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Electron Transfer. 118. Proton-Coupled Reductions of a Dinuclear Dimanganese (III, IV) Model for the Reactive Center in Photosystem II[1]

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The dinuclear Mn^{III}, Mn^{IV} model for the reactive center in photosystem II (PS II), $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$, undergoes rapid reductions by ascorbate, hydroquinone, and HSO_3^- to $2Mn^{2+}$ (aq) in aqueous media buffered by bipy–bipyH$^+$. Net changes of 3e$^-$ occur in each case. The ascorbate system involves a $Mn^{III}Mn^{IV}$–ascorbate complex ($Q = 1.4 \times 10^2$ M^{-1} at 23 °C) and exhibits $k_{limiting} = 8.8 \times 10^2$ s^{-1} in H_2O and 2.2×10^2 s^{-1} in D_2O for the initial redox act which, in this case, is rate-determining. Complex decay profiles generated by the reactions of hydroquinone and HSO_3^- are in accord with multistep processes in which the intermediate Mn states and the radicals derived from the reductant (semiquinone and $SO_3^{\bullet-}$) participate. The resulting patterns are autocatalytic in nature, with the active catalytic species appearing to be the $(Mn^{III})_2$ intermediate. Solvent kinetic isotope effects, (k_{H_2O}/k_{D_2O}) observed when solvent H_2O is replaced by D_2O, lie near 4.0 for the ascorbate reduction and for the initial step in the hydroquinone reduction but approach unity for the bisulfite reduction, pointing to coupled electron and proton transfers by the organic reductants but not by HSO_3^-. Plots of k_{obsd} vs mole fraction D_2O are very nearly linear for the reduction by ascorbate, indicating that, in this case, just one proton is transferred in the rate-determining step.

During the last 20 years, interest in the chemistry of tri- and tetrapositive manganese has grown impressively as an array of investigators have worked toward solutions to two still unanswered questions: (1) What is the detailed structure of the Mn-containing site involved in the photosynthetic conversion of water to O_2 (the characteristic process associated with Photosystem II)? (2) What is the molecular nature of the O_2-evolving and the regeneration steps comprising this system?[2]

The essentiality of manganese for O_2 evolution has long been recognized,[3] but it was not until 1970 that the current five "S-state" working model of PS II,[4] based upon Joliot's photosynthetic experiments with "chopped light",[5] was forwarded. These S-states, designated S_0 to S_4, are taken to differ from one another by successive absorption of light quanta and the delivery of single electrons, coupled, in some instances, by transfer of H$^+$, to the associated photosynthetic acceptor site, with the release of O_2 occurring only from S_4, which is then converted to S_0.

The PS II unit features four manganese atoms[6] ligated principally by O-donor centers.[7] EXAFS spectra point to Mn–Mn distances of 2.7 and 3.3 Å.[8] Attachment of manganese to the associated protein component may involve interaction with histidine, aspartate, or glutamic acid residues.[9]

A number of workers have noted that several μ-oxo-bridged complexes having the $Mn^{IV}(O)_2Mn^{III}$ unit exhibit key properties markedly resembling those of the manganese center in PS II. Similarities in metal–metal distances,[2g] in multiline EPR signals,[10] in *J* values pertaining to antiferromagnetic coupling between metal centers,[11] and in redox behavior,[12] taken in concert, favor the notion that essential aspects of the action of PS II may be elucidated from the study of such dinuclear derivatives. This view implies that the structural features required for O_2 evolution exist at least in part, in each of the dinuclear halves which comprise the Mn_4 unit. Among the nearly one hundred di- and polynuclear complexes of manganese which have been prepared as possible models for the active site in PS II,[2b] only the cationic species $[(bipy)_2Mn^{IV}(O)_2Mn^{III}(bipy)_2]^{3+}$ and the analogous 1,10-phenanthroline complex have thus far been reported to be associated with the generation of O_2 from water on illumination.[13] (Note, however, that such systems involve suspensions of the solid complex salts and also require the presence of an external oxidant such as Ce(IV).)

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Despite the prominence of $Mn^{IV}(O)_2Mn^{III}$ systems in guiding attempts to pinpoint the role of manganese in photosynthesis, broad knowledge concerning the reactions of these dinuclear complexes with a variety of simple redox species in aqueous media is not yet at hand. The present study deals with the reductions of $[(bipy)_2Mn^{IV}(O)_2Mn^{III}(bipy)_2]^{3+}$ (one of the more robust complexes of this type) with ascorbate, hydroquinone, and bisulfite. Although neither ascorbate nor hydroquinone is involved in PS II, ascorbate is of importance as a hydroxylase cofactor[14] and as an antioxidant,[15] whereas hydroquinone is of interest because of the intervention of the oxidized (semiquinone) form of this structural element in photosystem I.[16] Both reductants generally are oxidized with a net transaction of 2e, but this change is almost always accomplished in single-electron steps. The reaction of S(IV), which is capable of undergoing both 1e and 2e oxidations,[17] adds further detail.[18]

Experimental Section

Materials. L-Ascorbic acid, 2,2′-bipyridyl (bipy), deuterium oxide (99.9 atom percent D), and BES buffer (*N*,*N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid) were Aldrich products and were used without further purification, as were hydroquinone (Eastman) and sodium sulfite (Alfa).

The dinuclear $Mn^{III}Mn^{IV}$ complex $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2](ClO_4)_3 \cdot 2H_2O$, was prepared and purified as described by Cooper and Calvin;[19] λ_{max} was at 684 nm (ϵ = 558 M^{-1} cm^{-1}) with shoulders at 557 (449) and 526 nm (526). Lit.:[19] 684 (551), 555 s (455), 525 s (530). As reported,[19] aqueous solutions of this complex are stable only in the presence of bipyridyl buffer. Aqueous solutions in phosphate, acetate, or BES buffers decomposed within seconds, as did unbuffered solutions containing added bipyridyl.

Stoichiometric Studies. The stoichiometry of the reaction of hydroquinone with $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ ($Mn^{III}Mn^{IV}$) was determined spectrophotometrically at 684 nm. Measured deficient quantities of the reductant were added to a known excess of the oxidant in bipyridyl buffer. After reaction had ceased (30 s), decreases in absorbance were measured. These changes were then compared to those resulting from addition of an excess of the reductant. The analogous procedure, when applied to the $Mn^{III}Mn^{IV}$–HSO_3^- reaction, gave reproducible results only if performed under N_2 with solutions which had been rigorously deaerated. The $Mn^{III}Mn^{IV}$–ascorbate reaction, when carried out with excess oxidant, exhibited uncertain stoichiometry, probably reflecting a slow partial oxidation of dehydroascorbic acid after generation of the latter. For this system, excess reductant was taken. Following the reaction of interest, excess Fe(III) was added and was partially reduced, by the remaining ascorbate, to Fe^{II}, which was estimated as $[Fe(bipy)_3]^{2+}$ (ϵ_{max}^{522} = 8.5 × 10^3 M^{-1} cm^{-1}). Results are summarized in Table 1.

Kinetic Measurements. All reactions were rapid and were monitored, either at 684 or 350 nm, using a Durrum-Gibson stopped flow spectrophotometer interfaced with an OLIS computer system. Reactions were run under N_2 using solutions which had been rigorously deaerated, a precaution which was particularly important for reductions by HSO_3^-. Examination of decay curves in the range 350–800 nm disclosed no additional features not evident at the wavelengths of choice. Ionic strength was maintained at 0.10 M by addition of $NaClO_4$.[20] Solutions were buffered with bipy–bipyH⁺ mixtures; the total concentration, [bipy] + [$bipyH^+$], was 0.010–0.020 M, and the ratio [bipy]/[$bipyH^+$] ranged from 1.0 to 6.0. For reactions in D_2O, pD was calculated as $(pH)_{measured}$ + 0.40.[21a] Virtually all reactions were carried out with the reductant in excess. Reductions with ascorbate in greater than 10-fold excess yielded exponential decay curves. Pseudo-first-order rate constants greater than 50 s^{-1} were adjusted upward to accommodate the mixing rate associated with our stopped-flow instrument as described by Dickson.[21b] All reactions with hydroquinone and HSO_3^- gave complex curves requiring detailed analysis as described in the Results section.

Table 1. Stoichiometry of Reductions of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ [a]

reductant	[$Mn^{III}Mn^{IV}$], mM	[red], mM	Δ[ox], mM	Δ[red], mM	Δ[red]/Δ[ox]
hydroquinone[b]	1.60	0.50	0.32		1.56
	1.60	1.00	0.67		1.49
	1.60	1.50	1.02		1.47
	1.60	2.00	1.33		1.50
HSO_3^- [b,c]	0.75	0.28	0.185		1.51
	0.75	0.56	0.39		1.44
	0.75	0.84	0.57		1.47
	0.75	1.12	0.75		1.49
ascorbate[d]	1.70	5.0		2.50	1.47
	1.30	5.0		1.90	1.46
	0.25	1.13		0.35	1.40
	0.50	1.13		0.69	1.38
	0.70	2.25		1.05	1.50
	0.90	2.25		1.24	1.38

[a] Reactions were carried out at 25 °C in bipy–bipyH⁺ buffers (pH 4.9). [b] Measurements at 684 nm. [c] Reactions required rigorous deaeration of reagent solutions. Without deaeration, apparent stoichiometries, Δ[red]/Δ[ox], >2.4 were observed. [d] Excess ascorbate was estimated by reaction with Fe(III), forming $[Fe(bipy)_3]^{2+}$ (ϵ_{max}^{522} = 8.5 × 10^3) (see Experimental Section). Experiments with excess oxidant yielded apparent stoichiometries <0.90.

Additional Observations. Although the $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ complex can be stabilized in bipy–bipyH⁺ buffers, it suffers perceptible decomposition above pH 5.4 and below pH 4.3. Solution of its perchlorate in water is attended by a pronounced color change (green to red), by the disappearance of shoulders at 555 and 525 nm, and by diminution of the maximum at 684 nm. Similar, but more rapid, changes occur when solutions of the complex in 0.01 M bipy–bipyH⁺ are treated with an excess of the more basic buffers $HPO_4^{2-}/H_2PO_4^-$ or BES/BESH⁺. These conversions, when monitored at 684 nm, gave exponential decay curves. Estimated half-lives (pH 7.4, 20 °C) associated with the decays were 58 ms for treatment with 0.10 M phosphate and 5.3 s for treatment with 0.020 M BES.[22,23]

The apparent characteristics of the reductions of the $Mn^{III}Mn^{IV}$ complex were likewise highly dependent on stabilization with bipy–bipyH⁺. Typically, reduction, with 0.002 M hydroquinone, of the properly stabilized oxidant yielded a reproducible multistep profile (vide infra), whereas in the absence of bipy, this was degraded into a single component curve ($t_{1/2}$ = 33 ms at 20 °C).

The disproportionation of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ to $[Mn_3O_4(bipy)_4(OH_2)_2]^{4+}$ + Mn^{II}, which occurs at low pH's in the absence of bipy–bipyH⁺,[24] but not in its presence,[19] was briefly examined, both in H_2O and in D_2O (0.10 M HNO_3, 20 °C, 684 nm). Components of the resulting biphasic profiles exhibited *k* values of 12.4 ± 0.6 and 2.9 ± 0.1

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[14] Adams, E.; Frank, L. *Annu. Rev. Biochem.* **1980**, *49*, 1030.

[15] Cadenas, E. *Annu. Rev. Biochem.* **1989**, *58*, 79.

[16] See, for example: Brudvig, G. W.; Beck, W. F.; de Paula, J. C. *Annu. Rev. Biophys. Chem.* **1989**, *18*, 25.

[17] See, for example: (a) Yost, D. M.; Russell, H., Jr. *Systematic Inorganic Chemistry of the Fifth- and Sixth-Group Nonmetallic Elements*; Prentice-Hall: Englewood Cliffs, NJ, 1944; p 358. (b) Serala, R.; Stanbury, D. M. *Inorg. Chem.* **1990**, *29*, 3456.

[18] Related experiments with the same binuclear oxidant have been reported by: Monzyk, M. M.; Holwerda, R. A. *Inorg. Chem.* **1992**, *31*, 1969. The present work suggests that the spectral changes observed by these authors reflected conversions not of the complex at hand, but rather of a heterolysis or disproportionation product.

[19] Cooper, S. R.; Calvin, M. *J. Am. Chem. Soc.* **1977**, *99*, 6623.

[20] To avoid complications due to the slow precipitation of the $Mn^{III}Mn^{IV}$ complex as its perchlorate, this oxidant was dissolved in bipyridyl buffer and the reductant in 0.20 M $NaClO_4$. Optical disturbances resulting from mixing equal volumes of reagent solutions of different ionic strengths were slight and did not seriously interfere with the observation of kinetic profiles.

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[22] In experiments dealing with the reaction of unstabilized solutions of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ with $Co(bipy)_3^{2+}$ in BES buffers, Monzyk and Holwerda[18] report an unidentified [reductant]-independent rate component (k_0 = 0.16 s^{-1}). This corresponds reasonably closely to the decay of the oxidant in this buffer (k = 0.13 s^{-1}) in the absence of reductant.

[23] The $Mn^{III}Mn^{IV}$ dimer has been reported to undergo a combination of disproportionation and phosphato anation when treated with H_3PO_4, yielding a μ_2-HPO_4 derivative of $(Mn^{IV})_2$ and a μ_2-H_2PO_4 complex of $(Mn^{III})_2$. See: Sarneski, J. E.; Didiuk, M.; Thorp, H. H.; Crabtree, R. H.; Brudvig, G. W.; Faller, J. W.; Schulter, G. K. *Inorg. Chem.* **1991**, *30*, 2833.

[24] Sarneski, J. E.; Thorp, H. H.; Brudvig, G. W.; Crabtree, R. H.; Schulte, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 7255.

s^{-1} (H_2O) and 10.1 ± 0.3 and 0.57 ± 0.01 s^{-1} (D_2O). Note that only the slower contributer shows a substantial solvent isotope effect.[25]

Results

The close approach to 3:2 stoichiometry observed for the reductions by hydroquinone (H_2Q) and HSO_3^- (Table 1), in conjunction with the absence in the product of spectral features indicative of Mn^{III}, allows us to represent the predominant reactions as (1) and (2) (where Q = benzoquinone, and bipy ligands have been omitted). Similar stoichiometry for the reduction by ascorbic acid tells us that this reductant, in keeping with many other reports,[26] is undergoing a 2e⁻ oxidation to dehydroascorbate. Substantially lower stoichiometries noted with ascorbate taken in deficiency may be attributed to partial oxidative consumption of the dehydro compound under these conditions. Much higher stoichiometry for the HSO_3^- reduction in imperfectly deaerated solutions points to diversion of a rapidly oxidized reaction intermediate by dissolved oxygen, a conclusion in accord with highly variable induction periods observed for such preparations.

$$2[Mn^{III}(O)_2Mn^{IV}]^{3+} + 3H_2Q + 2H^+ \rightarrow 4Mn^{2+} + 4H_2O + 3Q \quad (1)$$

$$2[Mn^{III}(O)_2Mn^{IV}]^{3+} + 3HSO_3^- \rightarrow 4Mn^{2+} + 3SO_4^{2-} + H_2O + H^+ \quad (2)$$

The demonstrated rapid decomposition of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ in aqueous buffers other than bipy–bipyH⁺ underlines the necessity for carrying out experiments with this complex using solutions which have been suitably stabilized and leads us to question interpretations of kinetic measurements[18] which appear to have been performed on unstabilized samples.[27]

Representative kinetic curves generated by reductions of $Mn^{III}Mn^{IV}$ with hydroquinone and with HSO_3^- are shown as Figures 1 and 2. For all such reactions, slopes increase steadily as conversions get under way and then remain nearly constant until late in the reaction, finally decreasing in the final stages. However, reactions are not catalyzed by the products (Mn^{2+}, benzoquinone, or SO_4^{2-}).

Any proposed formulation must be in accord with the shapes of such curves and must also take into account the intervention of intermediate oxidation states of manganese, as well as the capacity of the reductants to partake in single-electron transactions. Data for 13 runs with hydroquinone are consistent with the sequence represented schematically as (3)–(8), in which Red• designates the radical semiquinone generated by removal of a single electron from the reductant. All steps are taken to be 1e⁻ changes, and all manganese species except Mn^{II} are considered to be dinuclear in line with evidence that electrochemical reduction of the oxidant at hand yields a $(Mn^{III})_2$ species,[13a] that reduction of its o-phenanthroline analog produces a $Mn^{II}Mn^{III}$ derivative,[28] and that nuclearity is preserved among the several oxidation levels of dinuclear catalase enzyme models.[2b,11c] Note also that bond connectivities appear to be retained among the various "S-states" involved in PS II.[29]

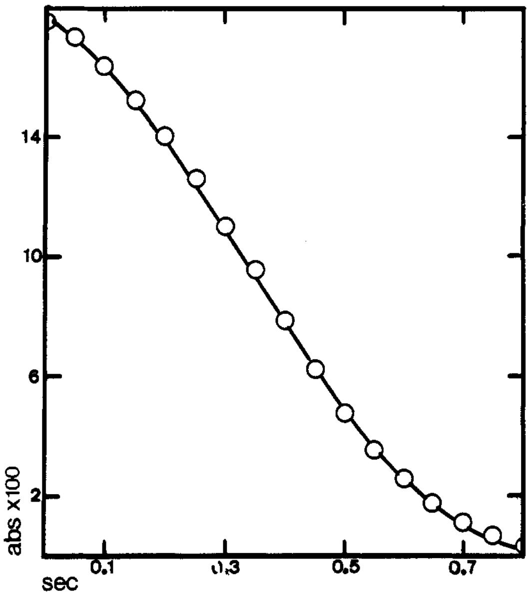

Figure 1. Kinetic profile (350 nm) for the reduction of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ (1.7×10^{-5} M) with hydroquinone (3.5×10^{-4} M) at 20 °C. pH = 4.76; μ = 0.10 M ($NaClO_4$). The $Mn^{III}Mn^{IV}$ solution was stabilized with bipy–bipyH⁺ buffer. The solid line is the experimental curve, whereas the circles are absorbances calculated from numerical integration of differential equations based on (3)–(8) in the text, taking the parameters listed in Table 2. Extinction coefficients used (M^{-1} cm^{-1}): $Mn^{III}Mn^{IV}$, 5.3×10^3; $(Mn^{III})_2$, 2.33×10^3; $Mn^{II}Mn^{III}$, 1.5×10^3. Optical path length = 2.0 cm.

$$Mn^{III}Mn^{IV} + Red \xrightarrow{k_3} (Mn^{III})_2 + Red^\bullet \quad (3)$$

$$(Mn^{III})_2 + Red \xrightarrow{k_4} Mn^{II}Mn^{III} + Red^\bullet \quad (4)$$

$$Mn^{III}Mn^{IV} + Red^\bullet \xrightarrow{k_5} (Mn^{III})_2 + Prod \quad (5)$$

$$(Mn^{III})_2 + Red^\bullet \xrightarrow{k_6} Mn^{II}Mn^{III} + Prod \quad (6)$$

$$Mn^{II}Mn^{III} + Red \xrightarrow{k_7} 2\ Mn^{II} + Red^\bullet \quad (7)$$

$$Mn^{II}Mn^{II} + Red^\bullet \xrightarrow{k_8} 2\ Mn^{II} + Prod \quad (8)$$

Expression of this sequence as a series of differential equations and numerical integration using an adaptation of the program KINSIM[30] yielded the concentrations of the participating species at 2-ms intervals during the course of each reaction, and incorporation of the extinction coefficients of $Mn^{III}Mn^{IV}$ (measured) and those of the two $(Mn)_2$ intermediates (estimated) yielded calculated values for the absorbance of the reaction mixture at each point.

Values of the rate constants and for the molar absorbance of $(Mn^{III})_2$ giving optimal agreement between calculated and

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(25) Rate constants for both components fall below the lower limit, 25 s^{-1} (25 °C, pH 2.3) reported for disproportionation of this $Mn^{III}Mn^{IV}$ complex in water. See: Carroll, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1992**, *114*, 8744.

(26) See, for example: Kustin, K.; Toppen, D. L. *Inorg. Chem.* **1973**, *12*, 1304. (b) Mushran, S. P.; Agrawal, M. C.; Mehrotra, R. M.; Sanehi, R. *J. Chem. Soc., Dalton Trans.* **1974**, 1460. (c) Pelizzeti, E.; Mentasti, E.; Pramauro, E. *Inorg. Chem.* **1976**, *15*, 2898. (d) Akhtar, M. J.; Haim, A. *Inorg. Chem.* **1988**, *27*, 1608. (e) Lannon, A. M.; Lappin, A. G.; Segal, M. G. *J. Chem. Soc., Dalton Trans.* **1986**, 619.

(27) In contrast, the voltammetry of solutions of the $Mn^{III}Mn^{IV}$ complex in aqueous phosphate solutions has been found to correspond to that in bipy–bipyH⁺ buffers despite partial disproportionation of this complex in the former medium. See, for example: (a) Thorp, H. H.; Sarneski, J. E.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 9249. (b) Thorp, H. H.; Brudvig, G. W.; Bowden, E. F. *J. Electroanal. Chem.* **1990**, *290*, 293.

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(29) See, for example: (a) Brudvig, G. W.; Crabtree, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 4586. (b) Vincent, J. B.; Christou, G. *Inorg. Chim. Acta* **1987**, *136*, L41.

(30) Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134. The original KINSIM program, for which we thank Dr. Carl Frieden, was developed for use on a VAX computer system. This was modified, using FORTRAN-77, to a "fixed-length" format and executed on an IBM 3081D system.

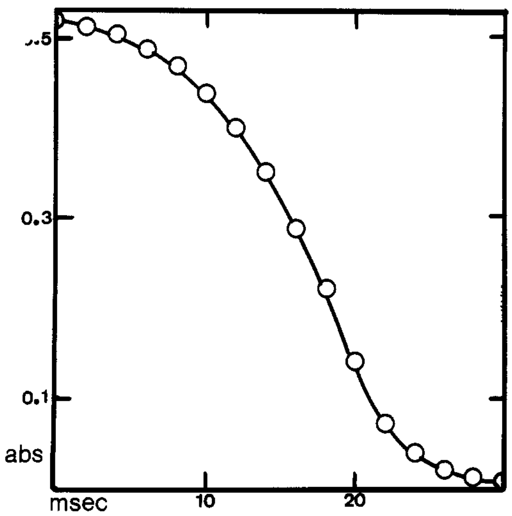

Figure 2. Typical kinetic profile (684 nm) for reaction of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ (5.0×10^{-4} M) with HSO_3^- (2.5×10^{-3} M) at 20 °C in H_2O. pH = 5.01; $\mu = 0.10$ M ($NaClO_4$). Solutions were rigorously deaerated and the oxidant stabilized with bipy–bipyH$^+$ buffer. The experimental curve (the solid line) is compared with absorbances (circles) calculated from integration of differential equations based on sequence (3), (4′), (4″), (5)-(8) in the text, taking parameters in Table 3. Extinction coefficients (M^{-1} cm^{-1}): $Mn^{III}Mn^{IV}$, 520; $(Mn^{III})_2$, 350; $Mn^{II}Mn^{III}$, 300. Optical path length = 2.0 cm.

Table 2. Kinetic Parameters for the Reduction of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ with Hydroquinone[a]

	in H_2O[b]	in D_2O[c]
k_3	$(16 \pm 3) \times 10^2$	$(4.2 \pm 0.3) \times 10^2$
k_4	$(5.8 \pm 0.8) \times 10^3$	$(2.1 \pm 0.2) \times 10^3$
k_5	4.3×10^7	1.7×10^7
k_6	1.9×10^6	0.9×10^6
k_7	1.0×10^6	3.8×10^5
k_8	5.0×10^7	1.9×10^7
$\epsilon_{Mn(3,3)}$[d]	$(2.3 \pm 0.2) \times 10^3$	$(2.3 \pm 0.1) \times 10^3$

[a] Parameters pertain to sequence (3)–(8) in text. Reactions were run at 20 °C; $\mu = 0.10$ M ($NaClO_4$); $\lambda = 350$ nm; [bipy] + [bipyH$^+$] = 0.010 M; $[Mn^{III}Mn^{IV}] = (1.70–3.80) \times 10^{-5}$ M; [HQ] = $(2.0–20.0) \times 10^{-4}$ M; k values are in M^{-1} s^{-1}. [b] pH = 4.36–5.32. [c] pD = 4.76–5.72. [d] $\epsilon_{Mn(3,3)}$ at 350 nm, in M^{-1} cm^{-1}.

observed profiles for reductions by hydroquinone are listed in Table 2. Absorbances calculated from these parameters (circles) are compared with the experimental curve in Figure 1.[31]

Data for 13 runs with HSO_3^- are correlated by a sequence very similar to (3)–(8). However, the detailed dependence on $[HSO_3^-]$ indicates that the reaction of $(Mn^{III})_2$ with HSO_3^- is subject to kinetic saturation and that for this system (4) must be replaced by the pair of steps (4′) and (4″) where $K_{4'}$ is the association

$$(Mn^{III})_2 + Red \overset{K_{4'}}{\rightleftharpoons} (Mn^{III})_2\,(Red) \qquad (4')$$

$$(Mn^{III})_2\,(Red) \xrightarrow{k_{4''}} Mn^{II}Mn^{III} + Red^{\bullet} \qquad (4'')$$

constant for the indicated addition compound, and $k_{4''}$ is the limiting (unimolecular) rate constant for electron transfer involving this adduct. Rate constants for reduction by HSO_3^-, obtained in an analogous manner, are found in Table 3. Calculated and observed profiles are compared in Figure 2.[32-34]

Table 3. Kinetic Parameters for the Reduction of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ with HSO_3^- [a]

	in H_2O[b]	in D_2O[c]
k_3, M^{-1} s^{-1}	$(2.0 \pm 0.2) \times 10^2$	1.7×10^2
$K_{4'}$, M^{-1}	$(4.5 \pm 1.0) \times 10^2$	4.5×10^2 [d]
$k_{4''}$, s^{-1}	$(2.8 \pm 0.3) \times 10^2$	2.3×10^2
k_5, M^{-1} s^{-1}	7.0×10^8	7.0×10^8
k_6, M^{-1} s^{-1}	1.0×10^7	1.0×10^7
k_7, M^{-1} s^{-1}	1.6×10^7	1.6×10^7
k_8, M^{-1} s^{-1}	8.0×10^8	8.0×10^8
$\epsilon_{Mn(3,3)}$, M^{-1} cm^{-1}	$(3.5 \pm 0.1) \times 10^2$	3.5×10^2

[a] Parameters pertain to sequence (3)–(8) in text, modified by incorporation of (4′) and (4″) in place of (4). Reactions were run at 20 °C; $\mu = 0.10$ M ($NaClO_4$); $\lambda = 684$ nm; [bipy] + [bipyH$^+$] = 0.010 M; $[Mn^{III}Mn^{IV}] = 5 \times 10^{-4}$ M throughout; $[HSO_3^-] = 0.001–0.004$ M. [b] pH = 4.39–5.28. [c] pD = 5.20. [d] Association constant, $K_{4'}$, taken to be the same in H_2O and D_2O.

Table 4. Kinetic Data for Reduction of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ with Ascorbate[a]

reactions in H_2O			reactions in D_2O		
[red], mM	pH	k, s^{-1} [b]	[red], mM	pD	k, s^{-1} [c]
0.20	4.85	24 (23)	0.50	5.25	14.0 (12.5)
0.35	4.85	39 (40)	1.00	5.25	23 (24)
0.50	4.85	60 (56)	2.0	5.25	41 (42)
0.75	4.85	83 (82)	4.0	5.25	69 (71)
1.00	4.85	104 (106)	6.0	5.25	91 (92)
1.50	4.85	145 (149)	7.5	5.25	108 (103)
2.0	4.85	195 (189)	1.00	5.37	27 (24)
1.00	4.97	105 (106)	1.00	5.48	25 (24)
1.00	5.08	110 (106)	1.00	5.69	23 (24)
1.00	5.29	100 (106)	1.00	4.89	20 (24)
1.00	4.49	101 (106)			

[a] Reactions were run at (23.0 ± 0.5) °C; $\mu = 0.10$ M ($NaClO_4$); $\lambda = 350$ nm; [bipy] + [bipyH$^+$] = 0.010 M; $[Mn^{III}Mn^{IV}] = 5.0 \times 10^{-5}$ throughout. [b] Parenthetical values were calculated using (9), taking $Q_{Ox\cdot Red} = 136$ M^{-1} and $k_{lim} = 8.8 \times 10^2$ s^{-1}. [c] Parenthetical values were calculated using (9), taking $Q_{Ox\cdot Red} = 122$ M^{-1} and $k_{lim} = 216$ s^{-1}.

Data pertaining to reductions by ascorbate are assembled in Table 4. All profiles are exponential, and there is no significant acidity dependence within the (relatively narrow) range examined. Rates are very nearly proportional to [reductant] at low concentrations of the latter, but there is a suggestion of kinetic saturation at higher concentrations. This effect becomes much more pronounced when the reactions are retarded by carrying them out in D_2O. The observed dependencies point to the formation of a complex between redox partners, reacting at a limiting rate k_{lim}, and is in accord with (9) where $Q_{Ox\cdot Red}$ designates the association quotient of the complex. Refinement, according

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(31) Rate constants for the reductions by hydroquinone (Table 2) were obtained from 13 runs each in H_2O and D_2O, with 40–60 data points taken in each run. Estimated uncertainties in k_3 and k_4 represent the range of values of these parameters giving optimum agreement between calculated and observed absorbances in the various runs. As expected, the quality of fit was much less sensitive to parameters assigned to k_5–k_8, pertaining to the later more rapid steps; agreement was perceptibly poorer when these values were increased or decreased by 25%. Absorbances of Mn^{2+}, the reductant, and the oxidation product were negligible at the wavelength used; ϵ for $Mn^{II}Mn^{III}$ were taken as less than 50% of that for $(Mn^{III})_2$. (Note also that the closeness of fit was quite insensitive to the value assigned to this parameter within the range 0 to $\epsilon_{Mn(3,3)}$.)

(32) The extended and variable induction periods observed for the Mn^{III}-Mn^{IV}–HSO_3^- reaction when deaeration was incomplete may be attributed to diversion of the $SO_3^{\bullet-}$ intermediate by traces of dissolved oxygen.

(33) The ϵ_{350} value estimated for $(Mn^{III})_2$ (2.3×10^3 M^{-1} cm^{-1}) from data pertaining to reductions with hydroquinone lies close to that reported by Sheats and co-workers[34a] (1.9×10^3) for the $(Mn^{III})_2$ complex $(Mn^{III})O(OAc)_2[HB(pz)_3]_2$, whereas ϵ_{684} from our HSO_3^- data (3.5×10^2) is somewhat greater than that reported (2.0×10^2) for analogous $(Mn^{III})_2$ complexes of triazacyclononane.[34b] Wieghardt[2b] has noted that the spectra of μ-oxo–bis(carboxylato) derivatives of $(Mn^{III})_2$ feature two intense bands near 400 and 600 nm which persist despite alterations in the remaining ligands. Note also that ϵ values reported for $Mn^{II,III}$ complexes have been found to be less than half those for the corresponding $(Mn^{III})_2$ species in the same ligand environment.[34c]

(34) (a) Sheats, J. E.; Czernuszewicz, R. S.; Dismukes, G. C.; Petrouleas, V.; Stubbe, J.; Armstrong, W. H.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 1435. (b) Hotzelmann, R.; Wieghardt, K.; Florke, U.; Haupt, H.-J.; Weatherburn, D. C.; Bonvoisin, J.; Blondin, G.; Girerd, J.-J. *J. Am. Chem. Soc.* **1992**, *114*, 1681. (c) Bodini, M. E.; Arancibia, V. *Polyhedron* **1992**, *11*, 2195.

$$k_{obsd} = (k_{lim}Q_{Ox \cdot Red}[Red])/(1 + Q_{Qx \cdot Red}[Red]) \quad (9)$$

to (9), of data taken in H_2O yields $k_{lim} = (8.8 \pm 1.3) \times 10^2$ s^{-1} and $Q_{Ox \cdot Red} = (1.36 \pm 0.22) \times 10^2$ M^{-1}, whereas the analogous treatment for data in D_2O gives $k_{lim} = (2.16 \pm 0.20) \times 10^2$ s^{-1} and $Q_{Ox \cdot Red} = (1.22 \pm 0.15) \times 10^2$ M^{-1}. As expected, the Q value is very nearly the same in the two solvents. Observed rates are compared to those calculated from the indicated parameters in this table. Further data concerning the solvent kinetic isotope effect on this reaction appear in Table 5, which summarizes rates observed in a series of H_2O-D_2O mixtures.

Discussion

The sequences proposed for reductions of our $Mn^{III}Mn^{IV}$ oxidant, both with hydroquinone and with HSO_3^-, are consistent with estimated stoichiometries and also accommodate the kinetic profiles observed for these conversions. The increases in rates as reactions proceed point to an autocatalytic process. However, since the final products are shown to be devoid of catalytic activity, the catalyst must be consumed in subsequent steps. In the suggested mechanisms, the intermediate designated $(Mn^{III})_2$ assumes a catalytic role, and its action is associated with intervention of the odd electron species, Red• (semiquinone or $SO_3^{\bullet -}$). In both systems the 1e⁻ reduction of $(Mn^{III})_2$ (k_4) is more rapid[35] than that of the starting reagent, $Mn^{III}Mn^{IV}$ (k_3), but in both cases Red• then reacts more rapidly with $Mn^{III}Mn^{IV}$ (k_5) than with $(Mn^{III})_2$ (k_6). Since (5) regenerates $(Mn^{III})_2$, there is a net increase in the latter until all of the $Mn^{III}Mn^{IV}$ is consumed. Catalysis of this type reflects a reversal of kinetic selectivities; i.e., the ratio $k_{3,3}/k_{4,3}$ exceeds 1.0 for both reductants but falls well below unity for the derived radical intermediates, a situation closely analogous to the autocatalytic reductions of carboxylate chelates of Cr(V) to Cr(III) with the same reagents,[36] each of which has been shown to proceed through a Cr(IV) intermediate.

Reductions by HSO_3^- appear to differ from those by hydroquinone principally by inclusion of the indicated preequilibrium step, (4′), at the $(Mn^{III})_2$ level. Although the calculated association quotient (4.5×10^2 M^{-1}) for this step is somewhat greater than may be attributed to simple outer-sphere interaction,[37] it may be that the $(Mn^{III})_2$–HSO_3^- adduct, as well as that formed from $Mn^{III}Mn^{IV}$ and ascorbic acid ($Q = 1.4 \times 10^2$), is further stabilized by hydrogen bonding involving one of the μ-oxo bridges.

Kinetic patterns for reductions by ascorbate are much simpler and therefore less instructive. The observed exponential profiles, along with the absence of any absorbance drops immediately after mixing, tell us simply that rates with this reagent are determined jointly by the reversible formation the $Mn^{III}Mn^{IV}$-ascorbate adduct and the first electron transfer act. Subsequent steps are rapid and therefore kinetically silent. In compensation, however, experiments dealing with solvent isotope effects are most informative with this reductant.

Variations in rate resulting from substitution of D_2O for solvent H_2O are expected to be slight for simple electron transfer reactions.[38] However, as pointed out by Albery[38] and, more specifically, by Binstead and Meyer,[39] much more dramatic effects will come into play when such transfer is coupled with the movement of a proton which is in equilibrium with solvent protons.[40]

Table 5. Rates for Reduction of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ with Ascorbate in H_2O–D_2O Mixtures[a]

mole % D_2O	k, s^{-1}	mole % D_2O	k, s^{-1}
0	60	75	27
25	49	100	14.0
50	39		

[a] Reactions were run at (23.0 ± 0.3) °C, $\mu = 0.10$ M ($NaClO_4$; $\lambda = 350$ nm; [bipy] + [bipyH⁺] = 0.010 M; $[Mn^{III}Mn^{IV}] = 5.0 \times 10^{-5}$ M; [ascorbate] = 5.0×10^{-4} M; $pH_{measured} = 4.85 \pm 0.01$.

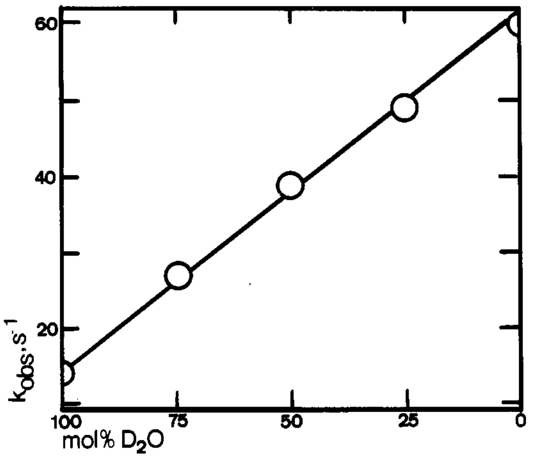

Figure 3. Reduction of $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ (5.0×10^{-5} M) with ascorbate (5.0×10^{-4} M) at 23 °C. Variation of reaction rate with isotopic composition of H_2O–D_2O mixtures. Observed pseudo-first-order rates are plotted vs mole fraction D_2O in solvent mixture. $pH_{measured} = 4.85 \pm 0.01$; $\mu = 0.10$ M. The oxidant solution was stabilized using bipy–bipyH⁺ buffer; [bipy] + [bipyH⁺] = 0.010 M. The regression line shown corresponds to the equation $k_{obs} = k_{D_2O} + k_{H_2O}(1 - f_{D_2O})$, where $k_{D_2O} = 14.2 \pm 0.4$ s^{-1} and $k_{H_2O} = 47.3 \pm 1.4$ s^{-1}.

Since a substantial isotope effect ($k_{H_2O}/k_{D_2O} = 4.0$) has been found to be associated with the initial redox step in the Mn^{III}-Mn^{IV}–ascorbate reaction (but not with the preassociation equilibrium), we may then infer that electron transfer from this reductant (to Mn) is nearly simultaneous with proton transfer (to ligated oxygen). Note also that the plot of k_{obsd} vs mole fraction of D_2O (Figure 3) is closely linear, a feature which has been shown to be characteristic of the transfer of just a single proton in the redox act.[41] Interestingly, both the magnitude of the isotope effect and the linearity of the plot of k vs f_{D_2O} correspond closely to the analogous features observed when the $Mn^{III}Mn^{IV}$ complex is reduced electrolytically using an edge-oriented pyrolytic graphite electrode.[42]

Each of the six steps in the proposed sequence for the Mn^{III}-Mn^{IV}-hydroquinone reaction (Table 2) is significantly retarded in D_2O ($k_{H_2O}/k_{D_2O} > 2$). The effect appears to be somewhat more pronounced for those steps (k_3, k_4, and k_7) involving hydroquinone itself rather than the semiquinone intermediate, suggesting that stretching of the O–H bond in the aromatic reductant contributes slightly less to the activation processes for reductions by the radical.

The reduction by bisulfite exhibits only a slight solvent isotope effect, with respect both to the overall conversion, and to individual

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(35) An estimated bimolecular rate constant for reaction of $(Mn^{III})_2$ with HSO_3^-, applicable at low concentrations of the latter, is 1.3×10^5 M^{-1} s^{-1}, obtained by multiplying K_4 (in Table 3), by $k_{4''}$.

(36) (a) Bose, R. N.; Rajasekar, N.; Thompson, D. M.; Gould, E. S. *Inorg. Chem.* **1986**, *25*, 3349. (b) Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Ibid.* **1988**, *27*, 1620.

(37) See, for example: Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, **1967**; p. 34.

(38) Albery, J. In *Proton Transfer Reactions*; Caldin, E., Gold, V.; Eds.: Wiley-Interscience: New York, 1975; Chapter 9.

(39) Binstead, R. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3287.

(40) Typically, the comproportionation reaction between ligated $[Ru^{IV}O]^{2+}$ and $[Ru^{II}(OH_2)]^{2+}$ species has been found[37] to exhibit an isotope effect, k_{H_2O}/k_{D_2O} of 16.1 at 25 °C, whereas the corresponding rate ratio approaches 20 for reduction of the same Ru(IV) complex with hydroquinone.[21]

(41) Albery, W. J.; Davies, M. H. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 167.

(42) (a) Manchanda, R.; Thorp, H. H.; Brudvig, G. W.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 494. (b) Kalsbeck, W. A.; Thorp, H. H.; Brudvig, G. W. *J. Electroanal. Chem.* **1991**, *314*, 335.

steps (Table 3). Proton transfer from S(IV), which is part of the net transformation, has therefore been decoupled from electron exchange in this instance. If such a transfer were to occur in a preliminary equilibrium, it would be reflected in a kinetic $[H^+]$-dependency, which is, however, not observed. It therefore must take place after the redox act(s).

In sum, our experiments have shown that the solutions of the PS II model, $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$, when properly stabilized, are reduced rapidly to $Mn^{2+}(aq)$, in a net transfer of $3e^-$ by ascorbate, hydroquinone, and HSO_3^-. Rates with ascorbate are determined by the initial redox step, whereas profiles with hydroquinone and HSO_3^- are in accord with six- and seven-step sequences, each involving catalysis by a $(Mn^{III})_2$ intermediate and the participation of radical species derived from the reductants. Electron and proton transfers appear to be coupled for the reactions with ascorbate and hydroquinone, but not for reduction by HSO_3^-. Thus, the capacity of the $Mn^{III}Mn^{IV}$ complex examined to undergo successive 1e changes, coupled with proton transfer, indicates that in its kinetic behavior, as well as in its structural features, it may be considered one of the more instructive models at hand for PS II.

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