DALTON

Kinetics of oxidation of thiosulfate ion with $[Mn^{IV}_2(\mu\text{-}O)_2(\mu\text{-}MeCO_2)(H_2O)_2(bipy)_2]^{3+}$ (bipy = 2,2′-bipyridine) and its hydrolytic derivatives

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The complex $[Mn^{IV}_2(\mu\text{-}O_2)_2(\mu\text{-}MeCO_2)(H_2O)_2(bipy)_2]^{3+}$ **1** (bipy = 2,2′-bipyridine) has been found to co-exist in rapid equilibrium with $[Mn_2O_2(H_2O)_4(bipy)_2]^{4+}$ **2** and $[Mn_2O_2(MeCO_2)(H_2O)_4(bipy)]^{3+}$ **3** in aqueous buffer containing an excess of bipy and $MeCO_2^-$ in the range pH 4.0–5.5. Equilibrium constants (mol dm^{-3}) for **1** $\rightleftharpoons$ **2** + $MeCO_2^-$ and **1** $\rightleftharpoons$ **3** + bipy are 10^{-2} and 10^{-3}, respectively. Water molecules co-ordinated to the manganese(IV) centres are stable at least up to pH 5.5. Reduction of the binuclear manganese(IV) species by thiosulfate ion proceeded *via* $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ **4**, in the presence of an excess of bipy. An excess of thiosulfate reduced complex **4** further and ultimately produced Mn^{II}. Rate constants for reduction of **1**–**3** to **4**, as determined under second-order conditions, increase with increasing number of water molecules at the manganese centre. A plausible mechanism is proposed and the relevance of the results to photosystem II discussed.

The active site of the transmembrane protein complex called photosystem II (PS II) contains an oxomanganese cluster, where water molecules are oxidised to oxygen.[1] Since water is the substrate of the catalytic oxidation, it must bind to or be present in the close vicinity of the oxomanganese cluster to be oxidised. It is also known that the manganese ions in the cluster are ligated by O and N atoms from amino acid residues.[2] Attempts to model the oxygen-evolving centre (OEC) in PS II have stimulated considerable research on the co-ordination compounds of high-valent manganese. As a result dinuclear oxomanganese(IV) cores have been assembled in both aqueous and non-aqueous media.[1b,3] However, the compound $[Mn_2O_2(MeCO_2)(H_2O)_2(bipy)_2]^{3+}$ **1** (bipy = 2,2′-bipyridine) is the first to include simultaneously a bridging ethanoate ligand, two oxo bridges and two water molecules, each directly co-ordinated to manganese(IV).[4] We initiated the present work with the belief that investigations on the kinetic and thermodynamic properties of **1** should be helpful in understanding the aqueous chemistry of higher-valent manganese clusters and their relevance in biological systems. In the long run, such knowledge may assist in the elucidation of the conditions that stabilise manganese–water bonds during oxidative charge build up[5] on the oxygen-evolving centre of PS II, and lead ultimately to the development of model compounds for the active site in the natural system.

Experimental

Materials

The complex salt hydrate $[Mn^{IV}_2O_2(MeCO_2)(H_2O)_2(bipy)_2][ClO_4]_3\cdot H_2O$ **1** was synthesized according to a known procedure[4a] involving oxidation of Mn^{2+} by Ce^{4+} in the presence of ethanoate and bipyridine. The crystals obtained were sufficiently pure and used without further purification (Found: C, 30.2; H, 3.1; N, 6.3. $C_{22}H_{25}Cl_3Mn_2N_4O_{19}$ requires C, 30.5; H, 2.9; N, 6.5%). Its equivalent weight found by iodometry (217) is in good agreement with the calculated value (216).

Sodium thiosulfate (A.R., BDH) was recrystallised from hot water. Its solutions in water were prepared and standardised by iodometry. They were always freshly prepared each day. Aqueous solutions of $NaNO_3$ and $MeCO_2Na$ (both A.R., BDH) were prepared in freshly boiled doubly-distilled water and standardised by passing through a Dowex 50W X8 strong cation-exchange column in the H^+ form and titrating the liberated acid with standard NaOH to a phenolphthalein end-point. 2,2′-Bipyridine (G.R., E. Merck) was used as provided. All other chemicals were of reagent grade.

Physical measurements and kinetics

All absorbances and electronic spectra were recorded with a Shimadzu (1601 PC) spectrophotometer using 1.00 cm quartz cells. The kinetics was monitored *in situ* at 550 nm in the thermostatted (25.0 ± 0.1 °C) cell-housing (CPS-240A). The ionic strength was 2.0 mol dm^{-3} ($NaNO_3$). A high ionic strength was necessary to keep the reaction rate within the limits of our measuring device. The reactions are very fast at any lower, standard ionic strength (*e.g.* 1.0 mol dm^{-3}). Solutions were buffered in the range pH 3.0–5.5 with mixtures of sodium ethanoate and 2,2′-bipyridine. The total 2,2′-bipyridine concentration, c_{bipy}(= [bipy] + [Hbipy$^+$]), being in the range 10–35 mmol dm^{-3}, and the total ethanoate concentration, c_{ea}(= $[MeCO_2^-]$ + $[MeCO_2H]$), being in the range 0.005–0.2 mol dm^{-3}. Solution pH values were measured with an Orion 710 A2 pH/ion meter and an Orion Ross combination (model 81-02) electrode. The linearity of the electrode was established using pH 4, 7 and 9 buffers. The electrode was calibrated to read $-\log[H^+]$ directly using a series of acid solutions at the ionic strength used for kinetic experiments. The $[H^+]$ in these solutions were determined by titration against standard NaOH solutions. The reaction kinetics was measured under second-order conditions using $[S_2O_3^{2-}]$ = [complex] = 0.10 mmol dm^{-3}. Reactions under first-order conditions using an excess of thiosulfate were too fast for conventional spectrophotometry; moreover, consecutive reactions complicated the kinetics.

Stoichiometric measurements

The reaction stoichiometry was determined under non-kinetic conditions in the presence of an excess of $Na_2S_2O_3$. Unspent $S_2O_3^{2-}$ was determined iodimetrically. Typically, complex **1** (1.0 mmol dm^{-3}) and $S_2O_3^{2-}$ (6.0 mmol dm^{-3}) were mixed at pH 4.5 and c_{bipy} = 6.0 mmol dm^{-3} and allowed to react until the solution became colourless. Formation of a polythionate was demonstrated according to a method of Kolthoff and Belcher.[6] It was reduced to $S_2O_3^{2-}$ by using an excess of KCN. Thiosulfate, thus formed was estimated iodimetrically.

Equilibrium measurements

The electronic spectra of the Mn^{IV}_2 complexes under different conditions indicated partial aquation of **1** to **2** and **3** [equations

$$\underset{\mathbf{1}}{[\mathrm{Mn^{IV}}_2\mathrm{O}_2(\mathrm{MeCO}_2)(\mathrm{H}_2\mathrm{O})_2(\mathrm{bipy})_2]^{3+}} + 2\mathrm{H}_2\mathrm{O} \overset{K_\mathrm{A}}{\rightleftharpoons} \underset{\mathbf{2}}{[\mathrm{Mn}_2\mathrm{O}_2(\mathrm{H}_2\mathrm{O})_4(\mathrm{bipy})_2]^{4+}} + \mathrm{MeCO}_2^- \qquad (1)$$

$$\mathbf{1} + 2\mathrm{H}_2\mathrm{O} \overset{K_\mathrm{B}}{\rightleftharpoons} \underset{\mathbf{3}}{[\mathrm{Mn}_2\mathrm{O}_2(\mathrm{MeCO}_2)(\mathrm{H}_2\mathrm{O})_4(\mathrm{bipy})]^{3+}} + \mathrm{bipy} \qquad (2)$$

(1) and (2)]. The overall equilibrium constants $K_\mathbf{A}$ and $K_\mathbf{B}$ were determined spectrophotometrically at 400 nm. The total complex concentration at equilibrium, $c_\mathbf{e} = [\mathbf{1}] + [\mathbf{2}]$ in the presence of an excess of bipy, but $[\mathbf{1}] + [\mathbf{3}]$ in the presence of an excess of ethanoate, and expressions (3) and (4) can be written where $A_\mathbf{e}$

$$c_\mathrm{t}(A_\mathbf{e} - A_\mathbf{0})^{-1} = [\mathrm{MeCO}_2^-][K_\mathbf{A}(\Delta\varepsilon)]^{-1} + (\Delta\varepsilon)^{-1} \qquad (3)$$

$$c_\mathrm{t}(A_\mathbf{e}' - A_\mathbf{0})^{-1} = [\mathrm{bipy}][K_\mathbf{B}(\Delta\varepsilon')]^{-1} + (\Delta\varepsilon')^{-1} \qquad (4)$$

represents the equilibrium absorbance of an aqueous solution of **1** in the presence of a fixed excess of bipy and varying $[\mathrm{MeCO}_2^-]$, $A_\mathbf{e}'$ is the equilibrium absorbance for an aqueous solution of **1** in the presence of a fixed excess of MeCO_2^- and varying [bipy] and $A_\mathbf{0}$ is the absorbance of an aqueous solution of pure **1** and was determined as described later; $\Delta\varepsilon = \varepsilon_\mathbf{1} - \varepsilon_\mathbf{2}$ and $\Delta\varepsilon' = \varepsilon_\mathbf{1} - \varepsilon_\mathbf{3}$, where the εs are the respective molar absorption coefficients of species indicated as subscripts. A plot of the left-hand side of equation (3) *vs.* $[\mathrm{MeCO}_2^-]$ should yield a straight line with slope $1/K_\mathbf{A}(\Delta\varepsilon)$ and intercept $1/\Delta\varepsilon$. Similarly, a plot of the left-hand side of equation (4) *vs.* [bipy] should be a straight line of slope $1/K_\mathbf{B}(\Delta\varepsilon')$ and intercept, $1/\Delta\varepsilon'$.

Determination of the second-order rate constant

Under the second-order reaction conditions the solution species absorbing at 550 nm are **1**, the two hydrolytic derivatives **2** and **3**, and the product complex $[\mathrm{Mn^{III}Mn^{IV}O_2(bipy)_4}]^{3+}$ **4**. Also, at any time (*t*), the total concentration of dimanganese(IV) species is, $c_t = [\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}]$, and solution absorbance at any time (*t*) is given by equation (5/6) where $c_\mathbf{0}$ is the initial

$$\begin{aligned} A_t &= \varepsilon_1[\mathbf{1}] + \varepsilon_2[\mathbf{2}] + \varepsilon_3[\mathbf{3}] + \varepsilon_4[\mathbf{4}] && (5)\\ &= \varepsilon_\mathbf{c}c_t + \varepsilon_4[\mathbf{4}] = \varepsilon_\mathbf{c}c_t + \varepsilon_4(c_\mathbf{0} - c_t) &&\\ &= (\varepsilon_\mathbf{c} - \varepsilon_4)c_t + \varepsilon_4 c_\mathbf{0} && (6)\end{aligned}$$

complex concentration and expressions (7)–(11) are valid.

$$\varepsilon_\mathbf{c} = \frac{\varepsilon_1[\mathrm{MeCO}_2^-][\mathrm{bipy}] + \varepsilon_2 K_\mathbf{A}[\mathrm{bipy}] + \varepsilon_3 K_\mathbf{B}[\mathrm{MeCO}_2^-]}{[\mathrm{MeCO}_2^-][\mathrm{bipy}] + K_\mathbf{A}[\mathrm{bipy}] + K_\mathbf{B}[\mathrm{MeCO}_2^-]} \qquad (7)$$

$$A_\infty = \varepsilon_4[\mathbf{4}]_\infty = \varepsilon_4 c_\mathbf{0} \qquad (8)$$

$$A_\mathbf{0} = \varepsilon_\mathrm{c} c_\mathbf{0} \qquad (9)$$

$$(A_t - A_\infty) = (\varepsilon_\mathbf{c} - \varepsilon_4)c_t \qquad (10)$$

$$c_t = (A_t - A_\infty)/(\varepsilon_\mathbf{c} - \varepsilon_4) \qquad (11)$$

Under second-order conditions[7] we can write equation (12)

$$1/c_t = 1/c_\mathbf{0} + kt \qquad (12)$$

where *k* is the second-order rate constant. Expression (13) then

$$(A_t - A_\infty)^{-1} = [\varepsilon_\mathrm{c}/(\varepsilon_\mathbf{c} - \varepsilon_4)A_\mathbf{0}] + kt(\varepsilon_\mathbf{c} - \varepsilon_4)^{-1} \qquad (13)$$

follows. Hence a plot of $(A_t - A_\infty)^{-1}$ *vs.* time (*t*) should yield a straight line with slope $= k(\varepsilon_\mathbf{c} - \varepsilon_4)^{-1}$, and *k* can be evaluated since $\varepsilon_\mathbf{c}$ and ε_4 are known.

Results and Discussion

Stoichiometry and reduction products

Non-kinetic conditions using an excess of thiosulfate indicated an overall 1:4 stoichiometry (14). Addition of an excess of

$$[\mathrm{Mn_2O_2(MeCO_2)(H_2O)_2(bipy)_2}]^{3+} + 4\mathrm{H}^+ + 4\mathrm{S_2O_3}^{2-} \longrightarrow 2\mathrm{Mn^{II}} + 2\mathrm{bipy} + 4\mathrm{H_2O} + \mathrm{MeCO_2}^- + 2\mathrm{S_4O_6}^{2-} \qquad (14)$$

KCN to the product solution generated extra $\mathrm{S_2O_3}^{2-}$ equal to half the amount of $\mathrm{S_2O_3}^{2-}$ consumed in reaction (14).This supports the correctness of equation (14) and the production of $\mathrm{S_4O_6}^{2-}$, which reacts with the excess of KCN according to equation (15). Stoichiometries other than (14) can occur in

$$\mathrm{S_4O_6}^{2-} + 2\mathrm{CN}^- + \mathrm{H_2O} \longrightarrow \mathrm{S_2O_3}^{2-} + \mathrm{SCN}^- + \mathrm{SO_4}^{2-} + 2\mathrm{HCN} \qquad (15)$$

oxidations of thiosulfate. However, formation of tetrathionate is probably the most common.[8] It might, however, be pointed out that the manganese product under kinetic conditions is $[\mathrm{Mn^{III}Mn^{IV}O_2(bipy)_4}]^{3+}$ not $\mathrm{Mn^{II}}$ (see kinetics).

Equilibrium studies

The electronic spectrum of complex **1** in bipyridine buffer at pH 4.5 agrees well with those reported by Reddy *et al.*[4a] However, we have noted that it depends appreciably on pH, $c_\mathbf{bipy}$ and $c_\mathbf{ea}$. Table 1 displays a representative variation of the equilibrium absorbance at 400 nm as a function of $[\mathrm{MeCO}_2^-]$ and [bipy]. Similar changes were observed at 550 nm. The $A_\mathbf{e}$ values for an aqueous solution of **1** in the presence of a fixed excess of bipy and varying $[\mathrm{MeCO}_2^-]$ were fitted by the polynomial $A_\mathbf{e} = a_1 + a_2[\mathrm{MeCO}_2^-] + a_3[\mathrm{MeCO}_2^-]^2 + \ldots + a_n[\mathrm{MeCO}_2^-]^n$. The value obtained for a_1 was taken as the absorbance for pure **2** and yielded ε_2. The value for $A_\mathbf{e}$ in the presence of a large excess of bipy decreases with increasing $[\mathrm{MeCO}_2^-]$ and ultimately becomes fairly constant at $[\mathrm{MeCO}_2^-] > 0.20$ mol dm^{-3}. This minimum value for $A_\mathbf{e}$ was used to evaluate ε_1. Similarly values of $A_\mathbf{e}'$ [defined in equation (4)] were fitted by a polynomial equation in [bipy] and ε_3 and ε_1 could be evaluated. The two values of ε_1 agree very well. The $\Delta\varepsilon$ and $\Delta\varepsilon'$ values in equations (3) and (4) were calculated using this ε_1 value and the $A_\mathbf{e}$ and $A_\mathbf{e}'$ data in Table 1. We thus obtained excellent straight lines ($r \geqslant 0.98$), which provided the values for $K_\mathbf{A}$, $K_\mathbf{B}$, ε_1, ε_2 and ε_3. Thus $K_\mathbf{A} = 0.01 \pm 0.001$ mol dm^{-3} and $K_\mathbf{B} = 10^{-3} \pm 10^{-4}$ mol dm^{-3}, while ε_1, ε_2 and ε_3 are 480, 700 and 720 dm^3 mol^{-1} cm^{-1} respectively at 550 nm and 2500, 3600 and 3750 dm^3 mol^{-1} cm^{-1} at 400 nm at 25 °C, $I = 2.0$ mol dm^{-3}. The values of ε_2 and ε_3 thus obtained agree very well with those found from the polynomial fitting technique. The excellent fit ($r \geqslant 0.98$) of the absorbance data in Table 1 by the linear equations (3) and (4) supports the presumption of equilibria (1) and (2) and indicates no deprotonation of the co-ordinated water molecules within the experimental range of pH.

Unusually water is present in the co-ordination sphere of $\mathrm{Mn^{IV}}$ in complex **1**. Two other manganese(IV) complexes containing water are[9,10] $[\mathrm{Mn^{IV}}_3\mathrm{O}_4(\mathrm{H_2O})_2(\mathrm{bipy})]^{4+}$ and its 1,10-phenanthroline analogue. The ligand sets in these complexes are sufficiently strongly donating to stabilise an unusually high-valent metal centre to the extent that the co-ordinated water remains fully protonated.[10] In a short communication Dave *et al.*[4b] reported that a millimolar solution of **1** in water is acidic (pH 1.6). Accordingly, they proposed deprotonation of the aqua ligands. However, these workers synthesized **1** by the disproportionation of $[\mathrm{Mn^{III}}_2\mathrm{O(MeCO_2)_2(H_2O)_2(bipy)_2}]^{2+}$ with 70% $\mathrm{HClO_4}$. They formulated the product as $[\mathrm{Mn^{IV}}_2\mathrm{O_2(MeCO_2)(H_2O)(bipy)_2}]\cdot 3\mathrm{HClO_4}\cdot\mathrm{H_2O}$ (no anions to balance cationic charge!), which contains three $\mathrm{HClO_4}$ of crystallisation. Obviously, its aqueous solution should be acidic, whether or not the

Table 1 Representative equilibrium absorbance of a solution of 0.20 mmol dm^{-3} of complex **1** at 400 nm

pH	c_{ea}/mol dm^{-1}	c_{bipy}/mol dm^{-3}	10^2-[$MeCO_2^-$]/ mol dm^{-3}	10^2[bipy]/ mol dm^{-3}	A_e	A_e'
4.5	0.21	0.035	7.5	1.91	0.530	
4.5	0.14	0.035	5.0	1.91	0.530	
5.0	0.04	0.024	2.5	1.91	0.556	
5.0	0.016	0.024	1.0	1.91	0.615	
5.5	0.005	0.020	0.59	1.91	0.685	
5.5	0.001	0.020	0.12	1.91	0.725	
4.5	0.208	0.025	7.5	0.137		0.722
4.5	0.208	0.010	7.5	0.546		0.671
5.0	0.117	0.010	7.5	0.792		0.621
4.5	0.208	0.025	7.5	1.37		0.563
4.5	0.210	0.035	7.5	1.91		0.540
5.0	0.208	0.030	7.5	2.40		0.532
5.0	0.117	0.035	7.5	2.77		0.530
5.0	0.088	0.035	7.5	3.23		0.530

aqua ligands deprotonate. However, the observed pH value corresponds to a surprisingly high [H^+] (= 2.5×10^{-2} mol dm^{-3}), which requires that 25 H^+ be released per molecule of complex **1**! Apparently, the complex has either adhered $HClO_4$ from the mother-liquor, or suffered extensive decomposition in aqueous solution. Overall, the results of Dave *et al.* are inconclusive on the question of the acidity of co-ordinated H_2O molecules. The present equilibrium studies indicate that the ethanoate bridge in **1** is fairly labile. Such lability is possibly a consequence of its structural characteristics. The $Mn^{IV}O_2Mn^{IV}$ ring departs from planarity due to the constraints exerted by the ethanoate bridge.[4a] This greatly weakens the antiferromagnetic interaction ($J = -43.7$ cm^{-1})[4] and destabilises the complex as a whole. Removal of the ethanoate bridge increases the stability and is therefore favoured. The lability of a bipy ligand in **1** is also noteworthy. The equatorial Mn–N distances in **1** are significantly longer than the axial ones, reflecting the *trans* influence of the bridging oxygen atoms on the equatorial nitrogen atoms.[4] This influence should weaken and labilise the equatorial Mn–N bond. The ethanoate bridge may further weaken the bond. Our equilibrium studies demonstrate that, contrary to the usual belief,[11] higher oxidation states of manganese can be quite labile in aqueous solutions.[12]

Kinetics

The overall reaction (14) must be a multistep process. It was reported earlier[4a] that the electronic spectrum of complex **1** dissolved in bipy–Hbipy$^+$ buffer (pH 4.5) slowly changes to that of the mixed-valence $[Mn_2O_2(bipy)_4]^{3+}$ complex **4**; after 72 h, 80% of **1** has changed to **4**. Under the present experimental conditions, however, solutions of **1** are stable at least up to an hour, which is substantially longer than required for the present kinetic measurements. Mixing of equimolar thiosulfate and **1** generated the spectrum of **4**, provided $c_{\mathrm{bipy}} > 0.01$ mol dm^{-3}. The product solution is further reduced if an excess of $S_2O_3^{2-}$ is used and the rate of such reduction is close (within 3%) to the known[13] rate of reaction of **4** with $S_2O_3^{2-}$ under similar conditions. However, the spectral and kinetic behaviours of the solution differ noticeably from those of **4**, if $c_{\mathrm{bipy}} < 0.01$ mol dm^{-3}. Apparently, the overall reaction (14) proceeds *via* the manganese(III,IV) complex **4**, which is eventually the end product if the reaction is carried out in the presence of an excess bipy and only 1 equivalent of $S_2O_3^{2-}$ [equation (16)]. However, **4** is

$$2\underset{\mathbf{1}}{[Mn_2O_2(MeCO_2)(H_2O)_2(bipy)_2]^{3+}} + 2S_2O_3^{2-} + 4bipy \longrightarrow$$
$$2\underset{\mathbf{4}}{[Mn^{III}Mn^{IV}O_2(bipy)_4]^{3+}} + S_4O_6^{2-} + 2MeCO_2^- + 2H_2O \quad (16)$$

either not formed or formed only partially if $c_{\mathrm{bipy}} < 0.01$ mol dm^{-3}.

Table 2 Second-order rate constants for the reaction of complex **1** with $S_2O_3^{2-}$ at 25.0 °C, $I = 2.0$ mol dm^{-3}, [complex] = [$S_2O_3^{2-}$] = 0.10 mmol dm^{-3}

pH	c_{bipy}/ mol dm^{-3}	c_{ea}/ mol dm^{-3}	10^3[bipy]/ mol dm^{-3}	10^2-[$MeCO_2^-$]/ mol dm^{-3}	k*/dm^3 mol^{-1} s^{-1}
4.50	0.035	0.3	19.1	10.8	11.4 (11.6)
4.73			23.5	14.7	9.7 (9.8)
4.92			26.6	18.0	8.60 (8.80)
5.00			27.6	19.2	8.30 (8.50)
5.17			29.7	21.8	8.10 (8.30)
5.33			31.2	23.8	7.60 (7.70)
5.50			32.2	25.5	7.40 (7.50)
4.50	0.01		5.5	10.8	25.6 (25.3)
	0.015		8.1		19.3 (19.3)
	0.020		10.7		16.3 (16.0)
	0.025		13.7		13.8 (14.0)
	0.030		16.4		12.5 (12.6)
	0.035	0.005	19.1	0.18	35.6 (35.1)
		0.015		0.54	28.5 (28.8)
		0.020		0.72	26.5 (26.6)
		0.025		0.91	25.1 (24.9)
		0.040		1.40	21.0 (21.3)
		0.050		1.80	19.8 (19.7)
		0.060		2.20	18.2 (18.5)
		0.070		2.50	17.8 (17.5)
		0.080		2.90	16.9 (16.7)
		0.100		3.60	15.3 (15.5)
		0.200		7.20	12.8 (12.7)

* Average of two or three determinations; standard deviation, 1.5–4%.

We have recently reported[13] the kinetics of reaction of complex **4** with an excess of $S_2O_3^{2-}$ and found **4** to be reduced to Mn^{II} according to equation (17). As expected, equations (16)

$$2[Mn^{III}Mn^{IV}O_2(bipy)_4]^{3+} + 6S_2O_3^{2-} + 8H^+ \longrightarrow$$
$$4Mn^{II} + 8bipy + 3S_4O_6^{2-} + 4H_2O \quad (17)$$

and (17) combined together give the stoichiometric equation (14) for the reaction of **1** with an excess of $S_2O_3^{2-}$. In all probability, therefore we have measured the kinetics of reaction (16) under second-order conditions and $c_{\mathrm{bipy}} > 0.01$ mol dm^{-3}. Plots of $(A_t - A_\infty)^{-1}$ *vs.* time (t) were found to be excellent straight lines ($r > 0.98$) for at least three half-lives. Values of the second-order rate constant k under different reaction conditions are collected in Table 2, which shows that k decreases with increasing [$MeCO_2^-$] and [bipy]. Such dependences further support the presumption of equilibria (1) and (2) and suggest reactions of **1**–**3** with $S_2O_3^{2-}$. Since the final reaction product under the experimental conditions is **4**, the reactions must be one-electron transfer processes, which should initially produce $[Mn^{III}Mn^{IV}O_2(MeCO_2)(H_2O)_2(bipy)_2]^{2+}$ **5** from **1**, and $S_2O_3^{2-}$ will be concomitantly oxidised to $S_2O_3^-$. Similar products will be formed from **2** and **3**.

How the one-electron reduction products of **1**–**3** are transformed to **4** may be speculated from the well known electrochemistry of $[Mn_2O_2(\mu\text{-}HPO_4)(bipy)_2(H_2PO_4)_2]$ **6**, which is a close analogue of **1**. The electrochemical reduction of **6** in phosphate buffer[12] produces first the manganese(III,IV) dimer **7**, equation (18). However, **7** is not stable and immediately changes

$$[Mn^{IV}{}_2O_2(\mu\text{-}HPO_4)(bipy)_2(H_2PO_4)_2] + e^- \longrightarrow$$
$$\underset{\mathbf{7}}{[Mn^{III}Mn^{IV}O_2(\mu\text{-}HPO_4)(bipy)_2(H_2PO_4)_2]^-} \quad (18)$$

to the dimer **4** [equation (19)], which may undergo further re-

$$[Mn^{III}Mn^{IV}O_2(\mu\text{-}HPO_4)(bipy)_2(H_2PO_4)_2]^- + 2bipy + H^+ \longrightarrow$$
$$[Mn^{III}Mn^{IV}O_2(bipy)_4]^{3+} + 3H_2PO_4^- \quad (19)$$

$$\underset{\mathbf{1}}{[\mathrm{Mn^{IV}{}_2O_2(MeCO_2)(H_2O)_2(bipy)_2}]^{3+}} + 2\mathrm{H_2O} \overset{K_A}{\rightleftharpoons} \underset{\mathbf{2}}{[\mathrm{Mn_2O_2(bipy)_2(H_2O)_4}]^{4+}} + \mathrm{MeCO_2}^- \quad (1)$$

$$\mathbf{1} + 2\mathrm{H_2O} \overset{K_B}{\rightleftharpoons} \underset{\mathbf{3}}{[\mathrm{Mn_2O_2(MeCO_2)(H_2O)_4(bipy)}]^{3+}} + \mathrm{bipy} \quad (2)$$

$$\mathbf{1} + \mathrm{S_2O_3}^{2-} \xrightarrow{k_1} \underset{\mathbf{5}}{[\mathrm{Mn^{III}Mn^{IV}O_2(MeCO_2)(H_2O)_2(bipy)_2}]^{2+}} + \mathrm{S_2O_3}^- \quad (20)$$

$$\mathbf{2} + \mathrm{S_2O_3}^{2-} \xrightarrow{k_2} \underset{\mathbf{8}}{[\mathrm{Mn^{III}Mn^{IV}O_2(H_2O)_4(bipy)_2}]^{3+}} + \mathrm{S_2O_3}^- \quad (21)$$

$$\mathbf{3} + \mathrm{S_2O_3}^{2-} \xrightarrow{k_3} \underset{\mathbf{9}}{[\mathrm{Mn^{III}Mn^{IV}O_2(MeCO_2)(H_2O)_4(bipy)}]^{2+}} + \mathrm{S_2O_3}^- \quad (22)$$

$$\mathbf{5} + 2\mathrm{bipy} \xrightarrow{\text{fast}} \mathbf{4} + \mathrm{MeCO_2}^- + 4\mathrm{H_2O} \quad (23)$$

$$\mathbf{8} + 2\mathrm{bipy} \xrightarrow{\text{fast}} \mathbf{4} + 4\mathrm{H_2O} \quad (24)$$

$$\mathbf{9} + 3\mathrm{bipy} \xrightarrow{\text{fast}} \mathbf{4} + 4\mathrm{H_2O} + \mathrm{MeCO_2}^- \quad (25)$$

$$\mathrm{S_2O_3}^- + \mathrm{S_2O_3}^{2-} \xrightarrow{\text{fast}} \mathrm{S_4O_6}^{3-} \quad (26)$$

$$\mathrm{S_4O_6}^{3-} + \mathrm{Mn^{IV}{}_2} \xrightarrow{\text{fast}} \mathrm{Mn^{III,IV}} + \mathrm{S_4O_6}^{2-} \quad (27)$$

Scheme 1

duction. We anticipate that chemical changes in $[\mathrm{Mn^{III}Mn^{IV}O_2(MeCO_2)(H_2O)_2(bipy)_2}]^{2+}$ **5** are analogous to those for **7** in solution and propose Scheme 1 as a plausible explanation for our results on the chemical reduction of **1** and its hydrolytic derivatives by $\mathrm{S_2O_3}^{2-}$ under second-order conditions at high $c_{\mathbf{bipy}}$. A $[\mathrm{Mn^{III}Mn^{IV}O_2(MeCO_2)}]^{2+}$ core analogous to those in **5** and **9** has been isolated.[14,15] Also it is well established from the kinetics of reduction of **4** by $\mathrm{NO_2}^-$ and $\mathrm{S_2O_3}^{2-}$ that deaquation of **8** by bipy rapidly produces **4** in aqueous bipy–Hbipy$^+$ buffer.[13,16] Hence, equation (24) represents a known chemical reaction. Condensation of $\mathrm{S_2O_3}^-$ with $\mathrm{S_2O_3}^{2-}$, followed by one-electron oxidation of the resultant $\mathrm{S_4O_6}^{3-}$ to $\mathrm{S_4O_6}^{2-}$ is also a well established general process[17] in the oxidation of $\mathrm{S_2O_3}^{2-}$ to $\mathrm{S_4O_6}^{2-}$. Equations (26) and (27) in Scheme 1 are therefore logical.

Reactions (19), (23) and (25) indicate the lability of the di-μ-oxo-μ-acido-dimanganese(III,IV) unit, $[\mathrm{Mn^{III,IV}{}_2O_2(\mu\text{-}acido)}]^{2+}$, and stability of the $\{\mathrm{Mn_2O_2}\}^{3+}$ core in complex **4**. Such lability, in turn, may be the reason for the rarity of this unit.[14,15]

For Scheme 1, one can derive equations (28) and (29). Values

$$k = \frac{k_1[\mathrm{MeCO_2}^-][\mathrm{bipy}] + k_2K_\mathbf{A}[\mathrm{bipy}] + k_3K_\mathbf{B}[\mathrm{MeCO_2}^-]}{[\mathrm{MeCO_2}^-][\mathrm{bipy}] + K_\mathbf{A}[\mathrm{bipy}] + K_\mathbf{B}[\mathrm{MeCO_2}^-]} \quad (28)$$

$$k([\mathrm{MeCO_2}^-][\mathrm{bipy}] + K_\mathbf{A}[\mathrm{bipy}] + K_\mathbf{B}[\mathrm{MeCO_2}^-]) = k_1[\mathrm{MeCO_2}^-][\mathrm{bipy}] + k_2K_\mathbf{A}[\mathrm{bipy}] + k_3K_\mathbf{B}[\mathrm{MeCO_2}^-] \quad (29)$$

of the second-order rate constant k, at fixed [bipy] (0.0191 mol dm^{-3}) but varying $[\mathrm{MeCO_2}^-]$, were used to plot the left-hand side of equation (29) against $[\mathrm{MeCO_2}^-]$. An excellent straight line ($r = 0.987$) was obtained as expected. Again the k data at fixed $[\mathrm{MeCO_2}^-]$ (0.0108 mol dm^{-3}) but varying [bipy] were used to plot the left-hand side of equation (29) against [bipy] and an excellent straight line was obtained ($r = 0.99$).

If $[\mathrm{MeCO_2}^-]$ and [bipy] in equation (28) are substituted with $c_{\mathbf{ea}}$ and $c_{\mathbf{bipy}}$ using equations (30) and (31) then one obtains equations (32)–(35). A plot of the left-hand side of equation (32) against [H$^+$] at constant $c_{\mathbf{ea}}$ and $c_{\mathbf{bipy}}$ yielded an excellent

$$[\mathrm{MeCO_2}^-] = K_{\mathbf{ea}}c_{\mathbf{ea}}([\mathrm{H}^+] + K_{\mathbf{ea}})^{-1}; \quad K_{\mathbf{ea}} = 1.8 \times 10^{-5}\ \mathrm{dm^3\ mol^{-1}} \quad (30)$$

$$[\mathrm{bipy}] = K_{\mathbf{Hbipy}}c_{\mathbf{bipy}}([\mathrm{H}^+] + K_{\mathbf{Hbipy}})^{-1}; \quad K_{\mathbf{Hbipy}} = 3.85 \times 10^{-5}\ \mathrm{dm^3\ mol^{-1}} \quad (31)$$

$$kD = A + B[\mathrm{H}^+] \quad (32)$$

$$A = K_{\mathbf{ea}}K_{\mathbf{Hbipy}}(k_1c_{\mathbf{ea}}c_{\mathbf{bipy}} + k_2K_\mathbf{A}c_{\mathbf{bipy}} + k_3K_\mathbf{B}c_{\mathbf{ea}}) \quad (33)$$

$$B = k_2K_\mathbf{A}K_{\mathbf{Hbipy}}c_{\mathbf{bipy}} + k_3K_\mathbf{B}K_{\mathbf{ea}}c_{\mathbf{ea}} \quad (34)$$

$$D = K_{\mathbf{ea}}K_{\mathbf{Hbipy}}(c_{\mathbf{ea}}c_{\mathbf{bipy}} + K_\mathbf{A}c_{\mathbf{bipy}} + K_\mathbf{B}c_{\mathbf{ea}}) + (K_\mathbf{A}K_{\mathbf{Hbipy}}c_{\mathbf{bipy}} + K_\mathbf{B}K_{\mathbf{ea}}c_{\mathbf{ea}})[\mathrm{H}^+] \quad (35)$$

straight line ($r = 0.98$) again supporting the validity of Scheme 1. In an attempt to evaluate the rate constants k_1, k_2 and k_3, all the k values in Table 2 were fitted by equation (29) with the help of a program (LINEQ) developed in FORTRAN 77 for simultaneous linear equations. Only k_1, k_2 and k_3 were treated as variables; $K_\mathbf{A}$ and $K_\mathbf{B}$ values obtained from spectrophotometric determinations were used. The best-fit values for the rate constants (dm^3 mol^{-1} s^{-1}) thus obtained are: $k_1 = 2.0 \pm 0.02$, $k_2 = 40 \pm 1$ and $k_3 = 145 \pm 4$ respectively at 25.0 °C and $I = 2.0$ mol dm^{-3}.

These values reproduce very well the experimental second-order rate constant k (see the parenthetical values in Table 2). The observed order of rate constants $k_1 < k_2 < k_3$ shows that the rate of oxidation increases with the increased number of water molecules attached to the manganese centre. Among complexes **1**–**3**, the maximum number (3) of water molecules at any manganese centre is present in **3**, which is oxidised with the highest rate constant k_3. A similar increase in kinetic activity with increased extent of aquation was observed previously for mono-[18] and bi-nuclear[13,16,19] manganese complexes. It is likely that increased aquation makes the oxidant more electron deficient, more closely approachable for attack by the reductant and more flexible with a reduced Franck–Condon barrier to electron transfer. Moreover, aquated complexes may form adducts stabilised by hydrogen bonding with the reductant.[16] The extent of such stabilisation increases with increasing number of $\mathrm{H_2O}$ molecules in the co-ordination sphere of the oxidising complex.

Conclusion

Kok *et al.*[5] showed that the OEC in PS II cycles among different combinations of oxidation states of manganese. Every step in the cycle is an one-electron step. The OEC must also be resistant to decomposition in aqueous media, but preferably be able to pick up water molecules in the process of oxidative charge build up. The present kinetic study shows that consecutive one-electron changes are possible in the model compound, that such models may be reasonably stable in aqueous solution, yet can undergo facile aquation. The stability of the water molecules in these models is noteworthy. The manganese ions in OEC are ligated to O and N atoms from amino acid residues.[2] The present investigation indicates that such Mn–O and Mn–N bonds may be quite labile and undergo rapid aquation. Whether or not such aquation provides the substrate water for the OEC is unclear from this study, but evidently higher-valent manganese ions, when aquated, oxidise at a faster rate. By analogy, water molecules (if present) in the OEC may be instrumental in the rapidity of its redox reactions. This role may be additional to the function of water as a redox substrate for OEC.

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