Kinetics of oxidation of hydrogen peroxide and ascorbic acid by a tribridged manganese(IV,IV) dimer in feebly acidic media

Anup Kumar Bhattacharya, Anath Bondhu Mondal, Anadi C. Dash, G.S. Brahma, and Rupendranath Banerjee

Abstract: In weakly acidic, aqueous buffer ($MeCO_2^-$+ bipy), the complex ion $[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}MeCO_2)(bipy)_2(H_2O)_2]^{3+}$, **1** (bipy = 2,2′-bipyridine), coexists in rapid equilibrium with its hydrolytic derivatives, $[Mn_2^{IV}(\mu\text{-}O)_2(bipy)_2(H_2O)_4]^{4+}$, **2**, and $[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}MeCO_2)(bipy)(H_2O)_4]^{3+}$, **3**. The solution quantitatively oxidizes hydrogen peroxide to oxygen and ascorbic acid to dehydroascorbic acid, itself being reduced to Mn^{II}. In the presence of excess reductant, the reactions follow simple first-order kinetics with no evidence for the accumulation of a significant amount of any intermediate manganese complex. The ascorbate anion shows overwhelming kinetic dominance over ascorbic acid, but no evidence is available for deprotonation of hydrogen peroxide. The preferred intimate mechanism for hydrogen peroxide is inner sphere but that for ascorbic acid is uncertain. For both reductants, increased extent of aquation leads to increased kinetic activity in the order: **1** < **2** < **3**.

Key words: kinetics, manganese, ascorbic acid, hydrogen peroxide, 2,2′-bipyridine.

Résumé : En milieu faiblement acide, tampon aqueux (acétate + bipyridine), le complexe ionique $[Mn(IV)_2(\mu\text{-}O)(\mu\text{-}MeCO_2)(bipy)_2(H_2O)_2]^{3+}$ (**1** dans lequel bipy = 2,2'-bipyridine) coexiste en équilibre rapide avec ses dérivés d'hydrolyse, $[Mn(IV)_2(\mu\text{-}O)(bipy)_2(H_2O)_4]^{4+}$ (**2**) et $[Mn(IV)_2(\mu\text{-}O)_2(\mu\text{-}MeCO_2)(bipy)_2(H_2O)_4]^{3+}$ (**3**). La solution oxyde quantitativement le peroxyde d'hydrogène en oxygène et l'acide ascorbique en acide déhydroascorbique alors que le manganèse est réduit en Mn(II). En présence d'un excès de réducteur, les réactions suivent une cinétique du premier ordre simple, sans accumulation de quantités significatives de complexes de manganèse intermédiaires. L'anion ascorbate présente une dominance cinétique importante par rapport à l'acide ascorbique, mais on n'a pas pu mettre en évidence de déprotonation du peroxyde d'hydrogène. La sphère interne correspond au mécanisme intime préféré pour le peroxyde d'hydrogène; celui pour l'acide ascorbique est toutefois incertain. Pour les deux réducteurs, une augmentation de l'aquation conduit à une activité cinétique accrue dans l'ordre **1** < **2** < **3**.

Mots clés : manganèse, acide ascorbique, peroxyde d'hydrogène, 2,2′-bipyridine.

[Traduit par la Rédaction]

Introduction

The oxygen-evolving complex (OEC) in photosystem II (PS II) consists of a manganese cluster that binds substrate water molecules and accumulates oxidizing equivalents in a cyclic sequence of reactions known as the Kok or the S-state cycle (1). The OEC is made up of four manganese ions (2), held together by μ-oxo and carboxylate bridges, and a tetrameric structure was recently proposed on the basis of EXAFS and EPR data (3). ESSEM $^{14}N/^{15}N$ labelling studies (4) and ^{15}N ENDOR spectroscopy (5) have shown that nitrogen-containing ligands are bound to manganese in PS II. Oxo- and carboxylato-bridged manganese dimers (6) containing N-donor ligands are therefore considered as "molecular bricks" for the OEC. Investigation of the kinetics, equilibrium, and mechanism of the ligand substitution and redox reactions of such complexes is intrinsically interesting.

In addition to their significance in light-driven oxidation of water molecules to oxygen, these complexes are novel oxidants useful for the mechanistic studies of electron transfer reactions of higher-valent manganese in solution. We recently investigated the kinetics of reduction of two dioxo-bridged manganese(III,IV) dimers (7) and the tribridged $[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}MeCO_2)(bipy)_2(H_2O)_2]^{3+}$ ion (**1**; bipy = 2,2′-bipyridine; see Fig. 1) in aqueous media (8–10). We thus found that the Mn_2^{IV} species in excess bipy generate a $Mn^{III}Mn^{IV}$ dimer, $[(bipy)_2Mn^{IV}(\mu\text{-}O)_2Mn^{III}(bipy)_2]^{3+}$, as intermediate while reacting with thiosulfate and hydrazine but not with nitrite. From the observed proton dependence, the intimate mechanism for hydrazine appeared to be inner sphere. In this paper, we report the kinetics of reduction of **1** and its aqua derivatives by ascorbic acid (H_2A) and hydrogen peroxide in an attempt to further explore the reactivity pattern of higher-valent oxo-bridged manganese complexes.

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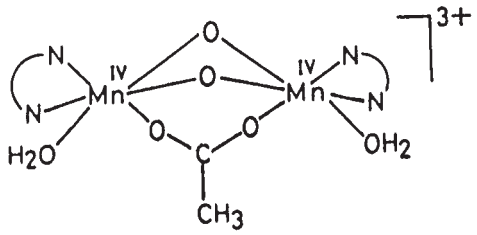
Fig. 1. Graphical structure for **1** drawn on the basis of its crystal structure.



Experimental

Materials

The solutions of hydrogen peroxide were prepared by dilution of 30% (w/v) stabilizer-free hydrogen peroxide (G.R., E. Merck) and were standardized by iodometry using starch indicator (11). L-Ascorbic acid (A.R., S.R.L) was used without further purification. All other materials including the complex ion **1** have been described earlier (8). Solutions were prepared in doubly distilled water, generally just before use.

Physical measurements and kinetics

Kinetics were measured with a stopped-flow spectrophotometer (HITECH SF-51), interfaced with an Apple-II GS personal computer for data acquisition and analysis of absorbance–time data for the first-order rate constants. Five hundred and twelve data points were collected by the stopped-flow apparatus for each experiment. Excess reducing agent maintained pseudo-first-order conditions in a mixed ($MeCO_2H/MeCO_2^-$ + $Hbipy^+$/bipy) aqueous buffer medium in the pH range 4.2–5.5. Each reported first-order rate constant is the average of three to five replicate measurements for a given reaction mixture. We measured the solution pH with an Elico (L 1120) pH-meter (8, 12). 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 measurements. Kinetics was measured at 25.0°C for hydrogen peroxide, but at 15.0°C for fast-reacting ascorbic acid.

Stoichiometries were determined under the kinetic conditions. An excess of a reducing agent, hydrogen peroxide or ascorbic acid, was added in a single portion to a solution of the Mn_2^{IV} complex **1**. The amount of hydrogen peroxide remaining after complete reaction was determined iodometrically(11). Ascorbate concentration in spent reaction mixtures was determined iodimetrically using starch indicator near the end point in a dilute sulphuric acid medium (13). Standard iodine solution rapidly and quantitatively oxidized ascorbic acid to dehydroascorbic acid (13, 14). Other materials present in the mixture did not interfere.

Results and discussion

Stoichiometry and reaction products

Each mole of the complex consumed two moles of H_2O_2 and thus suggests quantitative oxidation of H_2O_2 to O_2 (Table 1). The 1:2 stoichiometry was also observed for ascorbic acid (H_2A), indicating that dehydroascorbic acid (A), the most common oxidation product (14, 15) of H_2A, is produced in the present experiments.

Table 1. Stoichiometry of the reduction of Mn_2^{IV} complexes. [a]

$[Mn_2^{IV}]$	pH	[R]	$\Delta [Mn_2^{IV}]/\Delta[R]$
		R = H_2O_2	
0.2	4.53	0.8	0.48
0.6	4.79	1.4	0.52
0.8	4.85	1.8	0.49
1.0	4.96	2.4	0.47
1.2	5.12	2.8	0.51
			Avg. = 0.495 ± 0.02
		R = ascorbic acid	
0.2	4.48	0.7	0.49
0.4	4.52	1.2	0.47
0.9	4.87	2	0.52
1.2	5.05	2.8	0.48
1.6	5.23	3.8	0.51
			Avg. = 0.496 ± 0.02

[a] C_{bipy} = 35.0; all concentrations are in mmol dm^{-3} ; total volume, 100 mL.

Solution equilibria

The crystal structure of the complex salt **1**$(ClO_4)_3 \cdot H_2O$ shows a bridging ethanoate ligand, a bis(μ-oxo) bridge, and two water molecules, each directly coordinated to one manganese(IV) ion (16). The ethanoate bridge and a bipy ligand are labile and dissociate in aqueous solution according to eqs. [1] and [2] (8).

[1] $$[Mn_2^{IV}(\mu-O)_2(\mu-MeCO_2)(bipy)_2(H_2O)_2]^{3+} + 2H_2O$$
1
$$\overset{K_{12}}{\rightleftharpoons} [Mn_2^{IV}(\mu-O)_2(bipy)_2(H_2O)_4]^{4+} + MeCO_2^-$$
2

[2] **1** + 2 H_2O $\overset{K_{13}}{\rightleftharpoons}$
$$[Mn_2^{IV}(\mu-O)_2(\mu-MeCO_2)(bipy)(H_2O)_4]^{3+} + bipy$$
3

[3] $$MeCO_2H \overset{K_{ea}}{\rightleftharpoons} MeCO_2^- + H^+$$

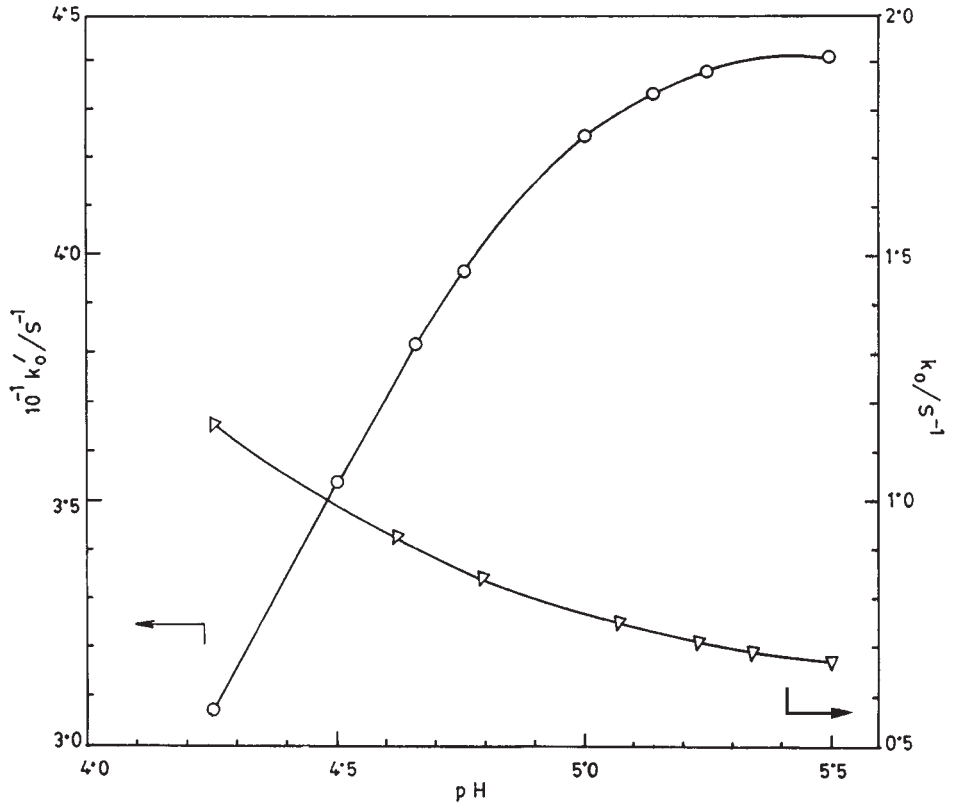
[4] $$Hbipy^+ \overset{K_{Hbipy}}{\rightleftharpoons} H^+ + bipy$$

The solution is otherwise stable under the present experimental conditions.

A labile ethanotate bridge is found also in the dinuclear Mn(III,IV) complex $[Mn_2(\mu\text{-}O)_2(\mu\text{-}MeCO_2)(\textit{fac}\text{-bpea})_2]^{2+}$ (bpea is *N*,*N*-bis(2-pyridylmethyl)ethylamine) and in its diferric analogue, $[Fe_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2(L)_2]^{2+}$ (L is substituted bpea) (17–19).

The chelating ligands in the complexes $[L'_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}L'_2]^{3+}$ (L′ = 2,2′-bipyridine and 1,10-phenanthroline) are also labile (7, 20). The binding sites in the S_3-state (the S-state notation (1) identifies the number of oxidizing equivalents stored in the manganese cluster in the water oxidation

Fig. 2. Variation of first-order rate constants for H_2O_2 with pH at a fixed C_{bipy}(0.035) and fixed C_{ea}(0.08) at 25.0°C (▽). Variation of first-order rate constants for ascorbic acid with pH at a fixed C_{bipy} (0.035) and C_{ea} (0.1) at 15.0°C (○).



complex of PS II) are labile and exchange ^{18}O-labeled water in less than 1 s (21). However, the bridging oxo-ligands are kinetically inert (22, 23). Interestingly, equilibrium as well as kinetic studies (8, 10) suggest that the coordinated water molecules in **1** and its aqua derivatives do not deprotonate, at least up to pH 5.5. Weak acidity of coordinated water is known also for $[Mn_3^{IV}(\mu\text{-}O)_4(bipy)_4(H_2O)_2]^{4+}$ (24) and $[Mn(pd)_2(H_2O)_2]^+$ (pd is pentane-2,4-dione). The latter complex has a pK_a value of 7.3 (25–27). The weak acidity observed is consistent with recent findings that the O—H bond strength in water coordinated to higher-valent manganese is comparable to the phenolic O—H bond strength in tyrosine (28, 29).

Kinetics and reaction schemes

All reactions in the presence of excess reducing agent obeyed first-order kinetics for at least 90% reaction. The first-order rate constants, k_0 for H_2O_2 and k_0' for ascorbic acid (see Table 2), increased with increasing concentration of the reducing agent but decreased with increasing [bipy] and [$MeCO_2^-$] at a fixed pH. However, pH change affects k_0 and k_0' differently. Increased pH decreases k_0 but increases k_0' (Fig. 2). The variations in k_0 can be explained on the basis of only equilibria [1]–[4], provided the hydrolytic derivatives **2** and **3** are kinetically more active than their parent, **1**. We therefore propose Scheme 1 as a simple model for the reaction of H_2O_2.

The pH dependence of the reactions of ascorbic acid can be reasonably explained if one assumes, along with equilibria [1]–[4], the deprotonation equilibrium of H_2A, eq. [8] (15), and an overwhelming kinetic dominance of the ascorbate ion, HA^-, over ascorbic acid, H_2A. (Scheme 2, eqs. [8]–[11]).

Scheme 1.

[5] **1** + H_2O_2 $\xrightarrow{k_A}$ Products (Mn^{II}, H^+, O_2)

[6] **2** + H_2O_2 $\xrightarrow{k_B}$ Products

[7] **3** + H_2O_2 $\xrightarrow{k_C}$ Products

Scheme 2.

[8] H_2A $\overset{K_a}{\rightleftharpoons}$ H^+ + HA

[9] **1** + HA^- $\xrightarrow{k_A'}$ Products (Mn^{II}, H^+, A)

[10] **2** + HA^- $\xrightarrow{k_B'}$ Products

[11] **3** + HA^- $\xrightarrow{k_C'}$ Products

Table 2. First-order rate constants for the reduction of Mn_2^{IV} complexes. [a]

pH	[bipy]	[$MeCO_2^-$]	[R]	k_0/s^{-1}
		Reducing agent (R), H_2O_2		
4.25	14.1	19.4	1.0	1.16 (1.13)
4.50	19.1	29.0	1.0	1.01 (0.99)
4.63	21.6	34.8	1.0	0.93 (0.91)
4.79	24.5	42.1	1.0	0.84 (0.82)
5.06	28.5	53.9	1.0	0.74 (0.73)
5.23	30.3	60.3	1.0	0.71 (0.69)
5.34	31.2	63.8	1.0	0.69 (0.68)
5.50	32.3	68.0	1.0	0.67 (0.66)
4.50	2.73	29.0	1.0	2.81 (2.68)
4.50	5.46	29.0	1.0	1.81 (1.78)
4.50	8.19	29.0	1.0	1.37 (1.43)
4.50	9.55	29.0	1.0	1.34 (1.32)
4.50	10.9	29.0	1.0	1.23 (1.24)
4.50	13.65	29.0	1.0	1.12 (1.26)
4.50	16.4	29.0	1.0	1.06 (1.09)
4.50	19.1	1.81	1.0	1.75 (1.76)
4.50	19.1	3.62	1.0	1.59 (1.61)
4.50	19.1	5.44	1.0	1.49 (1.50)
4.50	19.1	7.26	1.0	1.39 (1.41)
4.50	19.1	9.07	1.0	1.34 (1.33)
4.50	19.1	12.9	1.0	1.20 (1.22)
4.50	19.1	36.3	1.0	0.92 (0.94)
4.50	19.1	54.4	1.0	0.87 (0.86)
4.50	19.1	29.0	1.5	1.52 (1.48)
4.50	19.1	29.0	2.0	2.04 (1.98)
4.50	19.1	29.0	2.5	2.41 (2.47)
4.50	19.1	29.0	3.0	3.02 (2.97)
4.50	19.1	29.0	4.0	3.89 (3.96)
4.50	19.1	29.0	5.0	4.88 (4.95)
		Reducing agent, ascorbic acid		
pH	[bipy]	[$MeCO_2^-$]	[R]	$10^{-1}\ k_0'/s^{-1}$
4.25	14.1	24.2	1.0	3.07 (3.05)
4.50	19.1	36.3	1.0	3.54 (3.56)
4.67	22.4	45.8	1.0	3.81 (3.83)
4.75	23.8	50.3	1.0	3.99 (3.94)
5.00	27.7	64.3	1.0	4.25 (4.19)
5.13	29.3	70.8	1.0	4.35 (4.29)
5.25	30.5	76.2	1.0	4.39 (4.36)
5.50	32.3	85.1	1.0	4.41 (4.45)
4.50	2.73	36.3	1.0	5.18 (5.20)
4.50	5.46	36.3	1.0	4.40 (4.24)
4.50	8.19	36.3	1.0	3.99 (3.92)
4.50	9.55	36.3	1.0	3.84 (3.83)
4.50	13.65	36.3	1.0	3.65 (3.69)
4.50	17.2	36.3	1.0	3.62 (3.61)
4.50	19.1	1.81	1.0	3.99 (3.98)
4.50	19.1	3.63	1.0	3.91 (3.90)
4.50	19.1	5.44	1.0	3.87 (3.84)
4.50	19.1	13.8	1.0	3.68 (3.69)
4.50	19.1	23.6	1.0	3.57 (3.61)
4.50	19.1	54.4	1.0	3.43 (3.51)
4.50	19.1	36.3	1.5	5.21 (5.33)
4.50	19.1	36.3	2.0	7.21 (7.12)
4.50	19.1	36.3	2.5	8.96 (8.89)
4.50	19.1	36.3	3.0	10.5 (10.7)
4.50	19.1	36.3	4.0	14.3 (14.2)

Table 2. (*concluded*).

pH	[bipy]	[$MeCO_2^-$]	[R]	k_0/s^{-1}
4.50	19.1	36.3	4.5	16.2 (16.0)
4.50	19.1	36.3	5.0	17.8 (17.8)

[a]Temperature, 25.0°C for H_2O_2; 15.0°C for ascorbic acid. [Mn_2^{IV}] = 0.10; all concentrations are in mmol dm^{-3} except I = 1.0 mol dm^{-3} ($NaNO_3$); λ, 420 nm for H_2O_2; 380 nm for ascorbic acid. Values in parentheses are calculated rate constants.

Schemes 1 and 2 lead to eqs. [12] and [13], respectively.

$$[12]\quad k_0 = \frac{\{k_A[MeCO_2^-][bipy] + k_BK_{12}[bipy] + k_CK_{13}[MeCO_2^-]\}[H_2O_2]}{[MeCO_2^-][bipy] + k_{12}[bipy] + k_{13}[MeCO_2^-]}$$

$$[13]\quad k_0' = \frac{\{K_ak_A'[MeCO_2^-][bipy] + K_ak_B'K_{12}[bipy] + K_aK_{13}k_C'[MeCO_2^-]\}C_a}{\{[H^+] + K_a\}\{[MeCO_2^-][bipy] + K_{12}[bipy] + K_{13}[MeCO_2^-]\}}$$

where C_a (= [H_2A] + [HA^-]) is the total analytical concentration for ascorbic acid. Equation [12] leads to eq. [14] and eq. [13] leads to eq. [15].

$$[14]\quad k_0([MeCO_2^-][bipy] + K_{12}[bipy] + K_{13}[MeCO_2^-])/[H_2O_2] = k_A[MeCO_2^-][bipy] + k_BK_{12}[bipy] + k_CK_{13}[MeCO_2^-]$$

$$[15]\quad k_0'([H^+] + K_a)([MeCO_2^-][bipy] + K_{12}[bipy] + K_{13}[MeCO_2^-])/C_aK_a = k_A'[MeCO_2^-][bipy] + k_B'K_{12}[bipy] + k_C'K_{13}[MeCO_2^-]$$

[$MeCO_2^-$] = $C_{ea}K_{ea}/([H^+] + K_{ea})$ and [bipy] = $C_{bipy}K_{Hbipy}/([H^+]+K_{Hbipy})$, where C_{ea} = ([$MeCO_2^-$] + [$MeCO_2^-$]) and C_{bipy} = ([$Hbipy^+$] + [bipy]) are the total analytical concentration of ethanoate and 2,2′-bipyridine, respectively. Values for the left-hand sides of eqs. [14] and [15] may be calculated using known rate constants (Table 2) and equilibrium constants (Table 3). The calculated left-hand sides of eqs. [14] and [15] each yielded excellent straight lines (Figs. 3 and 4) when plotted against [bipy] or [$MeCO_2^-$], thus justifying the proposed schemes. The slopes and intercepts of the straight lines yielded the specific rate constants k_A, k_B, k_C, k_A', k_B' and k_C' displayed in Table 4 along with known rate constants for comparable reactions. The rate law derived for an equivalent scheme admitting significant kinetic contribution from H_2A contains an additional term, first order in [H^+]. Such a rate law does not fit the experimental data.

The K_{12} and K_{13} values are available only at 25.0°C and were used in computing the k_n' values for ascorbic acid at 15.0°C. This difference in temperature is unlikely to introduce serious error. We verified that a simultaneous increase or decrease to the extent of 50% in K_{12} and K_{13} changes k_1' by only 12% even when k_2' and k_3' are kept fixed to see what happens if the whole thrust of the change in the two equilibrium constants are put on k_1' alone. Similar were the cases for k_2' and k_3'.

Intimate mechanism

Ascorbic acid can act both as an inner-sphere as well as an outer-sphere reducing agent (30). In the present study, labile coordination sites present in the metal complexes may induce an inner-sphere mechanism but it is not a trivial matter to pinpoint the mechanism. For example, Bansch et al. (31) have shown that oxidation of ascorbic acid by $[Fe(H_2O)_6]^{3+}$ ion follows an outer-sphere path, and oxidation by the $[Fe(H_2O)_5(OH)]^{2+}$ ion proceeds by an H-atom transfer from HA^- although both H_2A and HA^- are known (32) to be good ligands for Fe(III). Obviously, presence of a labile coordination site and the ability of the reductant to bind to a metal centre are insufficient information to decide in favour of one of the two intimate mechanisms — inner sphere or outer sphere. However, an H-atom transfer mechanism may be discarded since the Mn_2^{IV} complexes have no OH group.

The simple first-order kinetics observed by us, without any indication of rate saturation, only implies the validity of the inequality, $Q_x[HA^-] << 1$ for every individual value of Q_x, the formation quotient for adducts that may form between HA^- and the $Mn^{IV}{}_2$ complexes, **1**, **2**, **3**. In our experiments the maximum value for [HA^-] is 3.6×10^{-3} mol dm^{-3}. The inequality, therefore, imposes an upper limit on Q_x, 30 dm^3 mol^{-1}. The observed situation is similar to those for reduction of $[Mn_2^{III,IV}(\mu\text{-}O)_2(bipy)_4]^{3+}$, **4**, by hydroquinone and HSO_3^-. No rate saturation was observed in these two reactions, as was also the case in the reaction between HSO_3^- and **4**, and that between HA^- and the one-electron reduced $Mn^{III}{}_2$ form of **4** (33). However, the $(Mn^{III}{}_2)$–HSO_3^- adduct (Q = 450 dm^3 mol^{-1}), as well as that formed from **4** and ascorbic acid, is strong enough to permit their kinetic detection (33). Apparently, the Q values may be sufficiently different to evade rationalization even in closely related systems.

Oxidation of hydrogen peroxide is generally inner sphere (34) excepting when the oxidant is very powerful and coordinatively saturated, such as $[Ni^{III}(bipy)_3]$ (35). For example, the reactions of H_2O_2 with moderately oxidizing (36)

Fig. 3. Variation of k_0 G / $[H_2O_2]$ with $[MeCO_2^-]$ at a fixed pH (4.50) and fixed C_{bipy} (0.035) (■). Variation of k_0 G / $[H_2O_2]$ with [bipy] at fixed pH (4.50) and fixed C_{ea} (0.08) (●). G = $[MeCO_2^-][bipy] + K_{12}[bipy] + K_{13}[MeCO_2^-]$. Other conditions: $[Mn_2^{IV}]$, 1.0×10^{-4}; *I*, 1.0; $[H_2O_2]$, 1.0×10^{-3}; temp., 25.0°C. All concentrations are in mol dm^{-3}.

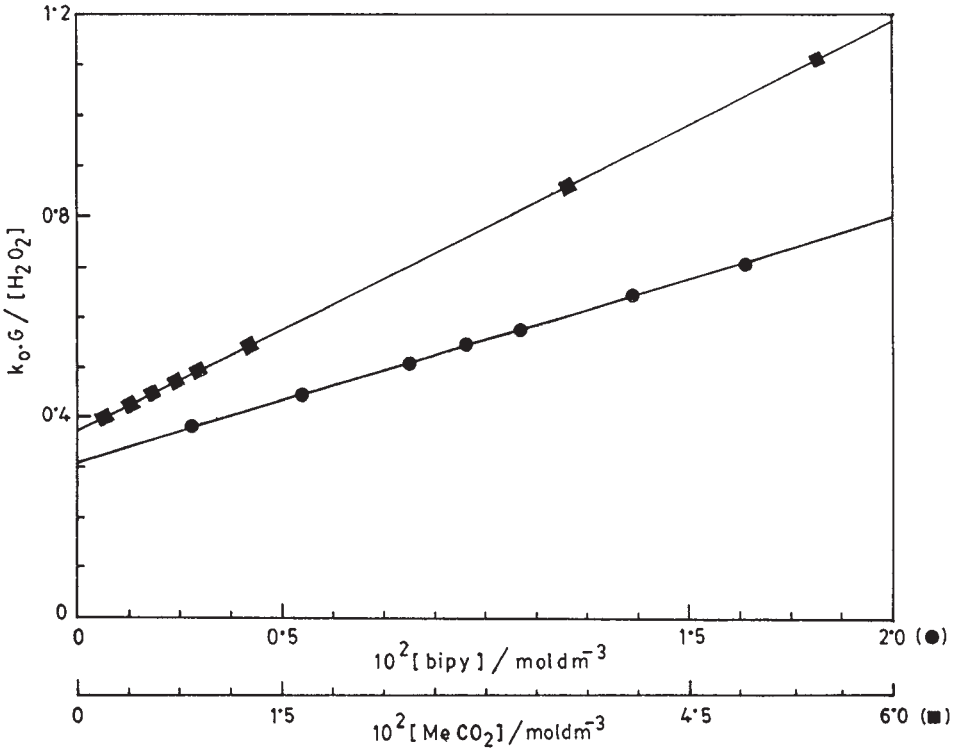


Table 3. Values of the equilibrium constants used.

Reaction	Temp./ °C	*I* / mol dm^{-3}	p*K*
Equation [1]	25	1.0	2.0[a]
Equation [2]	25	1.0	3.0[a]
Equation [3]	20	1.0	4.55[b]
Equation [4]	25	0.33	4.43[c]
	15	0.1	4.49[d]
Equation [8]	15	1.0	4.08[e]

[a]Reference 8 in the text.

[b]Reference 43. Change in temperature little affects the value; e.g, for $I \rightarrow 0$, the value over the temperature range 15–25°C is 4.756 ± 0.002 (44).

[c]Reference 45. Effect of *I* on p*K* is small; ±0.01 unit for a change in *I* from 0.33 to 0.1 mol dm^{-3}; cf. ref. 46.

[d]Reference 47. This value was used in calculations for ascorbic acid. Comparison with footnote *c* shows that the effect of temperature on p*K* is small.

[e]Reference 15 in the text.

complexes such as $[Mn(cydta)(H_2O)]^-$ (cydta is cyclohexyl ethylenediaminetetraacetate) (37) and solvolyzed **4** follow the inner-sphere path (7*d*, 36). Oxidation of potassium peroxymonosulfate to O_2 with solvolyzed **4** and its close analogues also follows the inner-sphere mechanism (38), and the same mechanism appears very likely for the reactions under the present investigation. Earlier examples of the inner-sphere mechanism for the Mn_2^{IV} complexes are their reactions with $N_2H_5^+$ (10).

In this study, no evidence is available for deprotonation of H_2O_2, though an inner-sphere mechanism implies a coordinated H_2O_2 and enhanced acidity. We recall that water molecules coordinated to Mn(IV) in **1** and its hydrolytic derivatives release no H^+ in the experimental range of pH. Similar behaviour is definitely expected for coordinated H_2O_2 and is not in contradiction with the proposed mechanism.

Table 4 shows that the kinetic activity of the Mn_2^{IV} complexes towards various reducing agents increases with increased extent of aquation in the order: **1** < **2** < **3**. Limburg et al. (38) as well as Banerjee and co-workers (7) noticed that, kinetically, **4** is a much inferior oxidant than its solvolyzed derivatives. Again, in a recent model for the mechanism of the OEC in PS II, it has been assumed that only the two terminal manganese atoms containing coordinated water in a ⊂-shaped tetranuclear cluster are redox active; the two central Mn^{4+} ions without coordinated water are inactive (23). A rationale for the greater kinetic activity of the aqua complexes was presented earlier (9).

Reduction of the Mn_2^{IV} complexes by $S_2O_3^{2-}$ and $N_2H_5^+$ produced the $Mn^{IV}Mn^{III}$ complex, **4**, as an intermediate, which subsequently oxidized additional molecules of reductant and thus decayed to Mn^{II}. No intermediate manganese complex could be detected in the present experiments. This, and the observed exponential profiles along with the absence of any absorbance drops immediately after mixing, suggests that generation of **4** and its subsequent reactions with ascorbic acid and hydrogen peroxide are kinetically insignificant in the present systems. It may be that the one-electron transfer products, the radicals $HO_2^•$ and $A^{-•}$ (generated in the rate-determining steps) rapidly react with the $Mn^{IV}Mn^{III}$ species. This is a strong possibility if the reactions are inner sphere, when rapid further reduction of the successor complex might

Fig. 4. Variation of k_0' D {[H^+] + K_a} / C_aK_a with [$MeCO_2^-$] at a fixed pH (4.50) and fixed C_{bipy} (0.035) (□). Variation of k_0' D {[H^+] + K_a} / C_aK_a [bipy] at a fixed pH (4.50) and fixed C_{ea} (0.1) (○). D = {[$MeCO_2^-$][bipy] + K_{12}[bipy] + K_{13}[$MeCO_2^-$]}. Other conditions: [Mn_2^{IV}], 1.0 × 10^{-4}; *I*, 1.0; C_{ea}, 1.0 × 10^{-3}; temp.,15.0°C. All concentrations are in mol dm^{-3}.

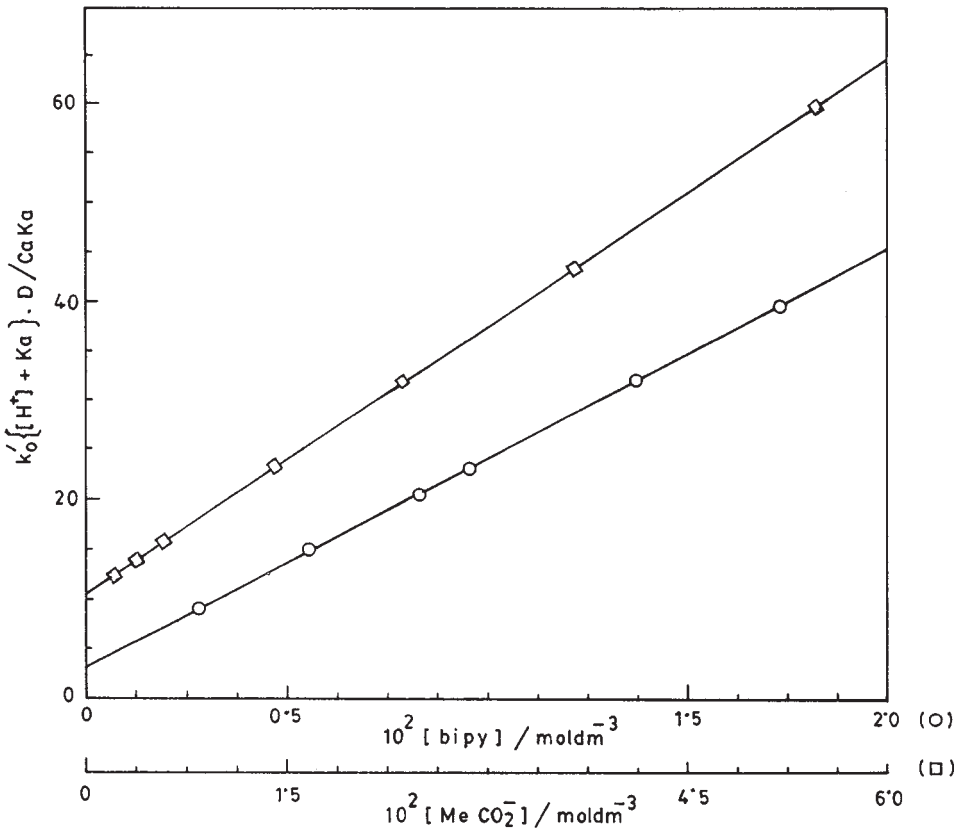


Table 4. Second-order rate constants (dm^3 mol^{-1} s^{-1}) for the reduction of different Mn_2^{IV} species by different reducing agents (R).

	Rate constant for			
R	**1**	**2**	**3**	Ref.
NO_2^-	(2.84 ± 0.13) × 10^{-3}	0.149 ± 0.007	2.07 ± 0.12	10
$N_2H_5^+$	—	(1.11 ± 0.08) × 10^{-3}	6.33 ± 0.2) × 10^{-3}	11
$S_2O_3^{2-}$	2.0 ± 0.02	40 ± 1	(1.45 ± 0.04) × 10^2	9
H_2O_2	(1.70 ± 0.08) × 10^2	(1.97 ±0.06) × 10^3	(1.02 ± 0.07) × 10^4	This work
HA^-	(4.22 ± 0.27) × 10^4	(5.62 ± 0.31) × 10^4	(9.20 ± 0.45) × 10^4	This work

occur before the radicals can escape into the bulk solvent (kind suggestion of a reviewer; see also ref. 39).

Such a mechanism, where the radicals are generated and consumed within the coordination sphere of the metal complex, is, however, closely analogous to and rarely distinguishable from a simultaneous two-electron transfer mechanism, proposed for different multinuclear manganese complexes. For example, Wieghardt et al. (40) isolated a peroxo-bridged complex, $[L_2'Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}O_2)]^{2+}$ (L′ = trimethyl-1,4,7-triazacyclononane), which releases molecular oxygen rapidly in aqueous solution at 20°C by an intramolecular two-electron oxidation of coordinated O_2^{2-} with concomitant reduction of Mn_2^{IV} to a binuclear Mn_2^{III} complex. Peroxo-bridged Mn_4 clusters have recently been proposed to represent the S_4 state, in which intramolecular two-electron oxidation of the peroxo-bridge produces O_2 and the S_0 state is regenerated (23). The S_3 to S_4 transition may also be described as a probable two-electron oxidation of substrate ligands according to the Hoganson and Babcock model (23). It appears that a mechanism involving a pair of electron acceptors becomes necessary when the driving force for electron transfer from a multielectron donor becomes too small for free-radical production (41). In such situations, binuclear complexes may provide a low-energy pathway for two-electron transfer. Nevertheless, ascorbic acid rarely undergoes two-electron transfer (42). One suggested example involves a ferriporphyrin dimer(41).

Conclusions

Rapid reduction of the complex ion $[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}MeCO_2)(bipy)_2(H_2O)_2]^{3+}$ and its hydrolytic derivatives with hydrogen peroxide seems to be inner sphere, but the intimate mechanism for the reduction by ascorbic acid is uncertain. An increased number of coordinated water molecules in-

creases the kinetic activity of the host Mn(IV) site in these model complexes, as in the OEC.

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