

Kinetics and mechanism of redox reactions of oxo-bridged complexes of higher-valent manganese

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Abstract. The dioxo-bridged $Mn^{III}Mn^{IV}$ complexes $[Mn^{III}Mn^{IV}(\mu-O)_2L_4]^{3+}$ (1^{3+} , $L = bipy = 2,2'$ -bipyridine; 2^{3+} , $L = phen = 1,10$ -phenanthroline) can be stabilized in aqueous solutions containing excess L in the range pH 4–6. Thus stabilized in solution, the parent complex coexists only with its aqua derivative $[Mn^{III}Mn^{IV}(\mu-O)_2L_3(H_2O)_2]^{3+}$ ($1a^{3+}$ for $L = bipy$; $2a^{3+}$ for $L = phen$) in rapid equilibrium. The solutions are novel oxidants and quantitatively oxidize NO_2^- to NO_3^- , $S_2O_3^{2-}$ to $S_4O_6^{2-}$, H_2O_2 to O_2 and $N_2H_5^+$ to N_2 . Simple first-order kinetics is observed except in reactions of the $bipy$ complex with NO_2^- , H_2O_2 and in the reaction of the $phen$ complex with $N_2H_5^+$. Reaction of the $bipy$ complex with NO_2^- produces the one-electron reduced intermediate $1a^{2+}$, while H_2O_2 gives the two-electron reduced intermediate $[Mn^{III}(bipy)_2(OH)(H_2O)]^{2+}$. It is concluded that (a) the aqua complexes are kinetically more active than their parents, (b) the $phen$ complexes react slower than the $bipy$ -complexes, (c) Mn^{2+} has no catalytic role, but intermediate manganese complexes and radical species may act as autocatalysts, (d) outer-sphere one-electron transfer occurs generally, but H_2O_2 prefers a two-electron pathway in its reactions with the dimers, (e) nuclearity is retained until one of the manganese in the dimers is reduced to the +2 state.

Keywords. Kinetics; manganese; oxidation; thiosulphate; nitrite; hydrogen peroxide; hydrazine.

1. Introduction

Oxo-bridged high-valent manganese dimers and oligomers are of interest as photosystem II models and redox catalysts. A great deal of activity among synthetic inorganic chemists has been directed towards the preparation of multinuclear oxo-bridged manganese aggregates. A variety of interesting species has thus been synthesized. While great emphasis has been laid on structural, spectroscopic and magnetic properties of these new materials, reactivity and kinetic studies appear rare^{1–5}

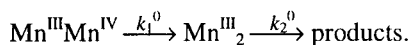
We summarize in this article results of our recent kinetic studies on redox reactions of different reducing agents with two $Mn^{III}Mn^{IV}$ dimers. These dimers are likely to represent the 'molecular bricks' for the formation of high nuclearity clusters and understanding their kinetic and mechanistic behaviour is therefore an essential step for a correct approach to larger systems.

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2. Results and discussion

In aqueous solutions the dimers $[\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}(\mu\text{-O})_2\text{L}_4]^{3+}$ ($\mathbf{1}^{3+}$, $\text{L} = \text{bipy} = 2,2'$ -bipyridine; $\mathbf{2}^{3+}$, $\text{L} = \text{phen} = 1, 10$ -phenanthroline) undergo complex reactions and thereby produce a complicated mixture of manganese species at equilibrium. However, only the parent dimers and their aqua derivatives $[\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}(\mu\text{-O})_2\text{L}_3(\text{H}_2\text{O})]^{3+}$ ($\mathbf{1a}^{3+}$ for $\text{L} = \text{bipy}$; $\mathbf{2a}^{3+}$ for $\text{L} = \text{phen}$) exist in rapid equilibrium within the range $\text{pH } 4.0\text{--}6.0$ maintained with an excess (HL^+-L) buffer. In such media the complexes are stable for at least $3\text{--}4 \text{ h}^{6-9}$. The solutions, thus stabilized, quantitatively oxidize NO_2^- to NO_3^- , $\text{S}_2\text{O}_3^{2-}$ to $\text{S}_4\text{O}_6^{2-}$, H_2O_2 to O_2 and N_2H_5^+ to N_2 . In all the cases, the final manganese product is manganese(II) if excess reducing agent is added. With less than the stoichiometric amount of the reductant, intermediate oxidation states of manganese may be detectable; for example, hydrogen peroxide generated an intermediate manganese(III) monomer, $[\text{Mn}^{\text{III}}(\text{bipy})_2(\text{H}_2\text{O})(\text{OH})]^{2+}$ from $\mathbf{1}^3$. This was detected by UV-VIS spectral studies¹⁰.

Oxidation of phen-complex generally follows simple first-order kinetics^{11,12}. First-order kinetics was observed also for the bipy-complex reacting with $\text{S}_2\text{O}_3^{2-}$. However, reactions of the bipy complex with NO_2^- and H_2O_2 followed biphasic kinetics; reaction of the phen complex with N_2H_5^+ is even more complex and generates sigmoid shaped absorbance-time graphs. The biphasic kinetics for the reaction of NO_2^- with the bipy complex was observed at 525 nm. Interestingly, the kinetics turned to simple first-order when monitored at 830 nm, the intervalence charge transfer band of the mixed valence complex $\mathbf{1}^{3+6}$. Reaction of the bipy-complex with NO_2^- generates a one-electron reduced iso-valent Mn^{III}_2 species, which is transparent to 830 nm radiation and hence does not interfere with the kinetic measurements. First-order kinetics is thus observed at 830 nm not at 525 nm. In the presence of excess NO_2^- , k_1^0 and k_2^0 are the observed first-order rate constants for the two consecutive steps seen at 525 nm. Between these two rate constants, k_1^0 is the same ($\pm 3\%$) as the first-order rate constant measured at 830 nm. Hence the reaction sequence is:



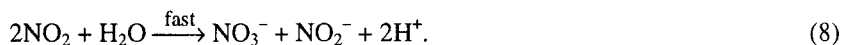
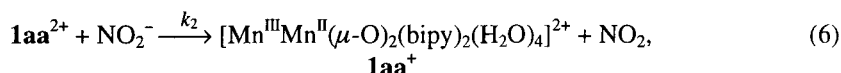
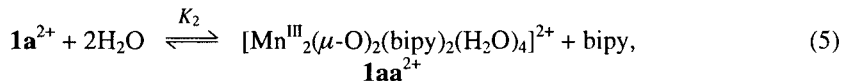
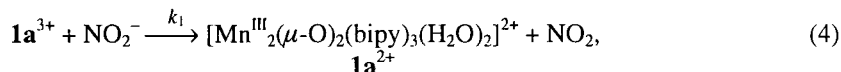
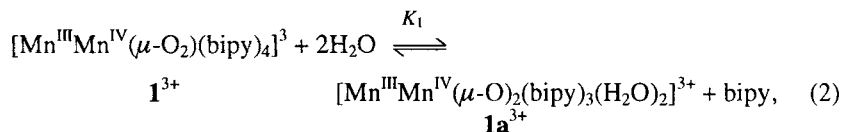
The observed dependence of k_1^0 and k_2^0 on $[\text{H}^+]$, $[\text{NO}_2^-]$ and $[\text{bipy}]$ fit satisfactorily in (1).

$$k_i^0 = \frac{k_i K_i [\text{NO}_2^-]}{[\text{bipy}]} \quad (i = 1, 2). \quad (1)$$

It may be explained by scheme 1, provided $K_i \ll [\text{bipy}]$, $C_{\text{bipy}} = ([\text{bipy}] + [\text{Hbipy}^+])$ and $C_{\text{N}} = ([\text{NO}_2^-] + [\text{HNO}_2]) \approx [\text{NO}_2^-]$.

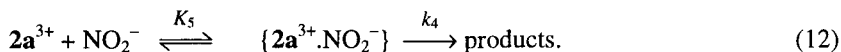
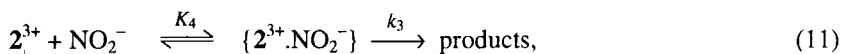
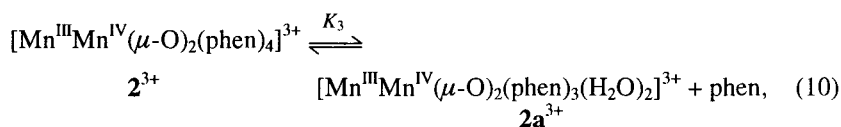
Ghosh and co-workers¹³ reported the rate constants for reduction of the $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ and Mn^{III}_2 dimers by HSO_3 and hydroquinone radicals. The values lie in the range $4.3 \times 10^7\text{--}8.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, but are expected to be much smaller for nitrogen dioxide. Hence the rapid disproportionation of NO_2 ((8), rate constant $\approx 10^8 \text{ M}^{-1}\text{s}^{-1}$) is preferred over its direct oxidation by higher-valent manganese complexes.

First-order rate constant k_3^0 for the reduction of the phen complex by NO_2^- exhibits complex dependence on $[\text{NO}_2^-]$ and $[\text{phen}]$. Plots of k_3^0 vs $[\text{NO}_2^-]$ suggests rate saturation at higher $[\text{NO}_2^-]$ and plots of $1/k_3^0$ vs $1/[\text{NO}_2^-]$ and vs $[\text{phen}]$ are linear. Equation (9) accommodates these observations satisfactorily and suggests scheme 2, which in turn leads to (9) provided $k_3 K_3 \ll k_4 K_3 K_5$.



Scheme 1.

$$k_3^0 = \frac{k_4 K_3 K_5 [\text{NO}_2^-]}{K_3(1 + K_5[\text{NO}_2^-]) + (1 + K_4[\text{NO}_2^-])[\text{phen}]}. \quad (9)$$



Scheme 2.

The k_4 -path should be a multi-step process consisting of steps analogous to (4) to (8). In fact schemes 1 and 2 are basically the same except that the aquation equilibrium and the adduct formation equilibria are more prominent for the phen complex ($I = 0.10 \text{ M}$) than they are for the bipy complex ($I = 1.0 \text{ M}$) under the experimental conditions. Stronger adduct may be a result of lower ionic strength, while higher value for K_3 may be a consequence of greater rigidity and steric bulk of phen. The best-fit values for $(K_3)^{-1}$, K_4 and K_5 are $3.6 \times 10^3 \text{ M}^{-1}$, 14 M^{-1} and 50 M^{-1} respectively at 30.0°C , $I = 0.1 \text{ M}$. The values for K_4 and K_5 lie within the range for outer-sphere association constants of several +3/-1

charge type adducts. The higher value of K_5 than K_4 appears to be due to hydrogen bonded interaction of NO_2^- with coordinated H_2O in $2\mathbf{a}^{3+}$ but not in 2^{3+} .

Added Mn^{2+} increases k_1^0 , k_2^0 , and k_3^0 because under the experimental conditions, Mn^{2+} scavenges bipy and phen and thus increases the concentrations of the kinetically active species $1\mathbf{a}^{3+}$ and $2\mathbf{a}^{3+}$. The amount of Mn^{2+} produced by the reduction of the complexes is however too small to affect the kinetics and Mn^{2+} is not an autocatalyst. This has been verified quantitatively.

Kinetics presented above demonstrates an overwhelming kinetic superiority of aqua derivatives over the parent complexes 1^{3+} and 2^{3+} . However, the parent complexes contribute appreciably to kinetics of reactions with thiosulphate and the observed first-order rate constants, k_4^0 and k_5^0 follow (13) and (14) respectively.

$$k_4^0 = (k_5 + k_6 K_1 / [\text{bipy}]) [\text{S}_2\text{O}_3^{2-}], \quad (13)$$

$$k_5^0 = (k_6 + k_8 K_3 / [\text{phen}]) [\text{S}_2\text{O}_3^{2-}]. \quad (14)$$

The corresponding reaction schemes proposed are schemes 3a and 3b.



Scheme 3a.

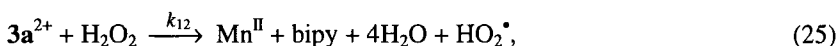
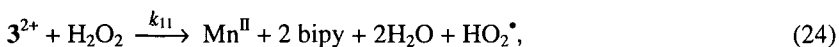
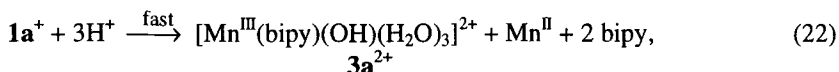


Scheme 3b.

They yield (13) and (14) provided the conditions $K_1 \ll [\text{bipy}]$ and $K_3 \ll [\text{phen}]$ are valid. Like the k_4 -path, k_5 - k_8 paths must also be multi-step processes, in which only the first act of electron transfer controls the measured k_i^0 ($i = 4$ -8); all subsequent steps are rapid. We presume that the $\{\text{Mn}_2\text{O}_2\}^{\text{II}}$ cores are retained except for the $\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{O}_2\}^+$ species, which are unstable in aqueous solutions. The presumption is supported by (a) earlier kinetic studies¹³, (b) the fact that nuclearity is preserved among the several oxidation levels of binuclear catalase enzyme models^{5,14}, (c) the fact that bond connectivities are retained among the various "S-states" involved in the photosystem II^{1,15,16} and (d) the fact that higher-valent manganese has a propensity to form and retain *bis*(μ -oxo) complexes in faintly acidic media¹⁷⁻¹⁹. The known electrochemistry of the binuclear manganese complexes also supports the hypothesis that nuclearity is retained^{6,20,21}.

Kinetics described so far have been interpreted in terms of $1e$ -transfer steps. The oxidation of hydrogen peroxide appears exceptional in this context. The observed biphasic kinetics along with the detection of $[\text{Mn}^{\text{III}}(\text{bipy})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$, 3^{2+} as an

intermediate strongly suggests 2e-reduction of the bipy complex by hydrogen peroxide. A plausible reaction scheme 4a is shown below.



Scheme 4a.

An obvious alternative for the k_9 - and the k_{10} -paths is one-electron transfer generating the Mn_2^{III} species followed by its fast reduction to $\text{Mn}^{\text{III}} + \text{Mn}^{\text{II}}$. However, we know no example where the Mn_2^{III} dimer of bipy is reduced fast enough to explain the formation of $\mathbf{3a}^{2+}$ as an intermediate via one-electron steps. This is why we prefer the two-electron transfer steps (19) and (20) over their one-electron alternatives.

One can derive equations (27) and (28) for the consecutive first-order rate constants k_6^0 and k_7^0 for the oxidation of H_2O_2 by the manganese(III,IV) dimer and the manganese(III) monomer respectively, if $[\text{bipy}]$ is \gg both K_1 and K_6

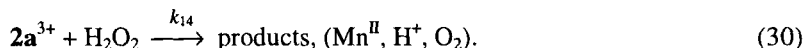
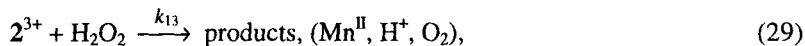
$$k_6^0 = \frac{(k_9[\text{bipy}] + k_{10}K_1)[\text{H}_2\text{O}_2]}{[\text{bipy}]} = (k_9 + k_{10}K_1/[\text{bipy}])([\text{H}_2\text{O}_2]), \quad (27)$$

$$k_7^0 = \frac{(k_{11}[\text{bipy}] + k_{12}K_6)[\text{H}_2\text{O}_2]}{[\text{bipy}]} = (k_{11} + k_{12}K_6/[\text{bipy}])([\text{H}_2\text{O}_2]). \quad (28)$$

These equations nicely agree with empirical relations connecting first-order rate constants and different concentration parameters.

Oxidation of H_2O_2 by the phen complexes $\mathbf{2}^{3+}$ and $\mathbf{2a}^{3+}$ should also be multi-step processes. So the observed monophasic kinetics indicates rapid conversion of the intermediates to final products, either because they are unstable or because they are kinetically very active. Absence of any known phen analogue for $\mathbf{3}^{2+}$ and $\mathbf{3a}^{2+}$ upholds the presumption. We note in this context that manganese(III)-phenanthroline monomers are rare, and both of the known species, $[\text{Mn}(\text{phen})\text{Cl}_3(\text{H}_2\text{O})]$ and $[\text{Mn}(\text{phen})_2\text{Cl}_2]^+$ are highly

putative in aqueous media^{22,23}. Scheme 4b, analogous to scheme 3b may therefore be proposed.



Scheme 4b.

The expression (31) derived for the scheme nicely reproduce the experimental values for the observed first-order rate constant k_8^0 .

$$k_8^0 = \frac{(k_{13}[\text{phen}] + K_3 k_{14})[\text{H}_2\text{O}_2]}{(K_3 + [\text{phen}])}. \quad (31)$$

The linear equations (1), (13), (14), (27) and (28) for k_x^0 ($x = 1, 2, 4-7$) yielded values for the constants k_1K_1 , k_2K_2 , k_5 , k_7 , k_6K_1 , k_8K_3 , k_9 , k_{11} , $k_{10}K_1$, and $k_{12}K_6$. Equation (9) was linearised and solved to yield K_3 , K_4 , K_5 , k_4K_5 and hence k_4 . The value for K_3 obtained from (9) was used in (31), which was transformed to (32) and yielded the value for k_{13} , K_3k_{14} , and hence k_{14} . Again (13) was derived assuming $K_1 \ll [\text{bipy}]$

$$k_8^0(K_3 + [\text{phen}]) = (k_{13}[\text{phen}] + K_3k_{14}) [\text{H}_2\text{O}_2]. \quad (32)$$

One can therefore estimate $K_1 < 1.4 \times 10^{-3}$ M. Hence the lower limits for k_1 , k_6 , and k_{10} were estimated. All these rate constants have been collected in table 1. It shows that the aqua complexes $1\mathbf{a}^{3+}$ and $2\mathbf{a}^{3+}$ are kinetically more active than their respective parents, 1^{3+} and 2^{3+} . A similar trend of reactivity is well known for the redox reactions of mononuclear manganese(III) complexes²⁴⁻²⁷ and the manganese(IV,IV) dimer, $[\text{Mn}_2(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{bipy})_2(\text{H}_2\text{O})_2]^{3+28}$. The possible reasons are: (a) replacement of a chelating ligand by the weaker donor H_2O makes the metal centre more open and electron deficient; (2) the precursor complexes for $1\mathbf{a}^{3+}$ and $2\mathbf{a}^{3+}$ may be stabilized by H-bond, not possible for 1^{3+} and 2^{3+} and (c) the metal-ligand bonds are more flexible in the aqua complexes, which therefore have lower Frank-Condon barriers. The phen complexes are more rigid than the bipy complexes. One can expect greater Frank-Condon barriers for phen complexes and hence lower rates of electron transfer as transpires from table 1.

Ghosh *et al*¹³ determined the kinetics for the reaction of the bipy-complex with HSO_3^- , hydroquinone and ascorbic acid. The rate constants (k_{AB} , say) they reported are comparable to k_iK_1/K_{Hbipy} ($i = 1$ and 6) determined by us. Table 2 represents k_{AB} values at 30°C along with some other relevant data. In this table, k_{AA} represents self-exchange rate constants for the reductants, and E_{AA} are corresponding one-electron reduction potentials (NHE). Simple Marcus crossrelation²⁹ suggests that a plot of $(\log k_{\text{AB}} - 0.5 \log k_{\text{AA}})$ against E_{AA} should be a straight line with slope = 8.47, if a group of similar reactions follow outer-sphere mechanism. Figure 1 shows that this expectation is fulfilled well by the reductants listed in table 2.

Table 1. Kinetic and equilibrium parameters.

	NO_2^-	$\text{S}_2\text{O}_3^{2-}$	H_2O_2
1^{3+}	—	$k_5 = 0.154 \text{ M}^{-1} \text{ s}^{-1} \text{ (b)}$	$k_9 = 13.5 \text{ M}^{-1} \text{ s}^{-1} \text{ (c)}$
$1a^{3+}$	$k_1 K_1 = 1.3 \times 10^{-1} \text{ s}^{-1} \text{ (a)}$ $k_1 > 0.9 \text{ M}^{-1} \text{ s}^{-1} \text{ (a)}$	$k_6 K_1 = 3.3 \times 10^{-3} \text{ s}^{-1} \text{ (b)}$ $K_1 < 1.4 \times 10^{-3} \text{ M} \text{ (b)}$ $k_6 > 2.3 \text{ M}^{-1} \text{ s}^{-1} \text{ (b)}$	$k_{10} = 0.191 \text{ s}^{-1} \text{ (c)}$ $k_{10} > 136 \text{ M}^{-1} \text{ s}^{-1} \text{ (b)}$
$1a^{2+}$	$k_2 K_2 = 1.3 \times 10^{-4} \text{ s}^{-1} \text{ (a)}$	—	—
2^{3+}	$K_3 = 3.9 \times 10^{-4} \text{ M} \text{ (d)}$ $K_4 = 14 \text{ M}^{-1} \text{ (d)}$	$K_3 < 8 \times 10^{-4} \text{ M} \text{ (a)}$ $k_7 = 0.405 \text{ M}^{-1} \text{ s}^{-1} \text{ (a)}$	— $k_{13} = 2.74 \text{ M}^{-1} \text{ s}^{-1} \text{ (c)}$
$2a^{3+}$	$k_4 K_5 = 1.65 \text{ s}^{-1} \text{ (d)}$ $K_5 = 50 \text{ M}^{-1} \text{ (d)}$ $k_4 = 3.3 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1} \text{ (d)}$	— $k_8 K_3 = 5.04 \times 10^{-4} \text{ s}^{-1} \text{ (a)}$ $k_8 = 1.29 \text{ M}^{-1} \text{ s}^{-1} \text{ (a)}$	— $k_{14} K_3 = 4.8 \times 10^{-3} \text{ s}^{-1} \text{ (c)}$ $k_{14} = 12.3 \text{ M}^{-1} \text{ s}^{-1} \text{ (c)}$
3^{2+}	—	—	$k_{11} = 2.18 \text{ M}^{-1} \text{ s}^{-1} \text{ (c)}$
$3a^{2+}$	—	—	$k_{12} K_6 = 4.87 \times 10^{-1} \text{ s}^{-2} \text{ (c)}$

(a)30.0°C, $I = 1.0 \text{ M}$, (b)30.0°C, $I = 2.0 \text{ M}$, (c)25.0°C, $I = 1.0 \text{ M}$, (d)30.0°C, $I = 0.10 \text{ M}$

Table 2. Second-order rate constants for the reactions of the bipy-complex.

Reductant	$k_{AB}, \text{M}^{-1} \text{ s}^{-1}$	$k_{AA}, \text{M}^{-1} \text{ s}^{-1}$	$E_{AA}/V \text{ (NHE)}$	$(\log k_{AB} - 0.5 \log k_{AA})$
NO_2^-	34.9	0.30	-0.87	1.80
$\text{S}_2\text{O}_3^{2-}$	85.5	2.3×10^5	-1.3	-0.75
HQ ⁻	160	7.0×10^5	-1.08	0.72
Hasc ⁻	1.2×10^5	3.5×10^5	-0.71	2.31
HSO_3^-	200	4.0	-0.72	2.0

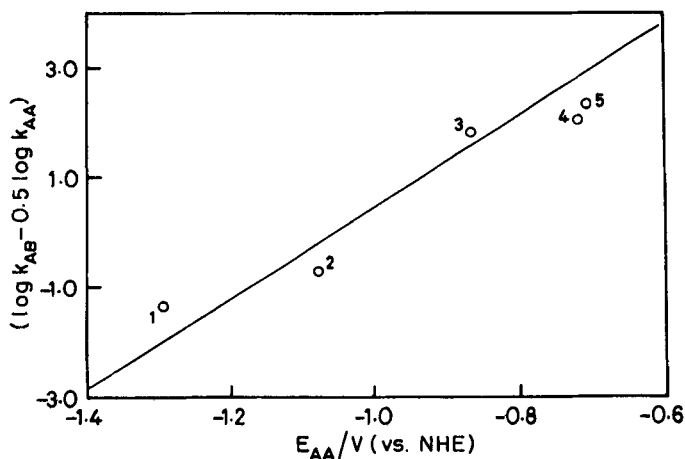
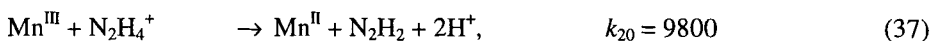
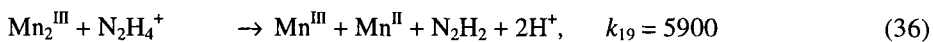
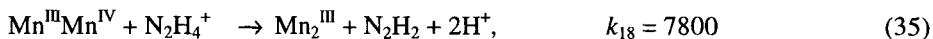
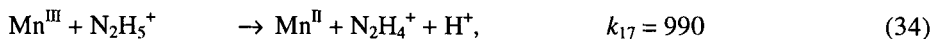
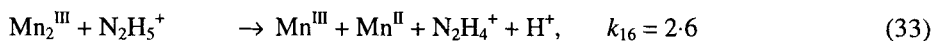
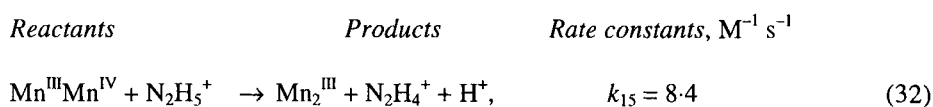


Figure 1. An approximate Marcus crossrelation for reduction of the bipy-complex by (1) $\text{S}_2\text{O}_3^{2-}$, (2) hydroquinone, (3) NO_2^- , (4) HSO_3^- and (5) Hasc⁻. The solid line is drawn with the theoretical slope, 8.47.

We have evidence that the oxidation of H_2O_2 by 1^{3+} and 2^{3+} is a two-electron transfer process. One-electron transfer appears unlikely due to the high thermodynamic barrier posed by the couple $\text{HO}_2^*/\text{H}_2\text{O}_2$ ($E = 1.7 \text{ V}$) for the weakly oxidizing bipy- and the phen-

complexes⁶. Calculations using simple Marcus relation show that one-electron transfer from H₂O₂ via an outer-sphere mechanism is not possible unless the self-exchange reaction for the couple HO₂[•]/H₂O₂ is impossibly high ($k_{AA} > 10^{10} \text{ M}^{-1} \text{ s}^{-1}$). Actually, one expects a small exchange rate since the value for the isoelectronic and isosteric species N₂H₄ and NH₂OH are very small. On this ground of low exchange rate the possibility of an outer-sphere, two-electron transfer mechanism also appears feeble in spite of the relatively low potential for the couple H₂O₂/O₂ (0.68 V). An inner-sphere, two-electron transfer mechanism thus seems highly plausible. The presumption is further supported by the formation of inner-sphere complexes by different manganese(III) species with H₂O₂³⁰⁻³³. Though there is no replaceable water molecule present in the [Mn₂(μ-O)₂L₄]³⁺ complexes, adduct formation with hydrogen peroxide can still occur through hydrogen bonding with the oxo-bridge. The distinction between inner-sphere and outer-sphere reactions is not appropriate in this case because there is no substitution in the metal coordination sphere, but the concept of strong overlap is still appropriate.

The absorbance-time profile (figure 2) for the reaction of N₂H₅⁺ with the phen complex suggests an auto-catalytic process. A reaction sequence that explains the observation is given below as scheme 5.



[complex] = $4.375 \times 10^{-5} \text{ M}$; $C_{\text{phen}} = 2.5 \text{ mM}$; [N₂H₅⁺] = 0.5 mM; pH = 4.51; I = 1.0 M; Temp., 30.0°C. ε values (M⁻¹ cm⁻¹): Mn^{III}Mn^{IV}, 2240; Mn₂^{III}, 1300; Mn^{III}, 700; Mn^{II}, 50

Scheme 5.

Expression of this sequence as a series of differential equations and numerical integration using the program KFSIM40³⁴ (kindly provided by Professor Carl Frieden) yielded the concentration of the participating species at desired time intervals during the course of the reaction, and incorporation of the extinction coefficients of Mn^{III}Mn^{IV} (measured) and those of the two Mn₂ intermediates (estimated^{13,35}) yielded the calculated values for the absorbance of the reaction mixture at each point.

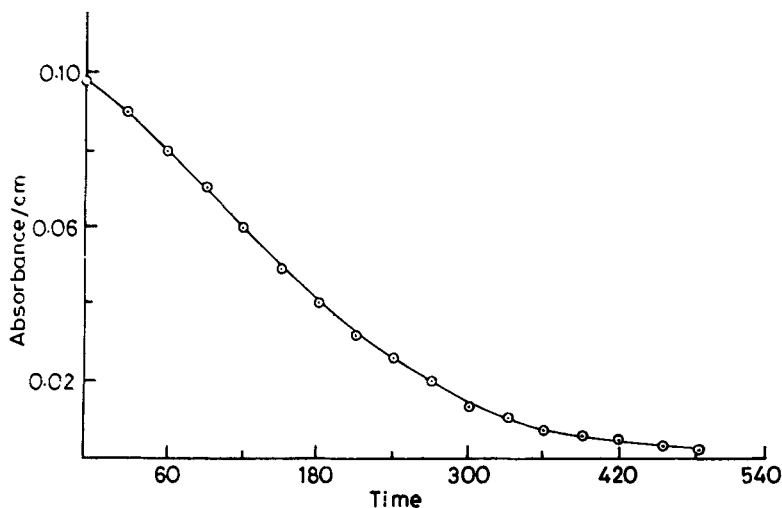


Figure 2. A typical comparison of calculated (solid line) vs experimental (circles) absorbance-time profile for the reduction of the manganese(III,IV)-bipy complex in solution by hydrazine (see scheme 5). (Time in seconds.)

Values of the rate constants and for the molar absorbances of manganese dimers at 410 nm giving optimal agreement between calculated and observed profiles are listed along with the scheme 5. The rate constants for the individual steps reveal that the auto-catalysis arises due to generation of Mn^{III} complex and the hydrazyl radical, N_2H_4^+ . The Mn^{III} complex is reduced by N_2H_5^+ at a rate ≈ 120 times faster than the parent $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ dimer, while the hydrazyl radical enhances the rate of consumption of higher-valent manganese species. Detailed dependence of the rate constants in scheme 5 on various concentration factors is now being explored.

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