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Oxidation of N^{III} and N^{-I} by an $\{Mn_4O_6\}^{4+}$ Core in Aqueous Media: Proton-Coupled Electron Transfer

Suranjana Das[a] and Subrata Mukhopadhyay*[a]

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$[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ ($\mathbf{1}^{4+}$; bipy = 2,2′-bipyridine) and its conjugate acid $[Mn_4(\mu\text{-}O)_5(\mu\text{-}OH)(bipy)_6]^{5+}$ ($\mathbf{1}H^{5+}$) quantitatively oxidise N^{III} (HNO_2 and NO_2^-) and N^{-I} (NH_3OH^+ and NH_2OH) to N^V (nitrate) and N^I (nitrous oxide), respectively, in aqueous solution (pH 2.0–6.0), with $\mathbf{1}H^{5+}$ reacting much faster than $\mathbf{1}^{4+}$. An uncommon feature of these reactions is the kinetic superiority of HNO_2 over its conjugate base NO_2^-. NH_2OH, however, behaves normally – the conjugate acid NH_3OH^+ is less reactive than NH_2OH. These reactions show remarkable kinetic isotope effects: the observed rate of N^{III} oxidation increases in D_2O media whereas the N^{-I} oxidation rate slows down in media enriched with D_2O. A search of the available data on the redox kinetics of multinuclear oxidants suggests that the title $\{Mn_4O_6\}^{4+}$ reduction by N^{III}, the rate of which is accelerated in D_2O, is the only one established so far. A hydrogen atom transfer (HAT) mechanism (1e, $1H^+$; electroprotic) is proposed.

Introduction

The oxygen-evolving complex (OEC)[1–5] oxidises water to molecular dioxygen in photosystem II (PS II) at the redox catalytic centre on the lumenal side of PS II, which includes four manganese ions, a calcium ion and a chloride ion.[6,7] The OEC cycles over five redox states S_0–S_4, where the index refers to the number of oxidising equivalents stored;[8,9] dioxygen is evolved in the $S_4 \rightarrow S_0$ transition.

Successive changes in the redox states of the Mn atoms in the OEC during this cycle are associated with protonation/deprotonation of the oxo bridges[10] and of the nearby amino acid residues as well as the simultaneous movements of proton and electrons within the OEC.[11]

The acid/base chemistry resulting from oxo-bridge protonations in synthetic multinuclear Mn complexes has been studied mostly in non-aqueous media.[12] It has also been demonstrated that oxo-bridge protonation sometimes increases the reactivity of a binuclear Mn oxidant[12d,12e] and completely quenches the catalase activity of an Mn^{IV} dimer.[12c] How such protonations affect the chemical behaviour of higher-valent synthetic Mn complexes is not known, despite the relevance of such knowledge to PS II. This is particularly true in water, the medium where PS II acts.

The title complex $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ ($\mathbf{1}^{4+}$; Figure 1) formally corresponds to the fully oxidised S_3 or S_4 state of OEC[2] [although involvement of an even higher state (Mn^V) is feasible in the water oxidation process],[13] which is stable in aqueous solution over a wide acidity range (pH 2.0–6.0). Its one-electron-reduced, mixed-valent $Mn^{IV}{}_3Mn^{III}$ form is an EPR spectroscopic model for the S_2 state,[14] which means that the electron-transfer reactivity of the title Mn tetramer will thus be instructive.

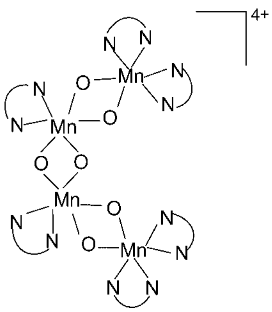

Figure 1. Schematic drawing of $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$. N-N = 2,2′-bipyridine.

We demonstrated recently that $\mathbf{1}^{4+}$ oxidises glyoxylic and pyruvic acid through an electroprotic mechanism and that the oxo-bridged protonated species $\mathbf{1}H^{5+}$ is a kinetically superior oxidant to $\mathbf{1}^{4+}$.[15] It therefore seemed worthwhile to investigate whether the relative acidities of the reducing agents influence the proton-coupled electron transfer mechanism as well as the reactivity of the oxo-bridged protonated oxidant. The present investigation was thus planned with two selected reducing agents, namely HNO_2 and NH_3OH^+ (and their conjugate bases), which have a sufficient separation in their pK_a values.[16,17] We further note that hydroxylamine[18] reduces the Mn ions in PS II whereas nitrite does not.[19]

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[a] Department of Chemistry, Jadavpur University,
Calcutta 700 032, India
E-mail: smukhopadhyay@chemistry.jdvu.ac.in

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Results and Discussion

Equilibrium Measurements

The measured pK_a values of these reducing acids in a 95% D_2O medium are 3.80 ± 0.10[20,21] and 6.40 ± 0.10 for nitrous acid and hydroxylammonium cation respectively. The reported pK_a values used in this investigation for HNO_2 and NH_3OH^+ in an H_2O medium are 3.00[16] and 6.00,[17] respectively. All the pK_a values are at 25.0 °C, I = 1.0 M ($NaNO_3$). The pH-metric titration of the title tetranuclear Mn oxidant, however, did not result in any ionisation constant in the pH interval 2.0–7.0.

Stoichiometric Analyses

Nitrate (NO_3^-) was detected as the oxidation product of nitrite whereas no red colouration was observed when the product solutions of the redox reaction of hydroxylamine were tested for nitrite or nitrate. The results of several stoichiometric experiments, under both kinetic ($T_R > 4[Mn^{IV}_4]$) and non-kinetic conditions ($T_R < 4[Mn^{IV}_4]$), are summarised in Table 1, which establishes a 1:4 stoichiometry (oxidant:reductant) for both the redox reactions, where T_R is the analytical concentration of the reducing agent defined as $T_R = [HNO_2] + [NO_2^-]$ for $[N^{III}]_T$ and $T_R = [NH_3OH^+] + [NH_2OH]$ for $[N^{-I}]_T$. The title Mn tetramer is not a powerful oxidant (see below) and it is clear from the ratio $\Delta[Mn^{IV}_4]/\Delta[T_R]$ (Table 1) that N_2O is the sole oxidation product of hydroxylamine – no further oxidation of N_2O to nitrite or nitrate was observed. The results of EDTA titrations of the product solutions revealed quantitative formation of Mn^{II} as the sole reduction product of Mn^{IV}. The likely Mn^{II} species under these reaction conditions is an Mn^{II}-bipy complex.[22] Optical spectra for the product solutions were superimposable on those of mixtures of $Mn(NO_3)_2$ and 2,2′-bipyridine under similar experimental conditions. Equations (1) and (2) are thus closest to our above observations.

$$[Mn_4O_6(bipy)_6]^{4+} + 4\,NO_2^- + 4\,H^+ \longrightarrow 4\,Mn^{2+} + 4\,NO_3^- + 6\,bipy + 2\,H_2O \quad (1)$$

$$[Mn_4O_6(bipy)_6]^{4+} + 4\,NH_2OH + 4\,H^+ \longrightarrow 4\,Mn^{2+} + 2\,N_2O + 6\,bipy + 8\,H_2O \quad (2)$$

Table 1. Stoichiometry of reduction of the Mn^{IV}_4 complex by N^{III} and N^{-I} (T = 25.0 °C, C_{bipy} = [Hbipy$^+$] + [bipy] = 3.0 mM).

$[Mn^{IV}_4]$ [mM]	pH	$[N^{III}]_T$ (= T_R) [mM]	$[N^{-I}]_T$ (= T_R) [mM]	$\Delta[Mn^{IV}_4]/\Delta[T_R]$
0.20	3.3	1.50		0.27
0.40	3.6	2.00		0.26
0.60	5.6	3.50		0.23
1.50	5.5	10.0		0.26
0.10	3.5	0.20		0.24
				average = 0.25 ± 0.02
0.20	2.5		2.00	0.23
0.50	4.5		4.00	0.24
0.80	5.0		6.00	0.27
1.30	5.3		10.0	0.23
0.20	5.1		0.60	0.23
				average = 0.24 ± 0.02

Kinetics

The decay in absorbance vs. time plots could be fitted with standard first-order decay curves at least up to three half-lives. The observed first-order rate constants (k_0) do not depend on the wavelength chosen for the measurements (380–500 nm) where only the oxidant absorbs sufficiently, the presence or absence of dissolved oxygen in the reaction medium or on the concentration of the Mn oxidant (0.05–0.30 mM). Averages of k_0 values from at least three measurements were taken and the average coefficients of variation (CV)[23] for these measurements were within 3%. The observed proton-dependences of k_0 in these two redox reactions is interesting (Table 2). For nitrite oxidation, k_0 values increase with an increase in acidity of the reaction medium whereas they decrease with increasing acidity for hydroxylamine oxidation until the very low pH region, where k_0 increases with a decrease in pH. We can suppose a superior kinetic reactivity of HNO_2 over NO_2^- from these trends whereas NH_2OH is superior to NH_3OH^+. However, the title complex (**1**$^{4+}$) may suffer protonation at very low pH, as was evident from its reaction with α-keto acids.[15] The species formed (**1**H^{5+}) may act as an additional oxidant in the low pH region despite being present in only a low concentration. Protonated oxidants always react quicker than their conjugate bases[24] within a system, and thus **1**H^{5+} is expected to react faster than **1**$^{4+}$. We measured several k_0 values in the presence of varying amounts of added bipy over the entire pH range for both the redox reactions. The lack of influence of added bipy on the observed rate of either reaction at any acidity rules out the possibility of bipy dissociation from the parent Mn complex in solution. We observed a linear variation of k_0 with T_R in the entire pH range studied and found no indication of rate saturation even at the highest T_R studied. Table 2 collects some representative k_0 values.

A strong pre-equilibrium (K) binding of the reducing species with the title oxidant followed by reaction of the intermediate thus formed with a second reducing species would lead to the observed kinetics (linear dependence of k_0 on T_R) provided that KT_R is much greater than 1, which requires a K value as high as 10^4 (lowest $T_R = 5.0 \times 10^{-3}$ M). However, the tetranuclear Mn oxidant is coordinatively saturated at each Mn centre and an inner-sphere attachment of reducing species seems unlikely. Moreover, d^3 Mn^{IV} is substitution inert and the oxidant retains its bipy ligands in aqueous solution in the entire pH range studied (see above), which means there is no scope for the formation of the aqua species that could lead to an inner-sphere mechanism in solution. We thus disregard this kind of pathway in the kinetics of the title redox reaction. The observed proton-

Table 2. Some representative first-order rate constants for the oxidation of nitrite and hydroxylamine by the title complex (0.10 mM) at T = 25.0 °C, I = 1.0 M ($NaNO_3$). The values in parentheses are calculated from Equation (9) using the rate constants reported in Table 3.

pH	T_R [M]	C_{bipy} [mM]	10^4k_0 [s^{-1}]
Nitrite			
2.50	0.05	3.0	491 (500)
2.82	0.05	3.0	197 (202)
3.14	0.05	3.0	74.0 (76.6)
3.78	0.05	3.0	11.2 (10.4)
4.18	0.05	3.0	3.44 (3.34)
4.75	0.05	3.0	0.74 (0.78)
5.15	0.05	3.0	0.28 (0.30)
5.56	0.05	3.0	0.11 (0.11)
4.69	0.025	3.0	0.43 (0.45)
4.69	0.075	3.0	1.39 (1.35)
4.67	0.10	3.0	1.81(1.89)
4.15	0.05	20	3.66 (3.62)
4.13	0.05	50	3.81 (3.82)
4.13	0.05	80	4.03 (3.82)
3.22	0.05	20	57.8 (59.6)
3.24	0.05	50	58.9 (56.0)
3.23	0.05	80	59.2 (57.8)
4.71	0.05	3.0	1.06[a]
4.70	0.05	3.0	1.39[b]
2.51	0.05	3.0	496 [a]
2.53	0.05	3.0	499 [b]
Hydroxylamine			
2.04	0.01	5.0	3.60 (3.58)
2.37	0.01	5.0	1.95 (1.92)
3.02	0.01	5.0	0.79 (0.84)
3.20	0.01	5.0	0.73 (0.76)
3.42	0.01	5.0	0.74 (0.74)
4.00	0.01	5.0	1.19 (1.12)
4.41	0.01	5.0	1.98 (2.10)
4.84	0.01	5.0	4.52 (4.69)
5.35	0.01	5.0	12.2 (12.4)
6.00	0.01	5.0	32.0 (32.2)
3.61	0.02	5.0	1.51 (1.58)
3.62	0.04	5.0	3.23 (3.18)
3.61	0.10	5.0	7.79 (7.90)
4.11	0.01	1.0	1.21 (1.30)
4.10	0.01	10	1.23 (1.28)
4.13	0.01	20	1.29 (1.34)
4.12	0.01	40	1.37 (1.32)
4.12	0.01	60	1.42 (1.32)
5.95	0.01	5.0	30.1[a]
5.93	0.01	5.0	30.5[b]
2.11	0.01	5.0	2.61[a]
2.12	0.01	5.0	2.08[b]
3.60	0.01	5.0	1.22[a]
3.62	0.01	5.0	1.05[b]

[a] I = 0.5 M ($NaNO_3$). [b] I = 0.1 M ($NaNO_3$).

dependence of k_0 on [H^+] could not be fitted to any type of reaction scheme with only one protic equilibrium, which means that Equations (3) and (4) need to be considered simultaneously, as shown in Scheme 1 for both the reactions under investigation.

Scheme 1 leads to the rate law in Equation (9), assuming that $K_1[H^+]$ is much less than 1. This scheme does not take into account any protonation equilibrium of HNO_2[25] to generate NO^+ [Equation (10)] or a disproportionation equilibrium of HNO_2[26] to generate NO and NO_2 [Equation (11)]. A reaction path involving NO would require an $[HNO_2]^2$ term in the rate law and NO^+ requires a third-order term $[Mn^{IV}{}_4][HNO_2][H^+]$. The equilibrium constants of these reactions are small, which might be the main reason for not obtaining the reactivities, if any, of these species. We therefore used $[N^{III}]_T = [HNO_2] + [NO_2^-]$. Except for NH_2OH and NH_3OH^+, no other pH-dependent N^{-I} species are known.

$$1^{4+} + H^+ \xrightleftharpoons{K_1} 1H^{5+} \qquad (3)$$

$$RH \xrightleftharpoons{K_a} R^- + H^+ \qquad (4)$$

$$1H^{5+} + RH \xrightarrow{k_1} \text{products} \qquad (5)$$

$$1H^{5+} + R^- \xrightarrow{k_2} \text{products} \qquad (6)$$

$$1^{4+} + RH \xrightarrow{k_3} \text{products} \qquad (7)$$

$$1^{4+} + R^- \xrightarrow{k_4} \text{products} \qquad (8)$$

Scheme 1. (RH = HNO_2 or NH_3OH^+).

$$k_0(K_a + [H^+])/T_R = k_1K_1[H^+]^2 + (k_2K_1K_a + k_3)[H^+] + k_4K_a \qquad (9)$$

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O \qquad K = 3.0 \times 10^{-7} \qquad (10)$$

$$2\,HNO_2 \rightleftharpoons NO + NO_2 + H_2O \qquad K = 6.0 \times 10^{-6} \qquad (11)$$

Plots of the left-hand side of Equation (9) resulted in a good polynomial fit of [H^+] for both redox reactions (Figure 2, r > 0.98), from which we obtain k_1K_1, $(k_2K_1K_a + k_3)$

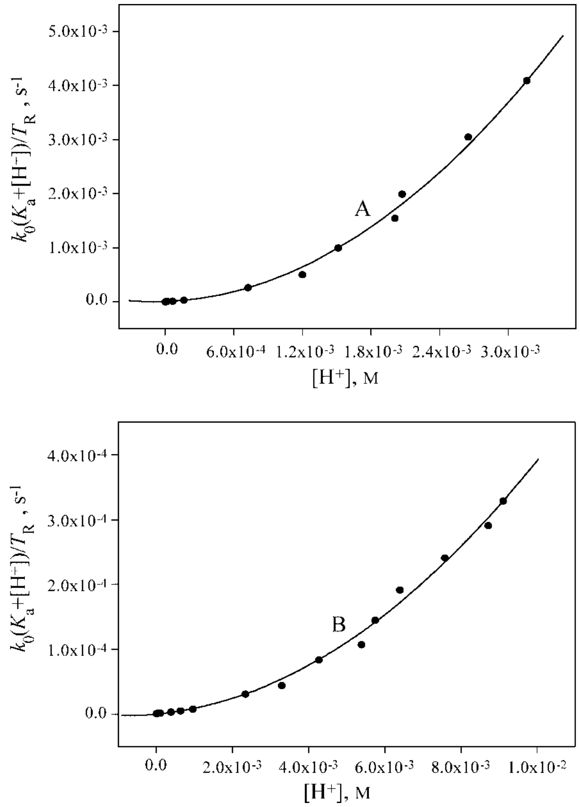

Figure 2. Plot of the left-hand side of Equation (9) vs. [H^+]. [complex] = 0.10 mM, T = 25.0 °C, I = 1.0 M. A: N^{III}, C_{bipy} = 3.0 mM; B: N^{-I}, C_{bipy} = 5.0 mM.

Table 3. Rate constants for the reduction of $\mathbf{1}^{4+}$ by nitrite and hydroxylamine at T = 25.0 °C, I = 1.0 M ($NaNO_3$).

	k_1K_1 [$M^{-2}s^{-1}$]	$k_2K_1K_a + k_3$ [$M^{-1}s^{-1}$]	k_4 [$M^{-1}s^{-1}$]
H_2O medium N^{III}	390 ± 20	$(8.2 \pm 0.5) \times 10^{-2}$	0
H_2O medium N^{-I}	3.43 ± 0.20	$(4.4 \pm 0.3) \times 10^{-3}$	$(6.6 \pm 0.4) \times 10^{-1}$
95% D_2O medium N^{III}	760 ± 45	$(5.0 \pm 0.3) \times 10^{-2}$	0
95% D_2O medium N^{-I}	0.65 ± 0.04	$(1.9 \pm 0.1) \times 10^{-4}$	$(5.5 \pm 0.3) \times 10^{-2}$

and k_4 (see Table 3). The non-existence of the k_4 path for the nitrite redox reaction, as determined by the above second-order polynomial, was further confirmed by plotting $k_0(K_a + [H^+])/(T_R[H^+])$ against $[H^+]$ (see electronic supporting information), which resulted in a good straight line ($r > 0.98$) with slope k_1K_1 and intercept $(k_2K_1K_a + k_3)$, in close agreement (within 5%) with the values reported in Table 3. On the other hand, the k_4 path was found to be significant for hydroxylamine redox above a pH of about 4, and a plot of T_R/k_0 against $[H^+]$ yielded a good straight line with slope $1/k_4$ and intercept $1/(k_4K_a)$ at pH ≥ 5.3 (see electronic supporting information). The value of k_4 determined in this way matches well with the values reported in Table 3.

It cannot be concluded, however, that, as $\mathbf{1}^{4+}$ does not react with NO_2^- (the k_4 path does not contribute to the overall rate), $\mathbf{1}H^{5+}$ would not oxidise NO_2^-. Protonated metal complexes are superior oxidants than their deprotonated analogues[20,24] and a finite contribution of k_2 path may therefore be anticipated, although kinetic resolution of the proton-ambiguous k_2 and k_3 paths is not possible. We also note that the k_1 path starts contributing towards the observed rate at pH ≤ 5.0 for the N^{III} redox reaction whereas for the N^{-I} redox reaction a more acidic environment is needed to ensure a finite contribution of the k_1 path (pH ≤ 4.0), as judged by the values of $k_1K_1[H^+]^2$ and $(k_2K_1K_a + k_3)[H^+]$ for both redox reactions at these pHs. Below pH 3.0, hydroxylamine is almost quantitatively present as cationic NH_3OH^+, whose oxidation by $\mathbf{1}H^{5+}$ is electrostatically more unfavourable than the oxidation of NH_2OH. Oxidation of cationic NH_3OH^+ requires higher concentrations of $\mathbf{1}H^{5+}$, which are produced at much lower pH than that required for the oxidation of neutral HNO_2 purely on charge grounds.

It should be noted here that a scheme comprising only HNO_2 as the active reducing species reacting with $\mathbf{1}H^{5+}$ (k_1) and $\mathbf{1}^{4+}$ (k_1') is an alternative to Scheme 1 and results in k_1K_1 and k_1' values identical to those reported in Table 3 (k_1' is similar to k_3 in Scheme 1, assuming the k_2 path is absent). However, this alternative cannot confirm the absence of the k_2 path in the nitrite redox reaction. The rate constants measured in presence of varying amounts of added $NaNO_3$ might be instructive here. At pH 4.7 (where $[NO_2^-] >> [HNO_2]$), k_0 increases substantially with a decrease in ionic strength of the reaction medium (Table 2), which indicates a reaction between opposite charges, therefore a finite contribution of the k_2 path may thus be anticipated ($\mathbf{1}H^{5+}$ is a stronger oxidant than $\mathbf{1}^{4+}$ and the k_4 path is absent in N^{III} oxidation), while at pH 5–6 the value of k_0 remains unaltered in the range I = 1.0–0.1 M ($NaNO_3$) for the N^{-I} redox reaction (Table 2), in line with the maximum contribution of the uncharged NH_2OH path (k_4) towards the overall rate at the highest pH extreme. Around pH 2.5, where $[HNO_2]$ is much greater than $[NO_2^-]$, the rate of the nitrite redox reaction was found to be independent of any variation in the ionic strength of the medium (Table 2), whereas at pH 2.1 or 3.6, where $[NH_3OH^+]$ is much greater than $[NH_2OH]$, the rate of hydroxylamine oxidation decreases significantly with decreasing ionic strength of the medium (Table 2). These observations qualitatively support the involvement of neutral HNO_2 and cationic NH_3OH^+ as reactive species with cationic $\mathbf{1}^{4+}$ or $\mathbf{1}H^{5+}$.

We can estimate K_1 to be between 10^{-9} and 10 from the fact that $K_1[H^+]$ is much less than 1 and the k_1K_1 values listed in Table 3. The fact that $K_1[H^+]$ is much less than 1 sets an upper limit for the pre-equilibrium binding of nearly 10 as the maximum $[H^+]$ used in this study is 10^{-2} M. Assuming the diffusion-controlled limit is 10^{11} $M^{-1}s^{-1}$, the lower limit of K_1 derived from the k_1K_1 values in Table 3 is around 10^{-9}. For comparison, we note that the reported pK_a of the analogous complex $[Mn^{IV}_4(\mu\text{-}O)_5(\mu\text{-}OH)(bpea)_4]^{5+}$ [bpea = *N*,*N′*-bis(2-pyridylmethyl)ethylamine] is –6,[12h] which shows that the bridging oxo group is much less basic. The strong acidity of the protonated oxo-bridge may thus be inferred. The Mn tetramer used here does not undergo any spectral change in the pH range 2.0–6.0 therefore spectral evaluation of its basicity was not possible.

It appears from Table 3 that the maximum value of k_3 is 4.4×10^{-3} $M^{-1}s^{-1}$ for N^{-I} oxidation while it is 8.2×10^{-2} $M^{-1}s^{-1}$ for N^{III} oxidation. The reactivity of NH_2OH is higher than NH_3OH^+ as the rate increases with pH while it decreases with an increase in pH for the N^{III} redox reaction. The maximum value of k_2K_1 for this latter reaction is 82 (much lower than k_1K_1), which clearly indicates that HNO_2 reacts much quicker with $\mathbf{1}H^{5+}$ or $\mathbf{1}^{4+}$ than NO_2^-. The overwhelming dominance of the reactivity of $\mathbf{1}H^{5+}$ is clear in both redox reactions.

Mechanism

The electrochemistry of $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ has been extensively studied by Dunand-Sauthier et al.[27] The cyclic voltammogram of $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ in bipy/Hbipy$^+$

buffer shows only an irreversible reduction peak near 0.40 V (vs. Ag/AgCl) which leads to the formation of $[Mn(bipy)_3]^{2+}$ species.[27] Attempts at electrolytic reduction resulted in decomposition of the tetranuclear complex into four Mn^{II} ions. Standard chemical reduction in solution also failed to achieve the monoreduced form $[Mn^{IV}{}_3Mn^{III}(\mu\text{-}O)_6(bipy)_6]^{3+}$.[14] Exhaustive reduction of $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ at 0.20 V (vs. Ag/AgCl) consumes almost eight equivalent of electrons per mole of the tetranuclear oxidant and leads to Mn^{II}.[27a] These authors have also shown an intermediate generation of the mixed-valent $[Mn^{III,IV}(\mu\text{-}O)_2(bipy)_4]^{3+}$ species during the conversion to Mn^{II}. This mixed-valent species could not, however, be generated selectively and quantitatively as the reduction of the tetranuclear and the mixed-valent species occurs at a very similar potential (approx. 0.4 V vs. Ag/AgCl).[27] We did not observe formation of any such spectrally characterisable binuclear intermediate during the chemical reduction of the title oxidant when reducing agents were used in either excess, deficit or stoichiometric amounts, see Equations (1) and (2).

We can conclude from the known electrochemical behaviour of the title tetranuclear Mn comlex that this species is not a powerful oxidant. The one-electron oxidation of NO_2^- or HNO_2 and NH_2OH or NH_3OH^+ is, however, highly endothermic. The one-electron oxidation potentials for NO_2^-/NO_2, HNO_2/NO_2, H^+, NH_2OH/NH_2OH^+ and NH_3OH^+/NH_2OH^+, H^+ couples are –1.04,[26] –1.22,[28] –0.91[29] and –1.30 V respectively.[28] An initial one-electron exchange between $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ and these reducing species is thus energetically unfavourable although we observe that these reducing agents smoothly reduce the Mn^{IV} oxidant to Mn^{II}. An inner-sphere attachment of the reducing species to the Mn^{IV} centres that could provide an alternative pathway is not likely as the d^3 Mn^{IV} atoms in the coordinatively saturated oxidant are substitution inert. However, it can be concluded from the known electrochemical behaviour of the tetranuclear Mn oxidant that the intermediate mixed-valent forms are too reactive. In fact, the very high reactivity of the most likely one-electron reduced species produced by cryogenic radiolytic reduction of $\mathbf{1}^{4+}$, namely $[Mn^{IV}{}_3Mn^{III}(\mu\text{-}O)_6(bipy)_6]^{3+}$, has been documented.[30] This species is very unstable even at low temperature (190 K).[30]

In order to further explore the electron-transfer mechanism we measured k_0 values in media enriched with D_2O and computed the second-order rate constants or their composites (Table 3) in the same way as in pure H_2O media; they showed kinetic isotope effects. Interestingly, we also note that the k_1K_1 path in N^{III} oxidation increases substantially in D_2O media whereas all the other rate constants or their composites decrease. A lowering of the rate in D_2O media is clearly indicative of an electroprotic mechanism.[31] Notably, we also found that the rate enhancement and rate decrease in H_2O/D_2O mixtures for N^{III} and N^{-I} oxidations, respectively, are linearly related ($r > 0.98$) to the D_2O content (Figure 3), which suggests transfer of a single proton in the slow steps.[32]

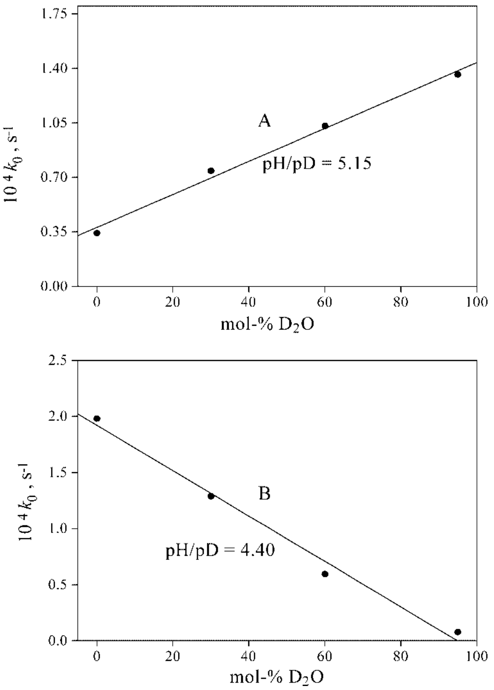

Figure 3. Effect of the amount of D_2O (mol-%) on k_0. [complex] = 0.10 mM, T = 25.0 °C, I = 1.0 M. A: N^{III}, $[N^{III}]_T$ = 0.05 M, C_{bipy} = 3.0 mM; B: N^{-I}, $[N^{-I}]_T$ = 0.01 M, C_{bipy} = 5.0 mM.

An initial one-electron transfer rate-limiting step in the overall eight electron transactions [Equations (5)–(8)] is proposed to result in the intermediate mixed-valent Mn species $Mn^{IV}{}_3Mn^{III}$, which is likely to be reduced quickly in the following steps by the excess reducing agents or the radicals generated at the rate-determining step. We did not observe any polymerisation in either redox reaction when the reactions were carried out in 6% v/v acrylonitrile, although this does not rule out the production of radicals as they may react faster with the one-electron reduced mixed-valent Mn species, which is itself very reactive.[30] The one-electron reduced species of $\mathbf{1}^{4+}$ or $\mathbf{1}H^{5+}$ would have much more basic oxo bridges that immediately accept a proton from the reaction medium, which could remove thermodynamic or kinetics barriers to further reduction.[33] A large increase in the basicity of oxo bridges after one-electron reduction of the bridge carrying higher valent Mn atoms in di- or polynuclear Mn complexes is well documented[34] and is a key feature in the redox steps of the Kok cycle in PS II.[1c,35] Radicals produced from one-electron oxidation of nitrite and hydroxylamine, namely NO_2 and NH_2OH^+, are well-documented in the literature and pathways leading to the formation of nitrate[16b,36] and nitrous oxide[37] are well-established facets of nitrogen chemistry.

It has been known for a long time that rate increases significantly with D_2O content in an H_2O/D_2O mixture if acid/base pre-equilibrium steps are involved prior to the rate-determining step.[38a–38c] D_2O has a smaller autoprotolysis constant than H_2O by a factor of about 5 and thus it is less basic than water,[38a] which means that the oxo bridges in the title oxidant will be able to compete with the solvent for the deuteron in D_2O more effectively than for the proton in H_2O. An increase in the K_1 value in D_2O is thus expected. In general, weak acids in H_2O become much weaker in D_2O,[38] and we found that reducing acids like glyoxylic, pyruvic, nitrous and hydroxylammonium cation have considerably higher pK_a's in D_2O.[15,20,21] We can thus reasonably expect a higher concentration of $\mathbf{1}H^{5+}$ in D_2O and the observed reversal in the rate constants k_1K_1 in the two redox reactions might be a result of competitive increase in the K_1 value and a decrease in the k_1 value (electroprotic mechanism).

It has been shown recently[39] that an inverse deuterium isotope effect ($k_H < k_D$) is observed during charge recombination between the fully reduced $FADH^-$ anion (FAD = flavin adenine dinucleotide) and the neutral (deprotonated) radical of the solvent-exposed tryptophan W306. This can be interpreted by a model of fast protonation equilibrium for the W306 radical that involves an increase in the pK_a of the radical in D_2O, which is 0.56-times that in H_2O buffer. The authors were able to kinetically separate the rate constants, and the rate constant for recombination via deprotonated radical was found to be higher in H_2O than in D_2O (1.4 times).

It seems likely that the second-order rate constants decrease to such a great extent that this overcompensates the effect of an increase in the K_1 value in D_2O for the N^{-I} redox reaction whereas it is unable to slow down the N^{III} redox reaction. The rate retardations in D_2O for the oxidation of glyoxylic and pyruvic acid by the title Mn oxidant are much smaller[15] than those observed in the oxidation of N^{-I}, which might indicate that the effect of an increase in K_1 is almost cancelled out by the decrease in rate constants in D_2O for the oxidations of these α-keto acids. A substantial decrease of K_a in D_2O (compared to that in H_2O) also contributes significantly to a remarkable decrease of the composite ($k_2K_1K_a + k_3$) for the N^{III} redox reaction in D_2O.

The contribution of reaction (8) in Scheme 1 (for $R^- = NO_2^-$) towards the overall rate is statistically insignificant (Table 3). Moreover, $(k_2K_1)_{max}$ is much lower than k_1K_1 for N^{III} oxidation, therefore we may reasonably expect that the k_3 path contributes significantly to the measured rate of N^{III} oxidation. The superior reactivity of HNO_2 over NO_2^- in reducing $\mathbf{1}^{4+}$ or $\mathbf{1}H^{5+}$ is thus clearly established. Both NH_2OH and NH_3OH^+, on the other hand, react with the tetrameric Mn oxidant. It appears that the presence of an H-atom in both these reducing agents is responsible for the observed reactivity and thus a hydrogen atom transfer (HAT) from the reducing acids may be mechanistically conceived to produce the radicals $NO_2^{\cdot}$ or $NHOH^{\cdot}$ along with the protonated oxo bridge in the mixed-valent $Mn^{IV}{}_3Mn^{III}$ species. The kinetic superiority of $\mathbf{1}H^{5+}$ may be due, at least in part, to its more oxidising nature than $\mathbf{1}^{4+}$ as well as a more facile movement of hydrogen or hydrogen ion through the H-bonding framework formed from the oxo bridges of $\mathbf{1}H^{5+}$ and the oxygen and hydrogens of the reducing species. The molecular mechanics computed structure of the OEC reveals a network of organised hydrogen-bonded species around the OEC[13a,13b,40] cluster, thereby providing an insight into the movement of protons and water in the site.

Experimental Section

Materials: The complex salt hydrate $[Mn_4(\mu\text{-}O)_6(bipy)_6][ClO_4]_4\cdot 2H_2O$ was synthesised following the literature procedure.[14] One of its water molecules is easily lost[14] therefore the elemental analyses of the material closely resemble the values expected for the monohydrate. The tetramer used here thus appears to be the monohydrate. $C_{60}H_{50}Cl_4Mn_4N_{12}O_{23}$: calcd. C 43.16, H 2.99, N 10.07; found C 43.39, H 3.03, N 10.00.

The preparation, standardisation and storage of sodium nitrite, hydroxylamine nitrate and sodium nitrate have been described previously.[20,41] 2,2′-Bipyridine was used as received from Sigma. D_2O (99.9 atom-% D) and DNO_3 (99+ atom-% D) were also purchased from Sigma. All other chemicals were of reagent grade and used as received. Doubly distilled, deionised and then freshly boiled water was used throughout.

Equilibrium Measurements: The acid dissociation constants of the reducing acids HNO_2 and NH_3OH^+ cation in 95% D_2O medium were determined by pH-metric titration using a Metrohm (736 GP Titrino) autotitrator at 25.0(±0.1) °C, I = 1.0 M ($NaNO_3$), as described previously.[20,41,42] To avoid nitrous acid decomposition in acidic media, solutions of $NaNO_2$ were titrated with DNO_3 while aliquots of hydroxylamine solutions (initially at pH 2 made by adding HNO_3) were titrated with carbonate-free NaOH. The reported values[16,17] of these ionisation constants in H_2O media were used. A similar pH-metric titration of $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ was performed in the pH range 2.0–7.0 to examine the basicity of its oxo bridges.

Stoichiometry Measurements: The stoichiometries of the reactions were measured with both an excess and a deficit of reducing agent. Reaction mixtures containing 6–15-times N^{III} over the Mn oxidant (0.05–1.50 mM) were allowed to react until the solutions became colourless (absorbance of less than 0.01 at 420 nm). Unreacted N^{III} in these product mixtures was determined colourimetrically. After appropriate dilution, the product solutions were treated with α-naphthylamine and sulfanilic acid. The red dye thus formed was estimated at 520 nm ($\varepsilon = 4.0\times10^4$ M^{-1}cm^{-1}).[43] We verified that bipyridine, Mn^{II} and ClO_4^- do not interfere in this coupling reaction. NO_3^- as the N^{III} oxidation product was qualitatively detected by the above-mentioned coupling reaction after adding Zn dust. For this purpose reaction mixtures were prepared with complex:N^{III} ratios of between 1:2 and 1:4. The Mn tetramer did not interfere in this colour reaction. Unreacted hydroxylamine was determined by titrating with standard $KBrO_3$ in the usual manner[44] when $Mn^{IV}{}_4$ (0.5–1.50 mM) was treated with (5–10 mM) N^{-I}. Formation of NO_2^- or NO_3^- as the N^{-I} oxidation product was also tested by the coupling reaction described above. Under non-kinetic conditions, 0.10–0.50 mM of the $Mn^{IV}{}_4$ complex was treated with a less than stoichiometric amount of the reducing agents. Unreacted $Mn^{IV}{}_4$ complex was measured at 420 nm ($\varepsilon = 7.5\times10^3$ M^{-1}cm^{-1}) when the reactions reached equilibrium. Mn^{II} in the product solutions was estimated by EDTA titrations using EBT as indicator.[45] For this purpose, excess reducing agent was treated with the Mn oxidant until the absorbance at 420 nm became less than 0.01 and then Mn^{II} was estimated. We verified that NO_2^-, NO_3^-, NH_2OH or bipy do not interfere in this complexometric titration.

Physical Measurements and Kinetics: Absorbance and electronic spectra were recorded with a Shimadzu (1601 PC) spectrophotometer using 1.00-cm quartz cells. The kinetics was monitored in situ with the instrument in "kinetic mode" at 420 nm in an electrically controlled thermostatted 25.0(±0.1) °C cell housing (CPS-240A). Reactions with $t_{1/2}$ less than 30 seconds were monitored using a Biologic SFM-03/QS stopped-flow spectrophotometer with DT-2801 data transmission system. The ionic strength was normally maintained at 1.0 M with $NaNO_3$. The excess 2,2′-bipyridine concentration, $C_{bipy} = [(Hbipy^+) + (bipy)]$ was in the range 1–80 mM and acted as a good buffer in the pH range studied (2.0–6.0), which was measured with an Orion-Ross Combined electrode system (Model 81–02) before and after the reaction. Excess bipyridine present in the reaction medium buffers the reaction within 0.05 pH units in the entire pH range studied for nitrite oxidation while for hydroxylamine oxidation a maximum pH increase of 0.15 units was seen when working at a pH below 3.0 but above pH 3.0 the pH drift was around 0.05 pH units. It is possible that HNO_2 in the low pH range and both bipyridine and hydroxylamine in the higher pH range act as good buffers.

The electrode calibration was described earlier to read $-\log_{10}[H^+]$ directly from a calibration curve constructed by plotting the pH-meter reading against $-\log_{10}[H^+]$.[46] For reactions in D_2O, pD was calculated as $pH_{measured} + 0.40$.[47] An excess of reducing agent was maintained in all the kinetic runs. The $\log_{10}$(absorbance) vs. time plots were found to be good straight lines for up to at least 90% completion of reactions and the observed rate constants (k_0) were calculated in the usual way.

Supporting Information (see also the footnote on the first page of this article): Linearisation of Equation (9) for the N^{III} redox reaction and evaluation of k_4 for the N^{-I} redox reaction from a linear plot at pH ≥ 5.3.

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