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Kinetics and mechanism of hydrazine oxidation by an oxo-bridged tetramanganese(IV) complex in weakly acidic media

Utpal Roy Choudhury, Saumen Banerjee and Rupendranath Banerjee *

Department of Chemistry, Jadavpur University, Calcutta 700 032, India.
E-mail: dsthcr28@cal2.vsnl.net.in

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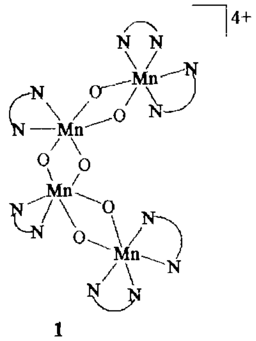
The complex $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ **1** (bipy = 2,2′-bipyridine) quantitatively oxidised $N_2H_5^+$ to N_2. With an excess of $N_2H_5^+$ the reaction proceeds through two parallel first-order paths. In one, **1** reacts with $N_2H_5^+$ and the rate is independent of $[H^+]$ and the concentration of bipy. In the other path, the rate decreases with increasing concentration of ligand and $[H^+]$. In this second path $[Mn_4(\mu\text{-}O)_6(bipy)_5(H_2O)(N_2H_4)]^{4+}$ appears to be the reactive species. The overall first-order rate constant k_0 decreases linearly with increased mole % of D_2O and k_0 in 98% D_2O is substantially (3.89 times) less than that in 0% D_2O. Transfer of one electron and one proton in the rate determining step is proposed for both the paths.

The oxygen-evolving complex (OEC) of photosystem II (PS II) is a tetrameric manganese cluster with a di(μ-oxo)dimanganese unit as its key structural feature.[1] The cluster cycles through five intermediate redox states from S_0 to S_4 as first observed by Kok *et al.*[2] Recent studies strongly suggest that in this cycle proton movement to a tyrosinase radical provides extra driving force relative to a purely outer-sphere electron transfer.[3]

The complex $[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+}$ **1** (bipy = 2,2′-bipyridine) is one of the different Mn^{IV}_4 clusters synthesized to model OEC.[4] Blondin *et al.*[5] prepared the reduced, mixed-valence $Mn^{IV}_3Mn^{III}$ form of **1** by cryogenic radiolysis. The mixed-valence cluster has a terminal Mn^{III} and is the best EPR spectroscopic model so far available for the 'S₂' state. Kinetic and mechanistic studies of the reduction of **1** thus appear interesting.



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Hydrazine, the presently chosen reductant, is useful for probing reaction mechanisms of inorganic complexes, and the mechanistic versatility noted in its reactions is attractive.[6] Furthermore, the estimated dissociation energy for the N–H bond of hydrazine (84 kcal mol^{-1})[7] and that of the O–H bond of tyrosine (86.5 kcal mol^{-1}) compare well and it is interesting to see whether hydrazine may take part in a proton coupled electron transfer, as tyrosinase does in PS II.

Experimental

Materials

The complex salt hydrate $[Mn_4(\mu\text{-}O)_6(bipy)_6][ClO_4]_4\cdot 2H_2O$ was synthesized according to a known procedure.[8] One of its water molecules is easily lost[8b] and the elemental analyses of the crystal closely adhered to that expected for the monohydrate formula, $[Mn_4(\mu\text{-}O)_6(bipy)_6][ClO_4]_4\cdot H_2O$. Calc. for $C_{15}H_{13}ClMnN_3O_6$: C, 42.73; H, 3.08; Mn, 13.03; N, 9.97. Found: C, 43.0; H, 3.10; Mn, 13.10; N, 9.79%. The absorption of 0.10 mmol dm^{-3} tetramer in an aqueous bipyridine buffer (pH 4.50, c_{bipy} = 5.0 mmol dm^{-3}) increase almost monotonously from 800 to 350 nm with a shoulder in between 420 and 430 nm (ε = 8630–8155 dm^3 mol^{-1} cm^{-1}). The spectral features reported[8b] in HNO_3 (pH 2.0) are similar, though the ε value at 420 nm is slightly lower at the lower pH. The equivalent weight measured iodometrically (211) is in good agreement with the value calculated (209) for the monohydrate. The compound used here in all the experiments thus appears to be the sufficiently pure monohydrate.

Preparation of hydrazine nitrate solution and volumetric measurement of its strength have been described earlier.[9] Such solutions are stable[10] and do not decrease in strength for at least a week at ≈27 °C. 2,2′-Bipyridine (Sigma) was used as received. All other chemicals were of reagent grade. Doubly distilled water was used throughout.

Stoichiometric measurements

Measurements were done in the range pH 4.2–5.1. Reaction mixtures containing 4.5–2.5 times hydrazine over the complex **1** were allowed to react until they became colourless (≤30 min). The hydrazine content in the spent solution was determined colorimetrically at 458 nm, after developing a yellow colour with *p*-dimethylaminobenzaldehyde (G.R., E. Merck, crystallised from alcohol) dissolved in a mixture of ethanol and concentrated HCl.[11] The final hydrazine concentrations used for calibration were (2–85) × 10^{-6} mol dm^{-3}. Gas evolved during the reaction was collected in a 10 mL micro-burette by downward displacement of water. The measured volume was corrected to NTP as usual.

Stoichiometric measurements were carried out with 100 mL, 1.0 mmol dm^{-3} complex solution, but only 10 mL, 0.10 mmol dm^{-3} complex solution was used in the kinetic experiments. The small volume of gas evolved (expected, 0.04 mL) had no effect on the measured absorbance, as verified from the unchanged absorbance on shaking the spectrophotometer cell. Nessler's reagent [alkaline potassium tetraiodomercurate(II)] was used to test qualitatively for ammonia. The test can detect 500 μg dm^{-3} of NH_3.

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Table 1 Stoichiometry of reduction of the Mn^{IV}_4 complexes by hydrazine (R)[a]

$[Mn^{IV}_4]$	pH	[R]	$\Delta[Mn^{IV}_4]/\Delta[R]$
0.2	4.20	0.8	0.52
0.4	4.50	1.0	0.48
0.8	4.75	2.4	0.53
1.2	4.90	4.2	0.51
1.4	5.10	6.2	0.49
			Average = 0.506 ± 0.021

[a] $c_{bipy} = 5.0$; all concentrations in mmol dm^{-3}.

Table 2 First-order rate constants[a] at 25.0 °C, I 1.0 mol dm^{-3} ($NaNO_3$)

pH	c_{bipy}/ mmol dm^{-3}	$[N_2H_5^+]$/ mmol dm^{-3}	$10^2k_0/s^{-1}$
4.50	5.00	2.00	0.80 (0.83)
4.63			0.87 (0.91)
4.78			1.03 (1.02)
4.92			1.23 (1.18)
5.00			1.30 (1.29)
5.14			1.60 (1.55)
4.22	1.00	2.00	1.84 (1.88)
4.50			2.40 (2.38)
4.70			3.02 (2.99)
4.80			3.45 (3.43)
5.01			4.70 (4.72)
4.51	2.00	2.00	1.40 (1.42)
4.75			1.80 (1.82)
4.80			1.96 (1.94)
5.08			2.92 (2.89)
4.86	1.00	2.00	3.82 (3.73)
	3.00		1.50 (1.54)
	7.00		0.88 (0.92)
	10.00		0.80 (0.78)
	15.00		0.70 (0.67)
4.23	1.00	2.00	1.85 (1.89)
	2.00		1.20 (1.17)
	15.00		0.55 (0.54)
4.86	5.00	2.00	1.08 (1.11)
		2.50	1.40 (1.38)
		3.00	1.64 (1.66)
		3.50	1.90 (1.94)
		4.00	2.19 (2.21)
		4.50	2.50 (2.49)

[a] Concentration of complex used 0.10 mmol dm^{-3}. Individual rate constants are averages from 2 or 3 experiments and k_0 values are reproducible within 5%. Calculated k_0 in parentheses lie within ±5% of the experimental value.

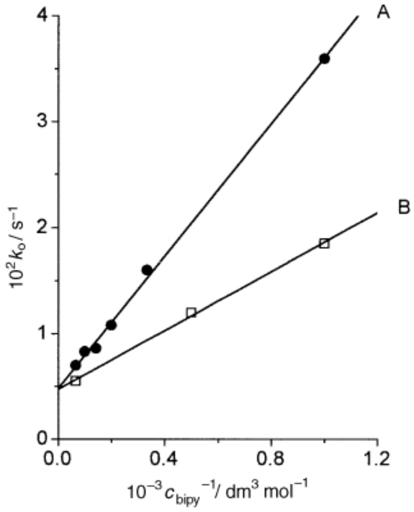

Fig. 1 Plots of k_0 *versus* $1/c_{bipy}$ at a fixed pH, [complex] = 0.10 mmol dm^{-3}, $[N_2H_5^+] = 2.0$ mmol dm^{-3}, $c_{bipy} = 1.0–15.0$ mmol dm^{-3}, $I = 1.0$ mol dm^{-3} and $T = 25.0$ °C. (A) pH 4.86, (B) pH 4.23.

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* in the 'kinetic mode' of the instrument at 420 nm in the electrically controlled thermostatted (25.0 ± 0.1 °C) cell-housing (CPS-240A). In this mode the change in absorbance is automatically and continuously recorded. For faster reactions, hydrazine solution (adjusted to desired pH) was directly injected into the spectrophotometer cell containing other components of the reaction mixture. The volume change due to mixing was minimal due to the use of a concentrated hydrazine solution. The ionic strength was 1.0 mol dm^{-3} ($NaNO_3$). Excess of bipyridine was added to the reaction mixture. The total 2,2′-bipyridine concentration, $c_{bipy} = ([bipy] + [Hbipy^+])$, was in the range 1–15 mmol dm^{-3} and acted as a weak buffer. Solution pH values ranged from 4.22 to 5.14 and were measured with an Orion-Ross Combination (model 81-02) electrode before and after the reaction. 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 was determined by titration against NaOH solutions.[12] For reactions in D_2O, pD was calculated[13] as $(pH)_{measured} + 0.40$. All the kinetics were determined with hydrazine in large excess.

Results and discussion

Measurements at different pH and different reactant ratios (complex : hydrazine) yielded ($\Delta[Mn^{IV}_4] : \Delta$[hydrazine]) = 0.506 ± 0.021 (Table 1). Qualitative analysis of the reaction mixture of NH_3 gave negative results, though 1.92 ± 0.11 (average of three experiments) moles of a gas were evolved per mole of the complex consumed. Hence the most likely oxidation product of $N_2H_5^+$ is dinitrogen according to the stoichiometric equation (1). The likely manganese(II) species under the experimental conditions are Mn^{II}–bipy complexes. Spectra for the product solution were practically superimposed on that of a mixture of $Mn(NO_3)_2$ and bipyridine under the reaction conditions of concentration and pH.

$$[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+} + 2\,N_2H_5^+ + 2\,H^+ \longrightarrow 4\,Mn^{II} + 6\,bipy + 2\,N_2 + 6\,H_2O \quad (1)$$

Kinetics

In the presence of an excess of reducing agent the reaction followed excellent first-order kinetics for at least 90% reaction and any initial drop in absorbance can be explained by the average first-order rate constants, k_0 (Table 2), and the estimated time required (≈5 s) for mixing the reagents. At a fixed pH, k_0 increases with decreasing c_{bipy} and plots of k_0 *versus* $1/c_{bipy}$ at a fixed pH are excellent straight lines ($r = 0.999$) with fixed intercept, independent of experimental pH. The slope of the line, however, decreases with decreasing pH [Fig. 1]. These observations suggest two parallel reaction paths, one independent of both c_{bipy} and $[H^+]$, while the rate for the other increased with decreasing $[H^+]$ and decreasing c_{bipy}.

The first path almost certainly corresponds to a reaction between complex **1** and $N_2H_5^+$. The inverse c_{bipy} dependence for the second path indicates a rapid ligand dissociation pre-equilibrium [eqn. (2), see Scheme 1] and greater kinetic activity

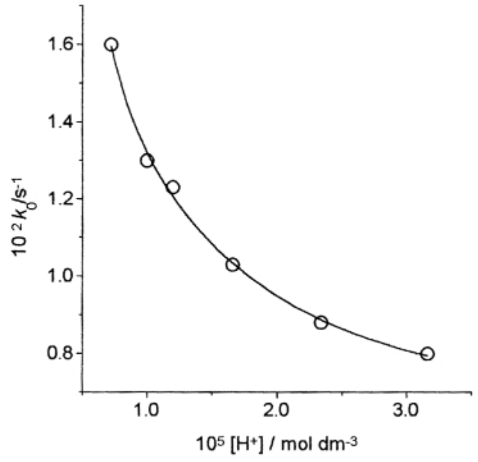

Fig. 2 Variation of k_0 with $[H^+]$ at a fixed $c_{bipy} = 5.0$ mmol dm^{-3}, [complex] = 0.1 mmol dm^{-3}, $[N_2H_5^+] = 2.0$ mmol dm^{-3}, $I = 1.0$ mol dm^{-3}, $T = 25.0$ °C.

of the aqua-derivative over its parent. Similar rapid[12,14] aquation equilibria are well known for a good number of oxo-bridged multinuclear manganese complexes of 2,2′-bipyridine and 1,10-phenanthroline (phen). Greater kinetic activity of the aqua-derivatives is also a well authenticated phenomenon for multinuclear and mononuclear manganese complexes.[14] Eqn. (2), which successfully explains the inverse dependence on c_{bipy}, does not however explain why k_0 decreases with increasing $[H^+]$ [Fig. 2]; indeed, it demands an opposite trend, increasing k_0 with increasing $[H^+]$. The observed kinetics, therefore suggest progressive generation of a species of strong kinetic activity as the pH is raised. It should be kinetically so active as to over-compensate the rate-retarding effect of decreasing $[H^+]$ one expects from eqn. (2).

$$[Mn_4(\mu\text{-}O)_6(bipy)_6]^{4+} + H^+ + 2H_2O \underset{\mathbf{1}}{} \xrightleftharpoons{K_1} [Mn_4(\mu\text{-}O)_6(bipy)_5(H_2O)_2]^{4+} + Hbipy^+ \quad (2)$$

$$\mathbf{1} \qquad\qquad \mathbf{2}$$

$$\mathbf{2} + N_2H_5^+ \xrightleftharpoons{K_2} [Mn_4(\mu\text{-}O)_6(bipy)_5(H_2O)(N_2H_4)]^{4+} + H^+ + H_2O \quad (3)$$

$$\mathbf{2'}$$

$$\mathbf{1} + N_2H_5^+ \xrightarrow{k_1} \text{Products, ultimately Mn}^{II}\text{, N}_2\text{, bipy} \quad (4)$$

$$\mathbf{2'} \xrightarrow{k_2} \text{Products, ultimately Mn}^{II}\text{, N}_2\text{, bipy} \quad (5)$$

Scheme 1

Evidently, a deprotonation equilibrium is necessary and one involving $N_2H_5^+$ appears plausible. We have no evidence so far for any deprotonated form of complex **1** or **2** in the experimental range of pH. Moreover, a deprotonated oxidant oxidises at a slower rate than its conjugate acid form.[15] Considering all these, Scheme 1 is proposed to account for the observed kinetics. We presume in eqns. (4) and (5) that an initial slow rate-determining reaction is followed by rapid reactions wherein intermediate higher-valent manganese complexes are rapidly reduced by hydrazine, or by the radicals produced from hydrazine. The follow-up reactions should be rapid because (a) the reducing agent may be a radical species in addition to hydrazine itself and (b) the possible intermediate complexes may possess high kinetic activity. For example, the $[Mn^{IV}_2Mn^{III}(\mu\text{-}O)_6(bipy)_6]^{3+}$ species is known to be putative.[5] Again a cluster break up is expected once one of the manganese atoms is reduced to the manganese(II) state.[16] It appears from the structure of **1** that tri- or di-nuclear complexes thus produced should bear 2–4 water molecules in the co-ordination.

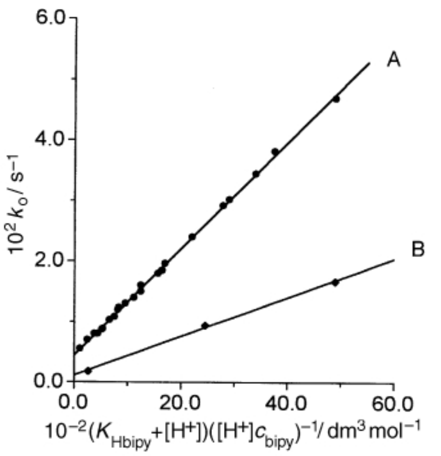

Fig. 3 Evaluation of k_1 and $k_2K_1K_2$. [complex] = 0.1 mmol dm^{-3}, $[N_2H_5^+] = 2.0$ mmol dm^{-3}, $c_{bipy} = 1.0$–15.0 mmol dm^{-3}, $I = 1.0$ mol dm^{-3}, $T = 25.0$ °C. (A) In 100% water; pH 4.22–5.14. (B) in 98 mole% D_2O; $pH_{measured} = 4.44$–4.61.

Such aqua complexes are known to possess high kinetic activity towards reduction reactions. Scheme 1 leads to eqn. (6), which

$$k_0 = \frac{(k_1[Hbipy^+] + k_2K_1K_2)[N_2H_5^+]}{[Hbipy^+] + K_1[H^+] + K_1K_2[N_2H_5^+]} \quad (6)$$

may be transformed to (7) provided $(K_1[H^+] + K_1K_2[N_2H_5^+]) \ll [Hbipy^+]$, where $[Hbipy^+] = c_{bipy}[H^+](K_{Hbipy} + [H^+])^{-1}$; K_{Hbipy} is

$$k_0 = \{k_1 + k_2K_1K_2(K_{Hbipy} + [H^+])(c_{bipy}[H^+])^{-1}\}[N_2H_5^+] \quad (7)$$

known (3.8×10^{-5} mol dm^{-3}) proton dissociation constant[17] of $Hbipy^+$ at 25.0 °C and I 0.33 mol dm^{-3}.

Plots of k_0 *versus* $(K_{Hbipy} + [H^+])(c_{bipy}[H^+])^{-1}$ are found to be excellent straight lines [Fig. 3] with intercept = $k_1[N_2H_5^+] = (0.44 \pm 0.012) \times 10^{-2}$ s^{-1} and slope = $k_2K_1K_2[N_2H_5^+] = (8.82 \pm 0.06) \times 10^{-6}$ mol dm^{-3} s^{-1}. Hence $k_1 = (2.22 \pm 0.06)$ dm^3 mol^{-1} s^{-1} and $k_2K_1K_2 = (4.41 \pm 0.03) \times 10^{-3}$ s^{-1} at 25.0 °C, I 1.0 mol dm^{-3}.

One can replace eqns. (3) and (5) with (8) and (9) to obtain

$$N_2H_5^+ \rightleftharpoons N_2H_4 + H^+ \quad (8)$$

$$\mathbf{2} + N_2H_4 \longrightarrow \text{Products} \quad (9)$$

a scheme, kinetically equivalent to Scheme 1. This is not an attractive alternative. The reaction kinetics require that complex **1** reacts with only $N_2H_5^+$ not N_2H_4. Selective reaction of **1** with $N_2H_5^+$ but that of **2** with N_2H_4 according to eqn. (9) appears most unusual. If a kinetically significant amount of N_2H_4 is available for reaction with **2**, then why should **1** not utilise it? Evidently, the concentration of free N_2H_4 must be kinetically insignificant for the present reaction systems.

At first sight the intimate mechanism of electron transfer in the k_1 path seems to be outer sphere since complex **1** is co-ordinatively saturated. Nevertheless, such a mechanism would be exceptional since reaction of $N_2H_5^+$ with an outer-sphere oxidant is unknown.[6] A different situation is not expected for complex **1** which is only a moderately strong oxidising agent reducible to Mn^{2+} at 0.6 V.[18] The reduction potential for $N_2H_5^+$–$N_2H_4^+$ can be calculated† to be −1.16 V. This highly unfavourable value is the most important stumbling block for

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† From the equilibrium constant ($K = 2.1 \times 10^{-20}$ mol dm^{-3}) for the overall reaction $N_2H_5^+ \rightleftharpoons N_2H_4^+ + H^+ + e$ which in turn is obtained as a product of two equilibrium constants, $K_a = 10^{-7.98}$ mol dm^{-3} for the reaction;[19] $N_2H_5^+ \rightleftharpoons N_2H_4 + H^+$ and $K_1 = 2 \times 10^{-12}$ for $N_2H_4 \rightleftharpoons N_2H_4^+ + e$.[20]

Table 3 First order rate constants[a] in different mole% D_2O

Mole% D_2O	$10^3k_0/s^{-1}$
0	7.0
48	4.2
98	1.8

[a] 25.0 °C; I 1.0 mol dm^{-3}; c_{bipy} 15 mmol dm^{-3}; $[Mn^{IV}_4] = 0.10$ mmol dm^{-3}; $[N_2H_5^+] = 2.0$ mmol dm^{-3}; $pH_{measured} = 4.44$.

Table 4 First order rate constants in 98 mole% D_2O, $[N_2H_5^+] = 2.0$ mmol dm^{-3}

$pH_{measured}$	c_{bipy}/mmol dm^{-3}	$10^3k_0/s^{-1}$
4.61	1.0	16.7
4.61	2.0	9.4
4.44	15.0	1.8

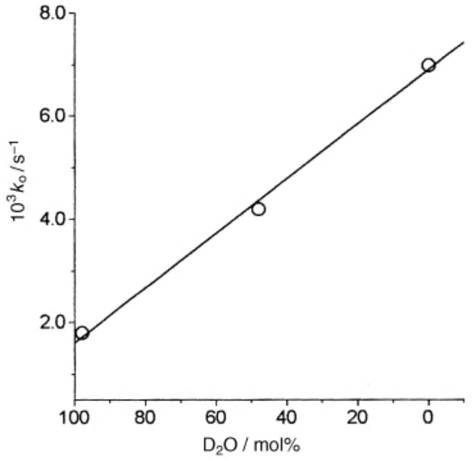

Fig. 4 Effect of mole% D_2O on k_0. [complex] = 0.1 mmol dm^{-3}, $[N_2H_5^+] = 2.0$ mmol dm^{-3}, $c_{bipy} = 15.0$ mmol dm^{-3}; $I = 1.0$ mol dm^{-3}; $T = 25.0$ °C; $pH_{measured} = 4.44$.

$N_2H_5^+$ to enter into an outer-sphere reaction; the expected self-exchange rate for $N_2H_5^+$ is also small[21] and further disfavours an outer-sphere reaction. To explore the mechanism, we measured some k_0 in media containing 0–98 mole% D_2O. The results are shown in Fig. 4 and Table 3. The ratio of k_0 in 0% D_2O to that in 98% D_2O is a substantial value (3.89 : 1). Variations in rate resulting from substitution of D_2O for solvent water are expected to be slight for simple electron transfer reactions. However, dramatic rate retardation is expected when such transfer is coupled with the movement of a proton which is in equilibrium with solvent protons.[22] It is also noticeable that the plot of k_0 *versus* mole fraction of D_2O [Fig. 4] is closely linear. According to Albery and Davies[23] this is indicative of the transfer of just a single proton in the redox act.

One cannot tell from Fig. 4 whether D_2O retards either or both the reaction paths, but further kinetics in 98 mole% D_2O medium [Fig. 3(B); slope = $(3.20 \pm 0.10) \times 10^{-6}$ mol dm^{-3} s^{-1}, intercept = $(0.12 \pm 0.04) \times 10^{-2}$ s^{-1}, $r = 0.999$] demonstrates nearly equal retardation for both. Interestingly, both the magnitude of the isotope effect and the linearity of the plot of k_0 *versus* mole% D_2O correspond closely to the analogous features observed when the $[Mn^{III,IV}_2(\mu\text{-}O)_2(bipy)_4]^{3+}$ complex **3** is reduced by ascorbic acid.[16b] Both the paths thus seem to involve simultaneous transfer of an electron and a proton in the rate determining step, which plausibly lead to the formation of $[Mn^{IV}_3Mn^{III}(\mu\text{-}O)_5(\mu\text{-}OH)(bipy)_6]^{4+}$ and its aqua derivative. These species are putative as found during electrochemical reduction[18] of **1** and from the cryogenic radiolytic studies of Blondin *et al.*[5] Hence we speculate rapid conversion of these mixed-valence $Mn^{IV}_3Mn^{III}$ cluster ultimately into Mn^{II} under the present experimental conditions and which thus explains the simple first-order reaction.

The present work illustrates that $N_2H_5^+$ ion may act as a reducing agent through a electroprotic pathway and thus exhibits significant kinetic activity.

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