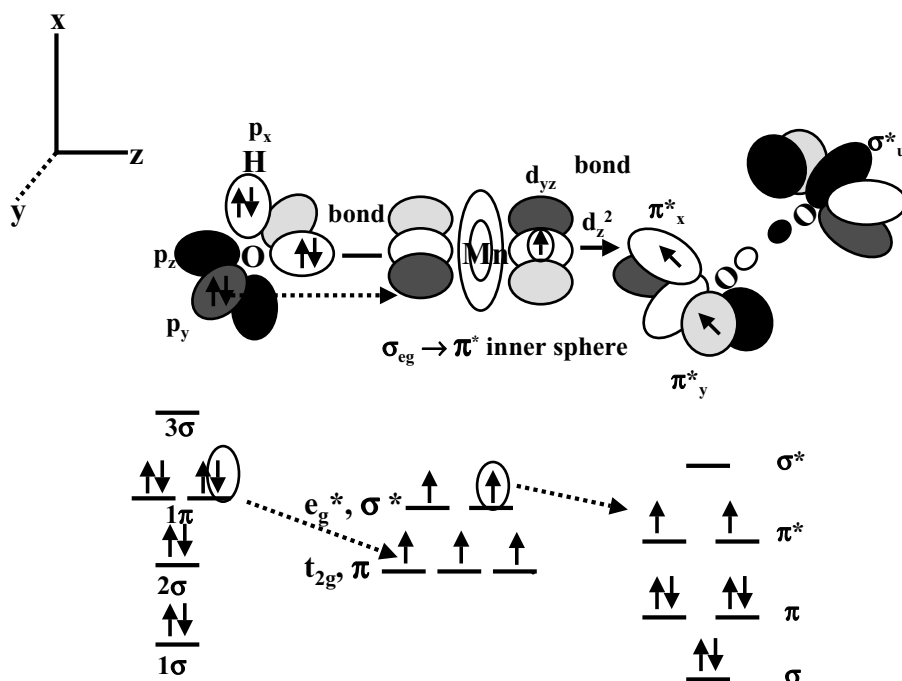
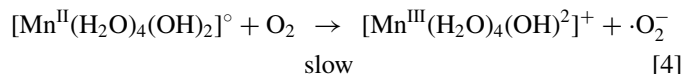
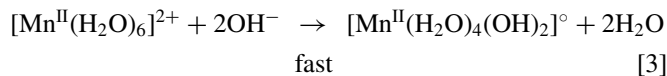


FIG. 5. Molecular orbital diagram (top) demonstrates the electron transfer process during the metal centered oxidation of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  by  $\text{O}_2$ . O atoms from ligands (on left) push electron density from the  $p_x$  and  $p_y$  orbitals to the  $d_{xz}$  and  $d_{yz}$  orbitals of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  to stabilize the higher oxidation state that results. However these do not donate to the  $\text{O}_2$  orbital. Instead the  $d_z^2$  orbital ( $e_g^*$ ) of  $\text{Mn}(\text{H}_2\text{O})_6^{2+}$  shares an electron with the  $\pi_x^*$  orbital of  $\text{O}_2$  to form a new sigma bond that is bent or angular Mn-O-O. Bottom part of the figure shows the orbital energy diagrams of each species. Note that Cartesian coordinate axes are drawn differently from Figure 1. Black and white lobes are in the  $xz$  plane and gray scale lobes are in the  $xy$  and  $yz$  planes.

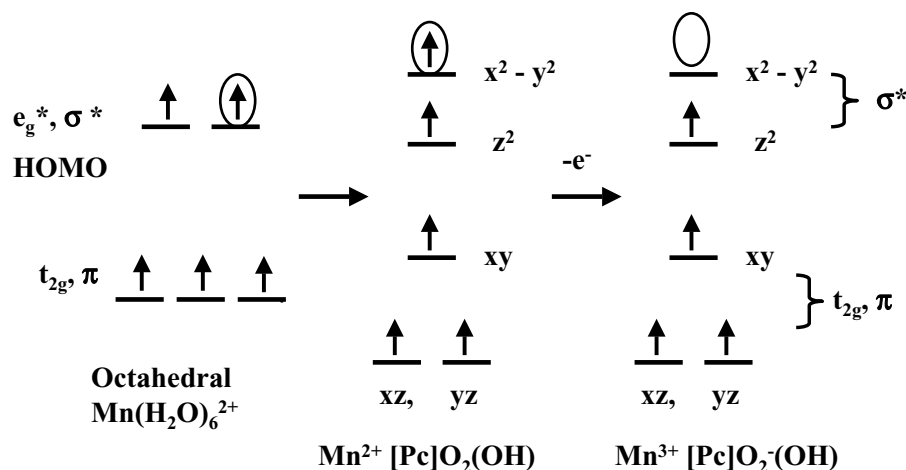


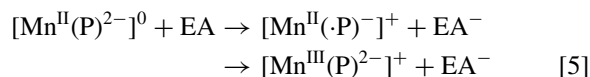
FIG. 6. Orbital energy diagram showing the change in energy and symmetry of Mn(II) orbitals from purely octahedral (left) to tetragonally distorted Mn(II) (center) to Mn(III) (right). This splitting is created by having different ligands (e.g., from all water ligands to a mixture of water and hydroxide ligands) bind to the Mn.

Equation 4 shows two hydroxide ions because there is a need to change the symmetry of  $Mn(H_2O)_6^{2+}$  from octahedral geometry (see below and Figure 6). In a recent review of Mn(II) oxidation, Morgan (2005) has indicated that the di-hydroxide species is the primary reactant. The schematic representation in Figure 5 is consistent with this rate law as O atoms from  $MnO_2$  or other higher oxidation state solid Mn compounds would replace the O atom from water or hydroxide ion as  $\pi$  donor ligands. This process is much faster once manganese minerals are formed because of their ability to complex the  $Mn(H_2O)_6^{2+}$  in solution. Organic chelates as well as bacterial spore coats (Mandernack et al. 1995a, 1995b; Bargar et al. 2000) are also able to complex the  $Mn(H_2O)_6^{2+}$  in solution, and thus they create a similar enhancement on  $Mn(H_2O)_6^{2+}$  oxidation rates.

In the chemical literature, one-electron transfer processes for oxidation of Mn(II) compounds are well known (e.g., Lever et al. 1981). Complexation of the  $Mn(H_2O)_6^{2+}$  by organic ligands has been shown to remove the octahedral symmetry of the Mn(II). Complexation rearranges the energies of the d orbitals to affect electron transfer. At least one d HOMO orbital must have more positive energy in the new geometry to initiate electron transfer. An energy-level representation similar to that for Mn-phthalocyanine complexes (pc = phthalocyanine which is a porphyrin-like molecule; Lever et al. 1981) is shown in Figure 6. This process shows the formation of the Mn(III) oxidation state and also shows the final orbital diagram for Mn(III) ( $d^4$ ), which is predicted by the Jahn-Teller theorem (Shriver et al. 1994). The bonding is bent Mn-O-O ("end on" attachment by  $O_2$ ) as described above in Figure 5.

The discussion above has been limited to metal-centered oxidations [direct electron transfer from Mn(II) compounds to  $O_2$ ]. However, one-electron transfers by ligand-centered oxidation can occur, but in a two-step process. These steps are the initial electron transfer from the ligand [bound to Mn(II)] to another electron acceptor, followed by electron transfer from Mn(II)

to the ligand. Figure 7 shows this two-step process for Mn(II) porphyrin complexes (Richert et al. 1988) where an electron from the  $x^2-y^2$  orbital of Mn in a square planar geometry transfers an electron into the porphyrin ligand. Equation 5 displays the process where P = porphyrin and EA = electron acceptor. This process is likely to happen in the environment at suboxic interface zones, where decomposition of organic matter occurs and creates unsaturated organic compounds for metal binding.



### One-Electron Transfer to Form Mn(III) Intermediates—Soluble and/or Solid

$Mn(H_2O)_6^{2+}$  oxidation (both chemical and microbial) generally results in Mn(III) as an intermediate. Mn(III) seems to be a forgotten intermediate in environmental processes although recent interest has accelerated. However, from a microbiological viewpoint, Mn(III) compounds are ideal reagents as Mn(III) compounds can act as electron acceptors forming soluble  $Mn(H_2O)_6^{2+}$  or as electron donors forming insoluble  $MnO_2$ . Figure 6 shows the conversion of Mn(II) organic complexes to Mn(III) ( $d^4$ ), which results in a tetragonally distorted geometry (2 long bonds on the z axis and 4 short bonds in the xy plane) rather than octahedral geometry with all six bonds equivalent. This electron configuration results in higher kinetic lability (ligand exchange) and reactivity for Mn(III) compounds than Mn(II) compounds. This coupled with the thermodynamically favored disproportionation reaction of inorganic Mn(III) to Mn(II) and Mn(IV) (eq. 6) has led environmental scientists to largely ignore Mn(III) compounds.



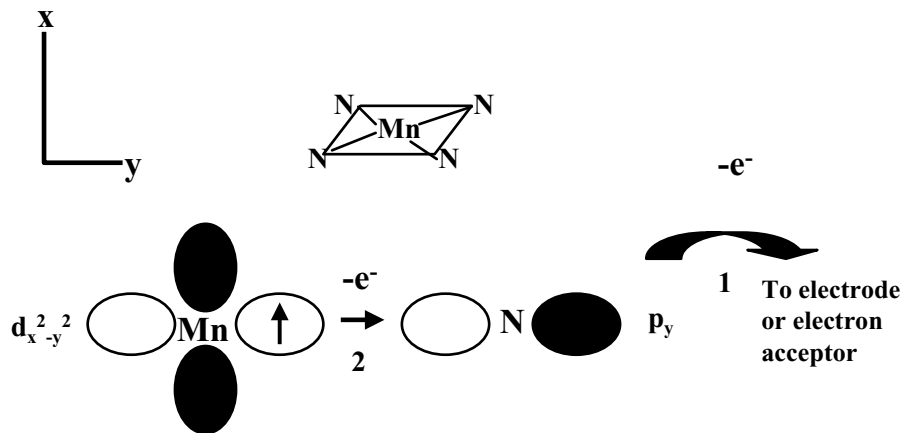


FIG. 7. Top diagram shows a square planar arrangement of ligands around Mn(II) in a porphyrin complex. The bottom diagram shows the movement of electrons from right to left in a ligand centered oxidation process. (1) shows the loss of an electron from the ligand binding Mn to an electrode or another electron acceptor orbital. (2) shows the loss of a Mn(II) electron from a  $d_{x^2-y^2}$  orbital to a ligand  $p_y$  orbital. Note that Cartesian coordinate axes are drawn differently from Figures 1, 4, and 5.

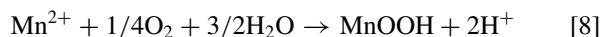
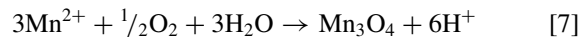
However, one of the best known chemical Mn(III) examples occurs in the Winkler titration to determine  $O_2$ . In this titration,  $O_2$  in a water sample is reacted with soluble  $Mn(H_2O)_6^{2+}$  under very basic conditions to form a brown solid Mn(III) precipitate. In the presence of iodide and acid, the  $I^-$  is then oxidized to  $I_2$ , which is then titrated with thiosulfate to determine  $O_2$ . This is an excellent quantitative example of the abiotic formation of Mn(III) from Mn(II)—a one-electron transfer. A host of researchers (e.g., Murray et al. 1985) have shown that the first formed precipitate of abiotic  $Mn(H_2O)_6^{2+}$  oxidation is a Mn(III) solid phase. Similar results have also been found for biological processes (e.g., Mandernack et al. 1995a) although  $MnO_2$  forms as well at moderately high pH.

Although the chemical literature has many examples of *soluble* Mn(III) complexes with inorganic and organic ligands, soluble Mn(III) has not been well studied by environmental chemists because of the widespread belief that once any Mn(III) forms it will disproportionate to  $Mn^{2+}$  and  $MnO_2$  (equation 6). However, polyphosphates such as pyrophosphate ( $P_4O_7^{4-}$ ) are known in the environment and they complex Mn(III) readily (Kostka et al. 1995). These ligands are likely organic decomposition products from ATP or ADP. Organic acids also bind Mn(III) but the stability of these Mn(III) complexes is not as good as pyrophosphate because the Mn(III) oxidizes the carboxylic acid functional group to  $CO_2$  (Klewicki and Morgan 1998, 1999; Luther et al. 1999). Hydroxamates, Fe(III) siderophores, also bind Mn(III) (Faulkner et al. 1994; Parker et al. 2004). Lastly, the photosystem II center has a cubic arrangement of Mn(II, III, IV) alternating with O atoms ( $Mn_4O_4$ ). Decomposition of the center in suboxic interface zones would release the various forms of Mn including Mn(III) as soluble entities.

Tebo et al. (2004) have reviewed  $Mn(H_2O)_6^{2+}$  oxidation to Mn(IV) in the environment, which appears to be mediated by a multicopper oxidase-like enzyme. Experimental results from

several methods show that Mn(III) is an intermediate in the process. Webb et al. (2002, 2005) using XANES measurements showed that Mn(III) is formed when  $Mn(H_2O)_6^{2+}$  oxidation is mediated by *Bacillus* sp. strain spores. Also, addition of pyrophosphate to the solution results in the formation of the Mn(III) pyrophosphate complex. Recently, Parker et al. (2004) showed that a pyoverdine siderophore, which is produced by a  $Mn(H_2O)_6^{2+}$  oxidizing organism, binds Mn(III). These workers concluded that two-sequential one-electron transfer reactions occur with the formation of a short-lived soluble or enzyme-complex Mn(III) intermediate.

Four electrons are required to fully reduce  $O_2$  to  $H_2O$  and break the O-O double bond. This fact coupled with evidence for one electron transfer processes for Mn indicate that isotopic enrichment experiments should not show significant quantities of oxygen from  $O_2$  in the Mn(III) and Mn(IV) phases produced. In fact, Mandernack et al. (1995b) showed that there was no indication of O atoms from  $O_2$  in their abiotic experiments that produced  $Mn_3O_4$  (equation 7) and  $MnOOH$  (equation 8) when a maximum of 25% could be expected based on the written reactions (equations 7 and 8) alone. However, when  $Mn(H_2O)_6^{2+}$  oxidizing bacteria were used, about 40–50% of the O atoms in  $MnO_2$  came from  $O_2$ . These latter reactions were allowed to age for 4 days to 1 year and are subject to uncertainty.



Based on the spatial orientation of the two  $Mn(H_2O)_6^{2+}$  HOMO orbitals above, one electron transfer processes appear to be most likely in environmental Mn processes. Because Cu undergoes one electron processes between  $Cu^{2+}$  and  $Cu^+$ , multicopper oxidase-like enzymes likely undergo one-electron transfer steps.

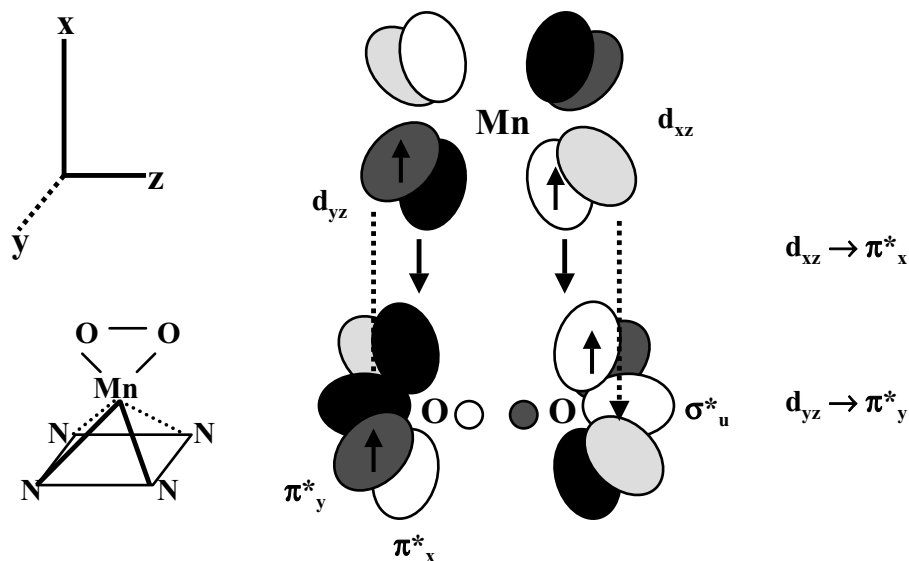


FIG. 8. Molecular orbital diagram (right) demonstrates the two-electron electron transfer process during the metal centered oxidation of Mn(II) by  $O_2$ . Both the  $d_{xz}$  and  $d_{yz}$  orbitals of Mn(II) donate an electron each to the  $\pi_x^*$  or  $\pi_y^*$  orbital of  $O_2$  (see arrows) Left part of the figure shows the geometry of the  $Mn^{2+}$  porphyrin complex. Note that Cartesian coordinate axes are drawn differently from Figure 1. Black and white lobes are in the  $xz$  plane and gray scale lobes are in the  $xy$  and  $yz$  planes.

### Possibility of Two-Electron Transfer in Mn(II) Oxidation

An example of a two-electron transfer process for metal-centered Mn(II) oxidation has been provided by Hoffman et al. (1978) using a Mn(II) porphyrin complex. Overall, this can be considered an oxidative addition of Mn(II) to  $O_2$  to form Mn(IV) and peroxide ion; i.e., Mn(II) loses two electrons to  $O_2$  as it adds the  $O_2$  into its coordination shell. This reaction is similar to that found in Vaska's complex (Vaska 1963), which has reversible  $O_2$  binding. Figure 8 is a schematic representation of the process. The Mn(II) complex is formally five coordinate (5 pairs of electrons donating to Mn) and exhibits side on bonding with  $O_2$ . Side on attack allows for overlap of both  $d_{yz} \rightarrow \pi_y^*$  and  $d_{xz} \rightarrow \pi_x^*$ ; i.e., one electron from the  $d_{xz}$  and  $d_{yz}$  orbitals of Mn(II) are donated to the appropriate  $\pi$  orbitals of  $O_2$ . This process cannot occur with angular "end on" bonding as in Figure 5 because of the bent Mn-O-O. If this  $MnO_2$  intermediate could react with another Mn(II) so that the second Mn could donate electrons to the  $O_2$ , then the O-O bonds in  $O_2$  would be broken

with formation of two M-O-M bridges in a four-membered ring (Cotton et al. 1999). Eventual release of  $MnO_2$  is then possible, which should result in 50% of the O atoms from  $O_2$  and the other 50% from water in the product  $MnO_2$ . This reaction sequence is represented by equations 9a-9e.

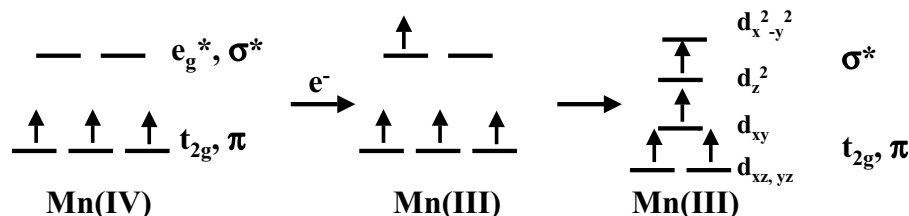
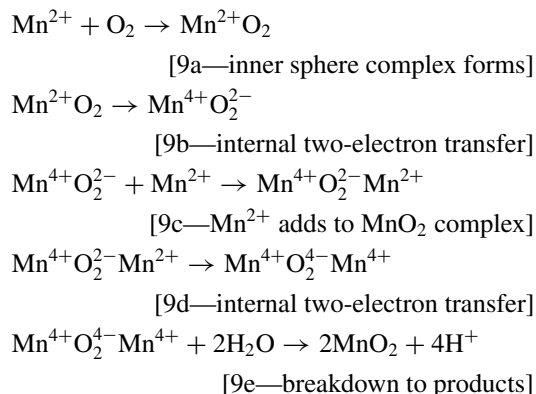


FIG. 9. Orbital energy diagrams depicting the change in energy and symmetry of Mn(IV) orbitals from purely octahedral (left) to octahedral Mn(III) (center) to tetragonally distorted Mn(III) (right). This latter splitting is predicted by the Jahn-Teller theorem.

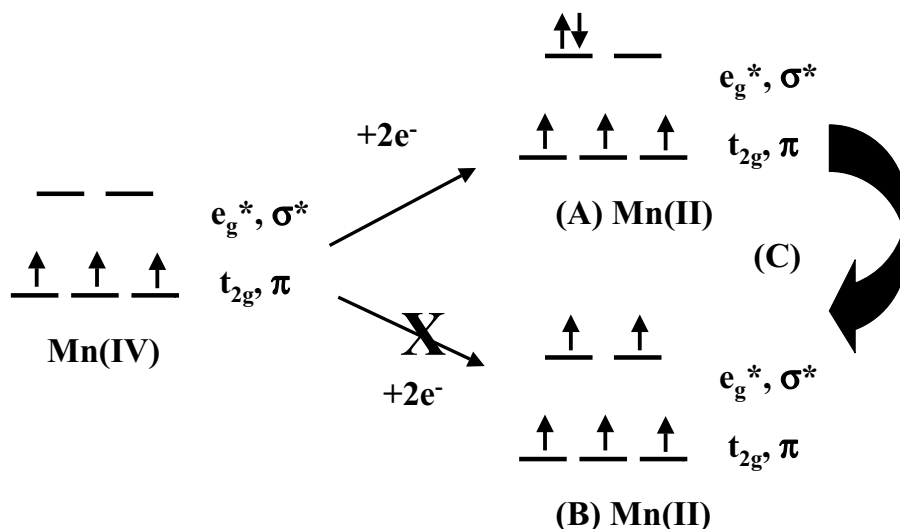


FIG. 10. Orbital energy diagrams showing the possible ways that Mn(IV) can add two electrons to its e<sub>g</sub><sup>\*</sup> orbital set. Accepting two electrons in one orbital is more likely and should result in (A) followed by electron rearrangement (C) to form (B) (O atom transfer is a possible mechanism). The X mark indicates that forming (B) directly is less likely and requires two different orbitals from a ligand to donate a single electron each to the e<sub>g</sub><sup>\*</sup> orbitals of Mn(IV). The latter process would be the reverse of that shown in Figure 8.

### MnO<sub>2</sub> Reduction

Based on the orbital discussion above, one-electron transfers are also likely for MnO<sub>2</sub> reduction to Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> with Mn(III) intermediate species being formed. Figure 9 shows that adding an electron to one of the e<sub>g</sub> orbitals results in Mn(III) compounds and an orbital rearrangement previously shown for Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> oxidation to form Mn(III) compounds (e.g., Figure 6). By contrast, Figure 10 shows that for a two-electron transfer to occur, the upper pathway (A) is more likely because two electrons as a lone pair can donate to an empty orbital with subsequent rearrangement (C) to form B. For B to form directly requires a reductant with 2 orbitals that can donate one electron each. To date, data on electron transfer processes during MnO<sub>2</sub> reduction appear sparse.

Electrochemical reduction of MnO<sub>2</sub> in sulfuric acid to MnOOH as an intermediate has been reported by Nijjer et al. (2000). Also, an one-electron transfer has been reported during the electrochemical reduction of MnO<sub>2</sub> by Ruppel et al. (2001). In these latter experiments, a polymeric form of MnO<sub>2</sub> was applied to a metal coupon and electrochemically reduced in the absence of bacteria and O<sub>2</sub>. Based on the quantity of MnO<sub>2</sub> applied to the metal coupon, an excess current of 2 to 5 times based on reduction directly to Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> was produced. Formation of Mn(III) with disproportionation to reform MnO<sub>2</sub> could account for the current increase.

Chemical studies (e.g.; Stone 1987; Luther et al. 1999) related to environmental processes have proposed that Mn(III) compounds form during MnO<sub>2</sub> reduction by organic reductants. Kinetic data indicate that a manganese-organic complex forms during reduction and that the complex contains Mn(III). However, trapping the intermediate complex has generally proved to

be difficult (Luther et al. 1999). Mn(III) appears to be produced during microbiological reduction of MnO<sub>2</sub> as shown by Tebo et al. (2004), who were able to use pyrophosphate to react with the Mn(III) formed.

However, in a kinetic study on the reduction of MnO<sub>2</sub> by nitrite to form nitrate and Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, Luther and Popp (2002) reported that O atom transfer was likely. This would result in a two-electron transfer as in equation 10. This reaction is inner sphere and



could occur as outlined in Figure 10 to form (A) first. NO<sub>2</sub><sup>-</sup> would react and remove an O atom from MnO<sub>2</sub>. This O atom is on the sigma bond axis and the Mn orbital binding with the O atom has σ (e<sub>g</sub><sup>\*</sup>) character. As NO<sub>3</sub><sup>-</sup> leaves the Mn, two electrons would remain with the Mn in a single e<sub>g</sub><sup>\*</sup> orbital. Electron rearrangement via (C) would then occur to form (B) as in Figure 10.

### CONCLUSIONS

Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> oxidation by O<sub>2</sub> occurs via an inner sphere process whereas Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> at circumneutral pH occurs via an outer sphere mechanism. An outer sphere process is symmetry forbidden for Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> based on analysis of the frontier molecular orbitals of the reactants. At higher pH, an inner-sphere process is also available for Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> oxidation. The bonding of O<sub>2</sub> to Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> in the precursor complex results in faster electron transfer for inner sphere processes than occurs in the outer-sphere process which occurs at lower pH. The bonding between the reactants in inner sphere processes is likely “end



on" bonding for O<sub>2</sub> to the metal with a bent M-O-O bond angle. Side-on bonding for O<sub>2</sub> to the metal is possible and could lead to two-electron transfers from Mn<sup>2+</sup> but requires stabilization of the Mn-O<sub>2</sub> bonding with organic ligands such as porphyrins. This would occur as an oxidative addition type reaction where the metal would give up two electrons to two different orbitals of O<sub>2</sub> and increase its local coordination environment. For two-electron transfers during Mn<sup>2+</sup> oxidation, multinuclear Mn complexes are required.

One-electron transfers are more likely to occur during the oxidation of Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> by O<sub>2</sub> and the reduction of MnO<sub>2</sub> than two-electron transfers. Both soluble and solid phase Mn(III) species can form as intermediates or stable species. From a microbiological viewpoint, Mn(III) compounds are ideal reagents as Mn(III) can act as an electron acceptor forming soluble Mn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> or as an electron donor forming insoluble MnO<sub>2</sub>. One-electron transfers are predicted based on the different spatial characteristics of the d<sub>z<sup>2</sup></sub> and d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbitals. The d<sub>z<sup>2</sup></sub> orbital has electron density on all three Cartesian coordinate axes (primarily the z axis) but the d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital has electron density only in the xy plane. Adding or losing two electrons simultaneously is not a facile process. However, O atom transfer can account for a two-electron transfer in MnO<sub>2</sub> reduction. Better knowledge of the structures of Mn intermediates and the types of reductant appears to be key for describing whether two one-electron transfer steps or a single two-electron step may be operative during MnO<sub>2</sub> reduction.

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