Solution Equilibria and Redox Reactivities of a Dioxo-bridged Manganese Complex

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The dinuclear complex $[(bipy)_2Mn^{III}O_2Mn^{IV}(bipy)_2]^{3+}$ (bipy = 2,2′-bipyridyl) **1** was stabilised in bipy–Hbipy$^+$ buffer where it coexists with the diaqua derivative $[(H_2O)_2Mn^{III}O_2Mn^{IV}(bipy)]^{3+}$ **2** (equilibrium constant K^H). Reduction of **1** by NO_2^- has been found to be kinetically insignificant, but that of **2** is rapid, quantitative and follows the sequence $Mn^{III}Mn^{IV} \xrightarrow{k_1} (Mn^{III})_2 \xrightarrow{k_2} Mn^{II}Mn^{III} \xrightarrow{fast} 2Mn^{II}$. In the presence of an excess of NO_2^-, first-order kinetics was observed at 830 nm, but a biphasic profile at 525 nm. At 30.0 °C and I = 1.0 mol dm^{-3}, $k_1K_1^H$ and $k_2K_2^H$ are 34.9 ± 0.8 and 3.3 ± 0.2 dm^3 mol^{-1} s^{-1} respectively. Added bipy retards, while Mn^{2+} accelerates, the reaction. The solution equilibria are much more complex for **1** in HNO_3 and H_3PO_4, but the known solution chemistry of **1** in such different media may be correlated by a unified reaction scheme.

The $\{Mn_2(\mu\text{-}O)_2\}^{3+}$ unit is considered[1–3] as a substructure of the polynuclear manganese oxo-aggregate present in the water oxidation catalytic site in photosystem II (PS-II). Naturally, therefore, structural, magnetic and spectral properties of several 'model' complexes bearing this unit have been explored.[4–12] However, quantitative studies on the reactivities of such heterovalent, dinuclear, higher manganese complexes are rare, though the kinetic behaviour of their mononuclear counterparts has been investigated in some detail.[13–17]

Tetrakis(2,2′-bipyridyl)-di-μ-oxo-dimanganese(III,IV) perchlorate **1** is one of the more robust complexes containing the $\{Mn_2(\mu\text{-}O)_2\}^{3+}$ core and is a useful structural model for PS-II.[18–24] We report herein the kinetics of its reactions with NO_2^- in aqueous acidic media buffered with bipy–Hbipy$^+$ (bipy = 2,2′-bipyridyl).

Experimental

Materials.—The complex $[\{Mn(bipy)_2O\}_2][ClO_4]_3\cdot 2H_2O$ was prepared according to the literature[18] and characterised by the known[18] molar absorption coefficients of its UV/VIS peaks.

Solutions of recrystallised $NaClO_4$, $NaNO_2$ and $NaNO_3$ (all G. R., E. Merck) were standardised as described earlier.[25,26] Sulfanilic acid, α-naphthylamine and 2,2′-bipyridyl were E. Merck products used without further purification. Reagent-grade chemicals, chromium(II)-scrubbed nitrogen gas and triply distilled water were used throughout. Manganese(II) nitrate (G. R., E. Merck) solutions were standardised volumetrically[27] after oxidising Mn^{2+} to MnO_4^-.

Physical Measurements and Kinetics.—All reactions were fairly rapid but could be monitored *in situ* in the thermostatted cell housing of a Shimadzu Graphicord (UV-240) spectrophotometer at 30.0 °C. Ionic strength was generally maintained at 1.0 mol dm^{-3} by adding $NaNO_3$. Solutions were buffered with bipy–Hbipy$^+$ mixtures; the total 2,2′-bipyridyl concentration c_{bipy} (= [bipy] + [Hbipy$^+$]), was in the range 0.0025–0.020 mol dm^{-3}. The pH was measured with a model 335 pH meter (Systronics, India) using a calibrated electrode.[14] All kinetic experiments were measured with the reductant in excess. Some solutions were rigorously deaerated with dinitrogen. Additional runs were made in the presence of added $Mn(NO_3)_2$, and with $NaNO_3$ partially replaced by $NaClO_4$.

Data Analyses.—Exponential decay curves were fitted by integrated first-order rate equations and the first-order rate constants, k_{obs}, evaluated. Biphasic kinetic profiles were graphically fitted[28] by equation (1) to yield first-order rate

$$A_t = P_1 e^{-k_f t} + P_2 e^{-k_s t} \quad (1)$$

constants k_f and k_s for the two consecutive first-order steps.

Stoichiometric Measurements.—The reaction stoichiometry was determined by spectrophotometric titration of the oxidant complex **1** with $NaNO_2$. The initial (A_0) reference absorbance at 684 nm was obtained from a bipy–Hbipy$^+$ buffered solution of the oxidant. Different amounts of $NaNO_2$ were mixed with oxidant solutions and allowed to react completely, *i.e.* till there was no absorbance change of the solution. The difference between the initial and final absorptions ($\Delta A = A_0 - A_\alpha$), corresponding to consumption of a stoichiometrically equivalent amount of the oxidant, was determined as a function of $NaNO_2$.

The stoichiometry in the presence of an excess of reductant was determined by measuring unreacted NO_2^- spectrophotometrically. For this purpose the reaction mixture was appropriately diluted and treated with sulfanilic acid and α-naphthylamine to form a red dye.[29] The absorbance of this dye was measured at 520 nm and the concentration of N^{III} obtained from a calibration curve (ε^{520} = 4.3 × 10^4 dm^3 mol^{-1} cm^{-1}).

Results and Discussion

Stoichiometry and Reaction Products.—Measurements with an excess of oxidant or an excess of reductant both indicated a 2:3 stoichiometry (see Table 1) and the overall reaction appeared to be as in equation (2).

$$2[Mn^{III}O_2Mn^{IV}]^{3+} + 3NO_2^- + 2H^+ \longrightarrow 4Mn^{2+} + 3NO_3^- + H_2O \quad (2)$$

Solution Equilibria.—In aqueous acidic media the complex may undergo extensive acid-catalysed aquation,[30] oxo-bridge protonation ($\mathrm{p}K_a \approx 2.3$),[18] dimer cleavage, disproportionation and core rearrangement. Consequently $[\mathrm{Mn^{IV}}_3\mathrm{O_4(bipy)_4(OH_2)_2}]^{4+}$ **A** and Mn^{2+} are produced from **1** in dilute $\mathrm{HNO_3}$.[20] When $\mathrm{HNO_3}$ is replaced by concentrated $\mathrm{H_3PO_4}$, a μ-$\mathrm{HPO_4}$ derivative of $(\mathrm{Mn^{IV}})_2$ **B** along with a polymeric μ-$\mathrm{H_2PO_4}$ complex of $(\mathrm{Mn^{III}})_2$ **C** is isolated.[21] However, complex **1** is reasonably stable in bipy–Hbipy$^+$ buffer at weakly acidic pH (3.5–5.5).[18,30] This well authenticated chemistry of **1** may be correlated in a sequence (3)–(8) which gives the overall reaction (9) identical to the stoichiometric equation determined from an EPR study.[20] This scheme accounts for the structural similarity of the basal part of **A** and **B** and is in accord with known chemistry of higher-valent manganese complexes.[6,7,31]

Aquation

$$\underset{\mathbf{1}}{2[(\mathrm{bipy})_2\mathrm{Mn^{III}O_2Mn^{IV}(bipy)_2}]^{3+}} + 2\mathrm{H}^+ + 4\mathrm{H_2O} \xrightleftharpoons{\mathrm{pH} \approx 4.0} \underset{\mathbf{2}}{2[(\mathrm{H_2O})_2(\mathrm{bipy})\mathrm{Mn^{III}O_2Mn^{IV}(bipy)_2}]^{3+}} + 2\mathrm{Hbipy}^+ \tag{3}$$

Oxo-bridge protonation

$$\mathbf{2} + \mathrm{H}^+ \xrightleftharpoons{\mathrm{pH} \approx 2.0} \underset{\mathbf{3}}{[(\mathrm{H_2O})_2(\mathrm{bipy})\mathrm{Mn^{III}O(OH)Mn^{IV}(bipy)_2}]^{4+}} \tag{4}$$

Dimer cleavage

$$\mathbf{3} + \mathrm{H}^+ + 2\mathrm{H_2O} \longrightarrow \underset{\mathbf{4}}{[\mathrm{Mn^{III}(bipy)(OH_2)_4}]^{3+}} + \underset{\mathbf{5}}{[\mathrm{Mn^{IV}(bipy)_2(OH)_2}]^{2+}} \tag{5}$$

Disproportionation

$$\mathbf{2} + \mathbf{4} \longrightarrow \underset{\mathbf{6}}{[(\mathrm{H_2O})_2(\mathrm{bipy})\mathrm{Mn^{IV}O_2Mn^{IV}(bipy)_2}]^{4+}} + \underset{\mathbf{7}}{[\mathrm{Mn^{II}(bipy)(OH_2)_4}]^{2+}} \tag{6}$$

Trimer formation

$$\mathbf{6} + \mathbf{5} \longrightarrow \underset{\mathbf{A}}{[\mathrm{Mn^{IV}}_3\mathrm{O_4(bipy)_4(OH_2)_2}]^{4+}} + \mathrm{Hbipy}^+ + \mathrm{H}^+ \tag{7}$$

Formation of Mn^{2+}

$$\mathbf{7} + \mathrm{H}^+ \rightleftharpoons \mathrm{Mn}^{2+} + \mathrm{Hbipy}^+ + 4\mathrm{H_2O} \tag{8}$$

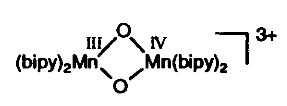
Overall reaction

$$\underset{\mathbf{1}}{2[(\mathrm{bipy})_2\mathrm{Mn^{III}O_2Mn^{IV}(bipy)_2}]^{3+}} + 4\mathrm{H}^+ + 2\mathrm{H_2O} \longrightarrow \underset{\mathbf{A}}{[\mathrm{Mn^{IV}}_3\mathrm{O_4(bipy)_4(OH_2)_2}]^{4+}} + 4\mathrm{Hbipy}^+ + \mathrm{Mn}^{2+} \tag{9}$$

Table 1 Stoichiometry of reduction of $[(\mathrm{bipy})_2\mathrm{Mn^{III}O_2Mn^{IV}(bipy)_2}]^{3+}$ by $\mathrm{NO_2}^-$ *

$[\mathrm{Mn^{III}Mn^{IV}}]$/ mmol dm^{-3}	$[\mathrm{NO_2}^-]$/ mmol dm^{-3}	pH	$\Delta[\mathrm{Mn^{III}Mn^{IV}}]/\Delta[\mathrm{NO_2}^-]$
0.50	2.00	4.3	0.71
0.20	0.80	4.8	0.63
0.80	2.00	5.0	0.63
0.50	2.00	5.0	0.69
0.50	1.50	4.9	0.72
			Average 0.68 ± 0.04

* Reactions were carried out at 30 °C in bipy–Hbipy$^+$ buffer systems and at $I = 1.0$ mol dm^{-3} ($\mathrm{NaNO_3}$). The media were perfectly deaerated by passage of purified dinitrogen.



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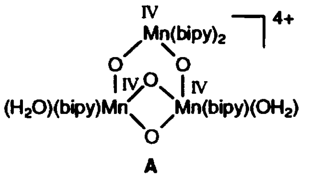

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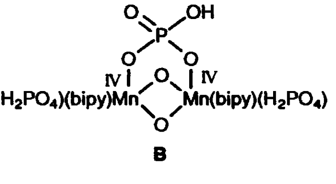

B

Kinetics.—For kinetic studies it is important to realise that reactions (4)–(8) may be avoided in the range pH 4.0–6.0 maintained with an excess of bipy–Hbipy$^+$ buffer and only two manganese species exist, *viz.* **1** and its diaqua derivative **2**. The interpretation of the kinetic results in this buffer may thus be greatly simplified.

Exponential decay curves were obtained at least up to 90% completion of reaction when monitored at 830 nm, but a biphasic profile was observed at 525 nm (Fig. 1). First-order rate constants, k_{obs}, extracted from absorbance data at 830 nm are in excellent agreement with k_{f}, the first-order rate constant for the faster step of the biphasic reactions at 525 nm under otherwise similar conditions. The k_{obs} values are compiled in Table 2 along with k_{s} values the first-order rate constant evaluated at 525 nm for the slower component reaction.

The rate constants k_{obs} ($= k_{\mathrm{f}}$) and k_{s} both increase with increasing concentration of $\mathrm{NO_2}^-$ and H^+, but decrease with increasing c_{bipy}. Plots of both k_{obs} and k_{s} against $[\mathrm{NO_2}^-]$ and against c_{bipy}^{-1} are excellent straight lines ($r > 0.99$) passing through the origin. Corresponding plots against $[\mathrm{H}^+]$ are also

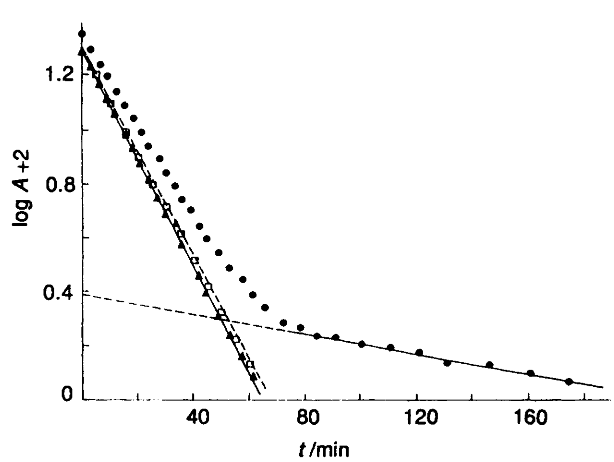

Fig. 1 Evaluation of first-order rate constants at 30.0 °C: [complex] = 0.4 mmol dm^{-3}, $[\mathrm{NO_2}^-] = 4.0$ mmol dm^{-3}, $c_{\mathrm{bipy}} = 0.010$ mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($\mathrm{NaNO_3}$), pH 4.75. (●) Measurements at 525 nm; (▲) measurements at 830 nm; (– – – □ – – –), the fast step calculated by consecutive analysis of the values at 525 nm, path length 1 cm

Table 2 Representative kinetic data for the reduction of the dinuclear manganese complex with NO_2^- [a]

pH	([bipy] + [Hbipy$^+$])/ mmol dm^{-3}	[NO_2^-]/ mmol dm^{-3}	$10^3\,k_{obs}$/ s^{-1}	$10^4\,k_s$/ s^{-1}
3.97	0.010	4.0	2.0 (2.03)	1.9 (1.92)
4.09			1.8 (1.67)	1.5 (1.58)
4.22			1.4 (1.37)	1.2 (1.30)
4.31			1.2 (1.22)	1.2 (1.15)
4.42 [b,c]			1.1 (1.06)	1.1 (1.00)
4.55			1.0 (0.92)	0.8 (0.87)
4.75			0.8 (0.78)	0.7 (0.74)
5.02 [c,d]			0.7 (0.66)	0.6 (0.62)
5.36			0.6 (0.59)	0.5 (0.56)
5.63			0.6 (0.56)	0.5 (0.53)
4.85		5.0	0.9 (0.91)	0.9 (0.86)
4.83		6.0	1.1 (1.11)	1.0 (1.05)
4.85 [b,c]		8.0	1.4 (1.42)	1.4 (1.37)
4.82		10.0	1.8 (1.86)	1.6 (1.76)
4.84		16.0	2.8 (2.94)	2.6 (2.78)
4.82		20.0	3.6 (3.70)	3.3 (3.50)
4.81		25.0	4.3 (4.67)	4.1 (4.42)
4.44	0.0025	4.0	4.5 (4.16)	4.2 (3.93)
4.40	0.005		2.4 (2.18)	2.3 (2.06)
4.42	0.0075		1.3 (1.42)	1.3 (1.34)
4.32	0.015		0.7 (0.80)	0.7 (0.76)
4.36 [c,d]	0.020		0.6 (0.57)	0.5 (0.54)
4.40 [e]	0.010		1.6 (1.57)	1.5 (1.48)
4.43 [f]			2.1 (2.00)	2.2 (1.89)
4.38 [g]			3.9 (3.96)	4.0 (3.74)

[a] Average (± 5%) of two to five experiments. Standard deviation 2–5%. Reactions were carried out at 30.0 °C and $I = 1.0$ mol dm^{-3} maintained by $NaNO_3$ except for runs *b*. Parenthetical values were calculated from equation (19). See text for definition of k_{obs} ($= k_f$) and k_s. [b] $I = 1.0$ mol dm^{-3} maintained by $NaNO_3$ as required along with 0.10 mol dm^{-3} $NaClO_4$. [c] For *b* and *d*, k_s and k_f do not significantly change from values calculated for the conditions in *a*. [d] Reaction mixture was purged with purified dinitrogen. [e] [Mn^{2+}] = 0.005 mol dm^{-3}. [f] [Mn^{2+}] = 0.010 mol dm^{-3}. [g] [Mn^{2+}] = 0.015 mol dm^{-3}.

excellent straight lines ($r > 0.98$) but have significant intercepts (Fig. 2). Added Mn^{2+} ion accelerates the reaction but partial substitution of $NaNO_3$ by 0.1 mol dm^{-3} $NaClO_4$, keeping the ionic strength unchanged (1.0 mol dm^{-3}), does not affect the rate. The rate is also not affected by ambient light, or whether the medium is purged with N_2 or not. However, gas-bubble formation and consequent interference with kinetic measurements are observed if the reaction mixture is kept for a long time in the light path of the spectrophotometer.

Our kinetic findings are consistent with the reaction sequence (10)–(15). It has been proposed that the band at 830 nm is due to a Mn^{III}–Mn^{IV} intervalence transition.[18] So the isovalent $(Mn^{III})_2$ dimer is transparent to 830 nm radiation and step (13) does not interfere with kinetic measurements. Hence first-order kinetics is observed at 830 nm in the presence of an excess of NO_2^-. At 525 nm, both complex **1** and the $(Mn^{III})_2$ intermediate absorb and a biphasic profile appears.

$$[(\mathrm{bipy})_2\mathrm{Mn^{III}O_2Mn^{IV}(bipy)_2}]^{3+} + \mathrm{H^+} + 2\mathrm{H_2O} \overset{K_1^{\mathrm{H}}}{\rightleftharpoons} [(\mathrm{H_2O})_2(\mathrm{bipy})\mathrm{Mn^{III}O_2Mn^{IV}(bipy)_2}]^{3+} + \mathrm{Hbipy^+} \tag{10}$$

$$[(\mathrm{H_2O})_2(\mathrm{bipy})\mathrm{Mn^{III}O_2Mn^{IV}(bipy)_2}]^{3+} + \mathrm{NO_2^-} \xrightarrow{k_1} [(\mathrm{H_2O})_2(\mathrm{bipy})\mathrm{Mn^{III}O_2Mn^{III}(bipy)_2}]^{2+} + \mathrm{NO_2} \tag{11}$$

$$[(\mathrm{H_2O})_2(\mathrm{bipy})\mathrm{Mn^{III}O_2Mn^{III}(bipy)_2}]^{2+} + \mathrm{H^+} + 2\mathrm{H_2O} \overset{K_2^{\mathrm{H}}}{\rightleftharpoons} [(\mathrm{H_2O})_2(\mathrm{bipy})\mathrm{Mn^{III}O_2Mn^{III}(bipy)(OH_2)_2}]^{2+} + \mathrm{Hbipy^+} \tag{12}$$

$$[(\mathrm{H_2O})_2(\mathrm{bipy})\mathrm{Mn^{III}O_2Mn^{III}(bipy)(H_2O)_2}]^{2+} + \mathrm{NO_2^-} \xrightarrow{k_2} [(\mathrm{H_2O})_2(\mathrm{bipy})\mathrm{Mn^{II}O_2Mn^{III}(bipy)(OH_2)_2}]^{+} + \mathrm{NO_2} \tag{13}$$

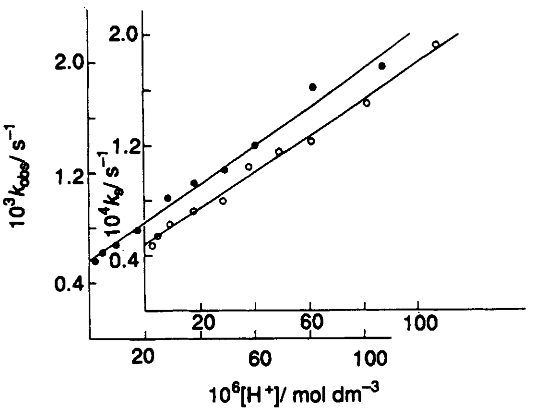

Fig. 2 Plots of k_{obs} and k_s against [H$^+$] at 30.0 °C: [complex] = 0.4 mmol dm^{-3}, $c_{bipy} = 0.010$ mol dm^{-3}, [NO_2^-] = 4.0 mmol dm^{-3}, I = 1.0 mol dm^{-3}

$$\mathrm{Mn^{II}Mn^{III}} + \mathrm{NO_2^-} \xrightarrow{\text{fast}} 2\mathrm{Mn^{II}} + \mathrm{NO_2} \tag{14}$$

$$2\mathrm{NO_2} + \mathrm{H_2O} \longrightarrow \mathrm{NO_3^-} + \mathrm{NO_2^-} + 2\mathrm{H^+} \tag{15}$$

The reaction sequence $Mn^{III}Mn^{IV} \longrightarrow (Mn^{III})_2 \longrightarrow Mn^{II}$-$Mn^{III} \longrightarrow 2Mn^{II}$ as proposed above is similar to those suggested by Gould and co-workers[32] for the reaction of I with HSO_3^-, hydroquinone and ascorbate. Our postulation that step (14) is fast compared to rate-determining steps (11) and (13) is also borne out by their studies, which show that step (14) is at least $\approx 10^3$ times faster than (11) and (13). We prefer the above sequence over two other alternatives, *viz.* $Mn^{III}Mn^{IV} \longrightarrow Mn^{II}Mn^{IV} \longrightarrow$ *etc.* and $Mn^{III}Mn^{IV} \longrightarrow Mn^{III}Mn^{II} \longrightarrow$ *etc.* This preference seems justified on two grounds. First, the odd electron in Mn^{III} is antibonding (e_g in an octahedral field) and hence its transfer necessitates considerable change in bond lengths about the manganese ion leading to slower electron transfer compared to Mn^{IV}. Secondly, electrochemical reduction of **1** and similar complexes with a $\{Mn_2O_2\}^{3+}$ core is known to produce an $(Mn^{III})_2$ dimer.[33] No $Mn^{II}Mn^{IV}$ or $Mn^{III}Mn^{II}$ dimer has ever been reported.

Again, the two-electron transfer process $Mn^{III}Mn^{IV} \longrightarrow Mn^{III}Mn^{II}$ can occur only with a large activation barrier due to significant structural reorganisations[34] which NO_2^- must undergo for concomitant formation of NO_2^+. Such a transfer is therefore less likely than two consecutive one-electron steps.

Gould and co-workers[32] also estimated the rate constants for reduction of complex **1** and the $(Mn^{III})_2$ dimer by HSO_3 and the hydroquinone radical. The values lie in the range 4.3×10^7–8.0×10^8 dm^3 mol^{-1} s^{-1}. It is expected[34] that NO_2 should react at a much slower rate than hydroquinone and HSO_3 radical while reducing **1** or $(Mn^{III})_2$, and hence prefer rapid disproportionation [equation (15); $k = 1.0 \times 10^8$ dm^3 mol^{-1} s^{-1}][35] over its direct reaction with higher-valent manganese complexes.

The reaction sequence (10)–(15) leads to equation (16) for k_f

$$k_x = \frac{k_n K_n^{\mathrm{H}}[\mathrm{H^+}][\mathrm{NO_2^-}]}{K_n^{\mathrm{H}}[\mathrm{H^+}] + [\mathrm{Hbipy^+}]} \tag{16}$$

($= k_{obs}$) and k_s where $n = 1$ for x = f and 2 for x = s. Assuming $K_n^{\mathrm{H}}[\mathrm{H^+}] \ll [\mathrm{Hbipy^+}]$ and $c_{\mathrm{NO_2^-}}$ ($= [\mathrm{NO_2^-}] + [\mathrm{HNO_2}]$) $\approx [\mathrm{NO_2^-}]$ under our experimental conditions, (16) reduces to

(17) where K_1 is the protonation constant[36] of bipy [equation

$$k_x = \frac{k_n K_n^H [H^+] c_{NO_2^-}}{K_1 c_{bipy} [H^+](1 + K_1[H^+])^{-1}} \qquad (17)$$

(18)]. Equation (17) may be rearranged to (19). Accordingly,

$$\text{bipy} + H^+ \rightleftharpoons \text{Hbipy}^+ \quad \log K_1 = 4.41 \qquad (18)$$

$$k_x = \frac{k_n K_n^H}{K_1} \frac{c_{NO_2^-}}{c_{bipy}} + \frac{k_n K_n^H [H^+] c_{NO_2^-}}{c_{bipy}} \qquad (19)$$

$k_n K_n^H$ can be evaluated from plots of k_x against $[H^+]$. At 30.0 °C, $I = 1.0$ mol dm^{-3}, $k_1 K_1^H = 34.9$ and $k_2 K_2^H = 3.3$ dm^3 mol^{-1} s^{-1}. The slope/intercept ratio of such plots should be K_1. The value of log K_1 thus estimated (4.40 and 4.45) is in excellent agreement with the literature value[36] and supports the proposed reaction pathway.

In these analyses we could not detect any kinetic activity of complex **1**. Aquation is known to enhance the redox reactivity of higher-valent manganese complexes and the aqua derivative often masks the kinetic significance of the parent complex. A typical example is $[Mn(OH_2)_2(acac)_2]^{2+}$ (acac = acetylacetonate) which completely swamps the kinetic activity of $[Mn(acac)_3]$ with its own while reacting with glyoxylate,[37] oxalate,[13] $H_2PO_2^-$ [38] and S^{IV}.[14] Apparently, the trend is maintained for the dinuclear complex **1** which we find to be much less active than its diaqua derivative **2**.

Added Mn^{2+} increases the reaction rate but does not alter the general shape of the absorbance *vs.* time plots at 525 and 830 nm. Evidently, Mn^{2+} is not an autocatalyst. It actually scavenges bipy as $[Mn(bipy)]^{2+}$ and thus promotes formation of the kinetically active diaqua $Mn^{III}Mn^{IV}$ complex, **2**. We have calculated the concentrations of $[Mn(bipy)]^{2+}$ under our experimental conditions using a formation constant $K = 502$ dm^3 mol^{-1} for $[Mn(bipy)]^{2+}$.[39] Such concentrations, when substracted from the analytical concentration of added 2,2′-bipyridyl, gave defined $c_{bipy} = [\text{bipy}] + [\text{Hbipy}^+]$. Such corrected c_{bipy} values fit excellently the k_x data in the absence of added Mn^{2+}.

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