Kinetics and Mechanism of Oxidation of Fe^{2+} by the Tris(biguanide)manganese(IV) Ion in Aqueous Acid Media

Basab Bijayi Dhar,[a] Ritam Mukherjee,[a] Subrata Mukhopadhyay,*[a] and Rupendranath Banerjee[a]

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Tris(biguanide)manganese(IV), $[Mn(LH_2)_3]^{4+}$ (LH_2 = biguanide, $C_2N_5H_7$), quantitatively oxidises Fe^{2+} to Fe^{3+} and is itself reduced to Mn^{2+} with almost quantitative (> 95%) release of biguanide. The reaction rate strongly depends on added Fe^{3+}; in the presence of externally added Fe^{3+}, the reaction shows a clear first-order dependence in $[Mn^{IV}]$, whereas in the absence of any added Fe^{3+}, an initial quick loss of Mn^{IV} is associated with a subsequent very sluggish decay. Two consecutive one-electron transfer inner-sphere steps are proposed for the entire redox process where $[Mn(LH_2)_3]^{3+}$, the initial one-electron-reduced product of Mn^{IV}, is believed to be a steady-state intermediate.

Introduction

The aqueous solution chemistry of mononuclear Mn^{IV} is very scarce due to the extreme paucity of soluble Mn^{IV} species. However, the recently reported[1] tris(biguanide)-manganese(IV) complex $[Mn(LH_2)_3]^{4+}$ (**1**; Figure 1, LH_2 = biguanide, $C_2N_5H_7$) is structurally well characterised and is a rare example of a water-soluble mononuclear Mn^{IV} complex that is stable over a wide range of acidity (10^{-6} to 2 M). Figure 2 displays its UV/Vis spectrum at pH 2.0. Some oxo-bridged di-, tri- and tetranuclear Mn^{IV} complexes[2] are also stable in aqueous solution and have interesting solution chemistry,[3] but their mononuclear counterparts are unknown.

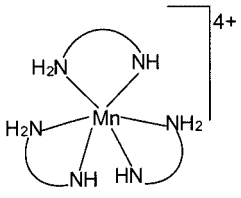

Figure 1. Structure of $[Mn(LH_2)_3]^{4+}$ (**1**)

We report here the kinetics of oxidation of Fe^{2+} by the title Mn^{IV} complex in aqueous acidic media to elucidate the mechanistic aspects of the process as a part of our continued interest[3] in the aqueous solution chemistry of higher-valent manganese species.

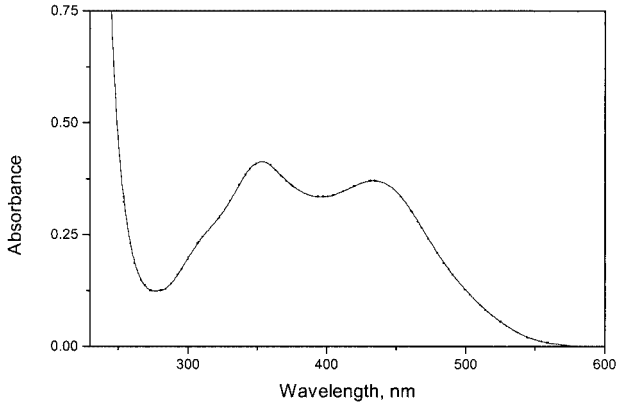

Figure 2. UV/Vis spectrum of 0.050 mM complex at pH 2.0

Results and Discussion

Equilibrium Studies

The built-in program of the Metrohm 736 GP Titrino autotitrator yielded two pK_a values for the title complex from the pH-titration curve: pK_{a1} = 5.30 ± 0.20 and pK_{a2} = 7.60 ± 0.30. The Mn^{IV} in the complex is coordinatively saturated and any deprotonation should thus arise from the ligand biguanide moiety, possibly from protons bound to sp^2 nitrogens as in an analogous Ag^{III} complex or in $[Co^{III}(am)(LH_2)_2]^{2+}$ (am = amino acids like glycine,

[a] Department of Chemistry, Jadavpur University, Calcutta 700032, India
E-mail: subrataju@vsnl.net

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alanine, etc.).[4a,4b] In $[Co^{III}(LH_2)_2(H_2O)_2]^{3+}$, however, coordinated water is deprotonated.[4c] Table 1 summarises the known acidity constants of some biguanide complexes.

Table 1. Deprotonation constants of metal biguanide complexes[a]

Metal complex	pK_{a1}	pK_{a2}	Reference
$[Ag^{III}(enbbg)]^{3+}$	3.80	6.30	[4a]
$[Co^{III}(gly)(LH_2)_2]^{2+}$	9.06	10.4	[4b]
$[Co^{III}(L\text{-ala})(LH_2)_2]^{2+}$	9.07	10.4	[4b]
$[Co^{III}(LH_2)_2(H_2O)_2]^{3+}$	5.86	7.92	[4c]
$[Mn^{IV}(LH_2)_3]^{4+}$	5.30	7.60	this work

[a] enbbg = ethylenebis(biguanide), gly = glycine, L-ala = L-alanine.

Stoichiometry and Reaction Products

The results of the stoichiometry experiments (Table 2) yielded $\Delta[Mn^{IV}]/\Delta[Fe^{2+}] = 0.49 \pm 0.03$ and $\Delta[Mn^{IV}]/\Delta[Fe^{3+}] = 0.53 \pm 0.04$. The product solution, after removing iron, displays a typical six-line EPR spectrum of Mn^{II} ($I = 5/2$). Hence, Equation (1) describes the overall redox process.

$$Mn^{IV} + 2Fe^{2+} \rightarrow Mn^{II} + 2Fe^{3+} \quad (1)$$

Iodometric determination of copper in the cupric biguanide precipitated from the product solution indicated release of more than 95% of the biguanide.

Kinetics

The reaction of complex **1** reacting with excess Fe^{2+} does not represent well-behaved kinetics; an initial quick loss in absorbance of **1** is followed by a sluggish phase, and the absorbance vs. time data do not follow first-order kinetics, as shown in Figure 3. In the presence of added Fe^{3+}, the initial loss in absorbance is prevented and the whole reaction course follows first-order kinetics (Figure 3) — the $\ln(A_t - A_\infty)$ vs. time plots were found to be linear to more than 90% completion of the reactions. In all kinetic runs A_∞ values were less than 0.01. Most of the kinetics were therefore determined in the presence of added Fe^{3+}. The first-order rate constants, k_o, defined by Equation (2) were obtained from least-squares slopes of these plots and are presented in Table 3. Moreover, a tenfold variation in the initial Mn^{IV} concentration (0.02 −0.20 mM) gave no change in the k_o values within experimental uncertainty (± 5%). This indicates a first-order decay of Mn^{IV} concentration.

$$-d[Mn^{IV}]/dt = k_o[Mn^{IV}] \quad (2)$$

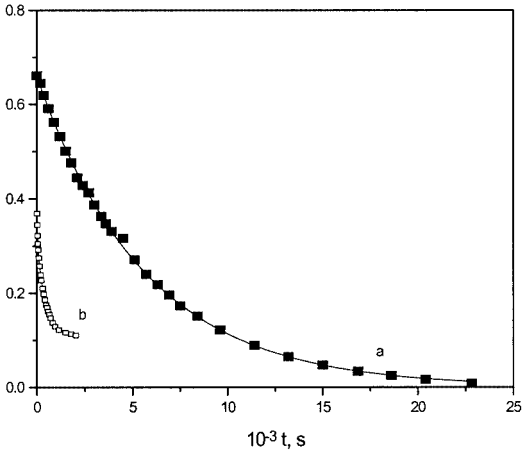

Figure 3. Absorbance vs. time graph for the reduction of $[Mn(LH_2)_3]^{4+}$ (0.10 mM) by Fe^{2+} (5.0 mM): a) in the presence of added Fe^{3+} (0.50 mM); b) in the absence of added Fe^{3+}; $[H^+]$ = 1.3 mM, I = 1.0 M, T = 25.0 °C

At fixed $[Fe^{3+}]_T$ (= $[Fe^{3+}]_{aq}$ + $[Fe(OH)^{2+}]_{aq}$) and $[H^+]$, the plot of $[Fe^{2+}]_T^2/k_o$ vs. $[Fe^{2+}]_T$, (= $[Fe^{2+}]_{aq}$ + $[Fe(OH)^+]_{aq}$) is a straight line with definite intercept and slope (Figure 4). Also, at fixed $[Fe^{2+}]_T$ and $[H^+]$, the plot of $1/k_o$ vs. $[Fe^{3+}]_T$ is a straight line with finite intercept. Plots of k_o versus $[H^+]$ at fixed $[Fe^{2+}]_T$ and $[Fe^{3+}]_T$ have a bell shape (Figure 5) indicating the involvement of at least two protic equilibria[5] in the reaction. We also observed that in the presence of 6% (v/v) acrylonitrile no polymeric products were formed, thus perhaps eliminating any detectable generation of free radicals during the reaction. Equations (3)−(8) provide a reasonable explanation of the kinetic observations.

Table 2. Stoichiometry of the reduction of $[Mn(LH_2)_3]^{4+}$ by Fe^{2+} at pH 2.4−2.7 and T = 25 °C; all concentrations are in mM

$[Mn^{IV}]$	pH	$[Fe^{2+}]_T$	$[Fe^{2+}]_{Left}$	$[Fe^{3+}]_{Produced}$	$\Delta[Mn^{IV}]/\Delta[Fe^{2+}]$	$\Delta[Mn^{IV}]/\Delta[Fe^{3+}]$
0.05	2.4	0.20	0.10	0.09	0.50	0.56
0.06	2.5	0.40	0.27	0.12	0.46	0.50
0.12	2.6	0.80	0.57	0.21 0.52	0.57	
0.20	2.6	1.20	0.73	0.38	0.48	0.57
0.28	2.7	1.30	0.73	0.57	0.49	0.49
					average: 0.49 ± 0.03	average: 0.53 ± 0.04

$$Fe^{2+}_{aq} \overset{K_a}{\rightleftharpoons} Fe(OH)^{+}_{aq} + H^{+} \quad (3)$$

$$[Mn(LH_2)_3]^{4+} + Fe^{2+}_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mn(LH_2)_3]^{3+} + Fe^{3+}_{aq} \quad (4)$$

$$[Mn(LH_2)_3]^{4+} + Fe(OH)^{+}_{aq} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Mn(LH_2)_3]^{3+} + Fe(OH)^{2+} \quad (5)$$

1

$$Fe^{3+}_{aq} \overset{K_h}{\rightleftharpoons} Fe(OH)^{2+}_{aq} + H^{+} \quad (6)$$

$$[Mn(LH_2)_3]^{3+} + Fe^{2+}_{aq} \xrightarrow{k_3} \text{Products} \quad (7)$$

$$[Mn(LH_2)_3]^{3+} + Fe(OH)^{+}_{aq} \xrightarrow{k_4} \text{Products} \quad (8)$$

Combining these equations leads to Equation (9), assuming a steady state for $[Mn(LH_2)_3]^{3+}$

$$k_o(K_a + [H^+])/(K_h + [H^+]) = (A + B[H^+] + C[H^+]^2)/(D + E[H^+] + F[H^+]^2) \quad (9)$$

where $A = [Fe^{2+}]_T^2 K_a^2 k_2 k_4$, $B = [Fe^{2+}]_T^2 K_a(k_2 k_3 + k_1 k_4)$, $C = [Fe^{2+}]_T^2 k_1 k_3$, $D = [Fe^{3+}]_T k_{-2} K_h K_a + [Fe^{2+}]_T K_h K_a k_4$, $E = [Fe^{3+}]_T(k_{-1} K_a + k_{-2} K_h) + [Fe^{2+}]_T(k_3 K_h + k_4 K_a)$ and $F = [Fe^{3+}]_T k_{-1} + [Fe^{2+}]_T k_3$.

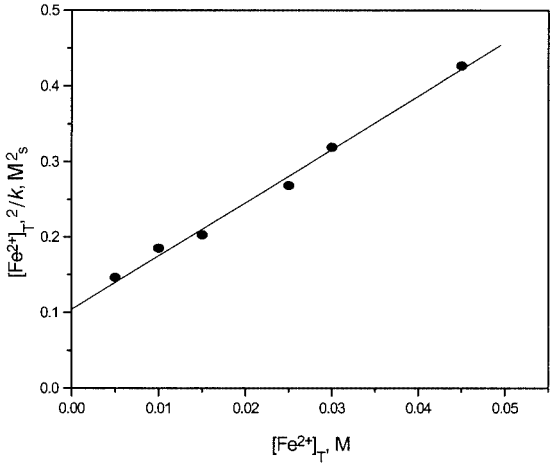

Figure 4. Plot of $[Fe^{2+}]_T^2/k_o$ vs. $[Fe^{2+}]_T$; [complex] = 0.10 mM, $[Fe^{2+}]_T$ = (5.0−45.0) mM, $[Fe^{3+}]_T$ = 0.50 mM, $[H^+]$ = 1.3 mM, I = 1.0 M, T = 25.0 °C

Table 3. First-order rate constants (k_o)[a] at T = 25.0 °C, I = 1.0 M ($NaClO_4$) and λ = 433 nm

$[H^+]$ (mM)	$[Fe^{2+}]_T$ (mM)	$[Fe^{3+}]_T$ (mM)	$10^4 k_o$ [s^{-1}]
1.56	30	1.00	21.6 (21.5)
2.90			18.0 (17.6)
5.27			16.1 (16.8)
8.19			17.3 (17.9)
12.1			20.0 (20.2)
1.30		0.50	28.4 (29.0)
2.23			23.9 (23.5)
5.14			20.8 (21.2)
7.60			22.2 (22.3)
10.1			22.7 (24.1)
12.6			25.7 (26.1)
1.56	45	1.00	38.7 (39.1)
3.37			31.7 (31.3)
5.27			29.7 (30.7)
8.19			32.0 (32.7)
11.2			36.5(35.9)
1.30	60	0.50	63.0 (65.1)
2.23			52.4 (52.2)
3.19			50.0 (48.0)
5.14			45.8 (46.6)
10.1			51.1(52.3)
12.6			56.8 (56.5)
15.1			61.5 (61.0)
1.19		0.30	80.4 (81.2)
4.10			56.5 (56.1)
8.06			58.5 (59.7)
12.0			69.0 (67.7)
15.0			77.6 (74.5)
1.30	5	0.50	1.79 (1.71)
	10		5.68 (5.41)
	15		11.0 (11.1)
	25		23.2 (23.3)
	30		28.2 (29.7)
	45		47.5 (49.9)

[a] Concentration of complex used: 0.10 mM. The k_o values calculated using Equation (9a) are given in parentheses.

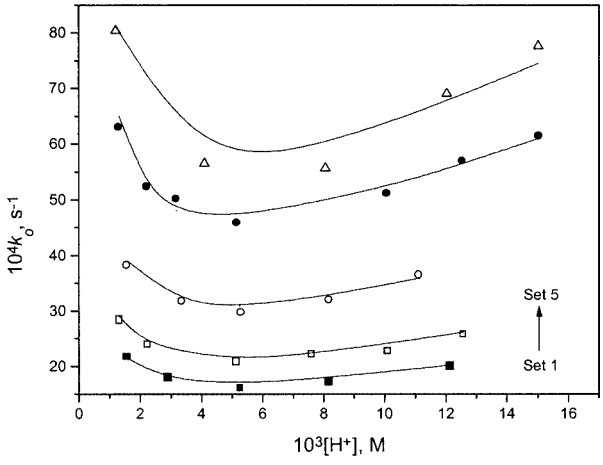

Figure 5. Plot of k_o vs. $[H^+]$; [complex] = 0.10 mM. set 1: $[Fe^{2+}]_T$ = 30.0 mM, $[Fe^{3+}]_T$ = 1.0 mM, $[H^+]$ = (1.5−12.2) mM; set 2: $[Fe^{2+}]_T$ = 30.0 mM, $[Fe^{3+}]_T$ = 0.50 mM, $[H^+]$ = (1.3−12.6) mM; set 3: $[Fe^{2+}]_T$ = 45.0 mM, $[Fe^{3+}]_T$ = 1.0 mM, $[H^+]$ = (1.5−11.2) mM; set 4: $[Fe^{2+}]_T$ = 60.0 mM, $[Fe^{3+}]_T$ = 0.50 mM, $[H^+]$ = (1.3−15.0) mM; set 5: $[Fe^{2+}]_T$ = 60.0 mM, $[Fe^{3+}]_T$ = 0.30 mM, $[H^+]$ = (1.2−15.0) mM. I = 1.0 M, T = 25.0 °C for all experiments

The plots of the left-hand-side of Equation (9) versus $[H^+]$ at different, fixed $[Fe^{2+}]_T$ and $[Fe^{3+}]_T$ are excellent straight lines (Figure 6; $r > 0.98$), which indicates that $C[H^+]^2 << (A + B[H^+])$ and $(E[H^+] + F[H^+]^2) << D$. Equation (9) therefore simplifies to Equation (10) as K_a $(= 10^{-8.1})$[6] $<<$ $[H^+]$.

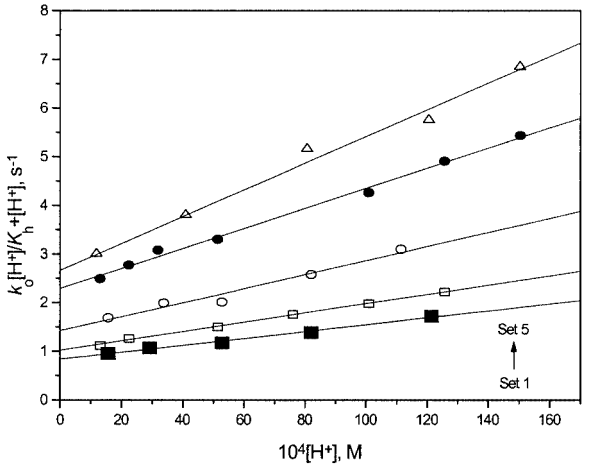

Figure 6. Plot of Y vs. $[H^+]$; [complex] = 0.10 mM; set 1: $[Fe^{2+}]_T$ = 30.0 M, $[Fe^{3+}]_T$ = 1.0 mM, $[H^+]$ = (1.5−12.2) mM; set 2: $[Fe^{2+}]_T$ = 30.0 mM, $[Fe^{3+}]_T$ = 0.50 mM, $[H^+]$ = (1.3−12.6) = mM; set 3: $[Fe^{2+}]_T$ = 45.0 mM, $[Fe^{3+}]_T$ = 1.0 mM, $[H^+]$ = (1.5−11.2) mM, Set 4: $[Fe^{2+}]_T$ = 60.0 mM, $[Fe^{3+}]_T$ = 0.50 mM, $[H^+]$ = (1.3−15.0) mM; set 5: $[Fe^{2+}]_T$ = 60.0 mM, $[Fe^{3+}]_T$ = 0.30 mM, $[H^+]$ = (1.2−15.0) mM. I = 1.0 M, T = 25.0 °C for all experiments

$$k_o[H^+]/(K_h + [H^+]) = (A + B[H^+])/D \quad (10)$$

The elaborated form of Equation (10) is:

LHS = Y (for example) = $[Fe^{2+}]_T^2\{K_a^2k_2k_4 + K_a(k_2k_3 + k_1k_4)[H^+]\}/[Fe^{3+}]_Tk_{-2}K_hK_a + [Fe^{2+}]_TK_hK_aK_4$

or

$$[Fe^{2+}]_T^2/Y = (k_{-2}K_hK_a/a)\,[Fe^{3+}]_T + (k_4K_hK_a/a)\,[Fe^{2+}]_T \quad (11)$$

where $a = K_a^2k_2k_4 + K_a(k_2k_3 + k_1k_4)[H^+]$. Equation (11) explains the observed linear plots of $[Fe^{2+}]_T^2/k_o$ versus $[Fe^{2+}]_T$ at fixed $[Fe^{3+}]_T$ and $[H^+]$ and also the linear plots of $1/k_o$ versus $[Fe^{3+}]_T$ at fixed $[Fe^{2+}]_T$ and $[H^+]$. From the linear plots of Y versus $[H^+]$ (Figure 6), the slopes and intercepts yielded, respectively, $B/D = \{[Fe^{2+}]_T^2(k_2k_3 + k_1k_4)/K_h([Fe^{3+}]_Tk_{-2} + [Fe^{2+}]_Tk_4)\}$ and $A/D = \{[Fe^{2+}]_T^2K_ak_4k_2/K_h([Fe^{3+}]_Tk_{-2} + [Fe^{2+}]_Tk_4)\}$. The slope/intercept of these plots yield B/A $[= (k_2k_3 + k_1k_4)/K_a\,k_2k_4] = 92.6 \pm 2.0\ M^{-1}$ at 25.0 °C and I = 1.0 M. We determined A/D and B/D values at different, fixed $[Fe^{2+}]_T$ and $[Fe^{3+}]_T$. These values were used to plot $[Fe^{2+}]_T/(A/D)$ vs. $[Fe^{3+}]_T/[Fe^{2+}]_T$ and $[Fe^{2+}]_T/(B/D)$ vs. $[Fe^{3+}]_T/[Fe^{2+}]_T$. As expected, these were found to be good straight lines ($r > 0.98$) and yielded k_{-2}/k_4 (= 28.0 ± 2.0) and k_2 $[= (1.28 \pm 0.1) \times 10^4\ M^{-1}s^{-1}]$ from their slopes and intercepts using known K_a and K_h $(= 10^{-2.7})$[7] values. The composite constants $(k_3k_2 + k_4k_1)/k_4$ $[= (1.0 \pm 0.01) \times 10^{-2}]$ and $(k_3k_2 + k_4k_1)/k_{-2}$ (= 3007 ± 150) were also determined from the slopes and intercepts.

Equations (12)−(16) can explain the kinetic observations equally well. Here, Fe^{2+} hydrolysis is neglected and replaced by the deprotonation equilibrium of **1**.

$$[Mn(LH_2)_3]^{4+} \underset{}{\overset{K_a}{\rightleftharpoons}} [Mn(LH_2)_2(LH)]^{3+} + H^+ \quad (12)$$
1 **1a**

$$[Mn(LH_2)_3]^{4+} + Fe^{2+}_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mn(LH_2)_3]^{3+} + Fe^{3+}_{aq} \quad (13)$$

$$[Mn(LH_2)_2(LH)]^{3+} + Fe^{2+}_{aq} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Mn(LH_2)_3]^{3+} + Fe(OH)^{2+}_{aq} \quad (14)$$
1a

$$Fe^{3+}_{aq} \overset{K_h}{\rightleftharpoons} Fe(OH)^{2+}_{aq} + H^+ \quad (15)$$

$$[Mn(LH_2)_3]^{3+} + Fe^{2+}_{aq} \xrightarrow{k_3} \text{Products} \quad (16)$$

Proceeding in the same way as above gives $k_1 = (1.0 \pm 0.01) \times 10^{-2}\ M^{-1}s^{-1}$, $k_2 = 21.5 \pm 0.5\ M^{-1}s^{-1}$ and $k_{-2}/k_3 = 28.0 \pm 2.0$.

Mechanism

We like to allow less importance to Equations (12)−(16) as it is unusual[8] that a deprotonated species of a higher valent transition metal complex is more reactive (k_2) than its conjugate acid (k_1). Further, this flouts the well-known fact that $Fe(OH)^+_{aq}$ is much more reactive than Fe^{2+}_{aq} in redox reactions and $Fe(OH)^+_{aq}$ is a kinetically reactive species even in moderately acidic media.[6]

The value of k_2 evaluated from Equations (3)−(8) indicates a very high reactivity of $Fe(OH)^+_{aq}$ in reducing the title Mn^{IV} complex. A similar situation has been found with the reduction of Ni^{IV}-oxime.[6] There, $Fe(OH)^+_{aq}$ is about 10^5 times more reactive than Fe^{2+}_{aq}. Although it was not possible to extract the absolute value of k_4, we expect it also to be high. Our results also indicate, at best, a poor contribution of Fe^{3+}_{aq} (k_{-1} path) in reoxidising the Mn^{III} species; $Fe(OH)^{2+}_{aq}$ (k_{-2} path) is almost wholly responsible for this. The pattern of reactivity established with Fe^{III}, Mn^{III}, Ag^{II} and Co^{III} as inner-sphere oxidants also revealed a significant contribution of the M−OH path to the overall rate.[9] In contrast, aqua complexes generally predominate for outer-sphere reactions, with little or no contribution from the M−OH path. In the present case, the hydroxo species $Fe(OH)^{2+}_{aq}$ and $Fe(OH)^+_{aq}$ are kinetically superior to their corresponding conjugate acids. Such a situation is likely with inner-sphere reactions, possibly by hydrogen bonding of the OH group to an NH or NH_2 group of the ligand biguanide.

Experimental Section

Materials: The complex salt $[Mn(C_2N_5H_7)_3]_2SO_4(NO_3)_6{\cdot}3H_2O$ was prepared by a known procedure.[1] The crystals obtained were sufficiently pure, as indicated by satisfactory elemental analysis (calcd. C 11.63, H 3.88, N 40.71; found C 11.3, H 3.9, N 39.9). A stock solution of $Fe(ClO_4)_2$ was prepared by dissolving pure iron powder (G. R., E. Merck) in a slight stoichiometric excess of $HClO_4$ under an N_2 atmosphere. These solutions were prepared just prior to use for kinetic measurements. This solution was estimated by the dichromate oxidation method.[10] $Fe(ClO_4)_3$ solutions were prepared by dissolving freshly precipitated $Fe(OH)_3$ in a stoichiometric excess of $HClO_4$. In solution, Fe^{3+} was estimated by measuring the absorbance of $[Fe(SCN)]_{aq}^{2+}$ (ε = 5000 $M^{-1}cm^{-1}$) at 460 nm after the addition of NH_4SCN solution.[11,12] The free-acid content in both of these iron solutions were measured by passing them separately through a Dowex 50 W X-8 strong cation-exchange resin in the H^+ form to obtain $[H^+]$ equivalent to the metal-ion concentration along with free acid and then subtracting the metal equivalent from these. An aqueous solution of $NaClO_4$ (G. R., E. Merck) was standardised by passing through a Dowex 50 W X-8 strong cation-exchange resin in the H^+ form and titrating the liberated acid with standard NaOH to a phenolphthalein end-point. The total acid content of the reaction mixtures was calculated as added acid plus that produced by the hydrolysis of ferric ion. All other chemicals were of reagent grade and used as received. Doubly distilled, freshly boiled water was used throughout.

Physical Measurements and Kinetics: All absorbances and electronic spectra were recorded with a Shimadzu (1601 PC) spectrophotometer using 1.00 cm quartz cells. The kinetics were monitored in situ in the "kinetic mode" of the instrument at 433 nm, one of the absorption peaks (Figure 2) of the complex **1**, in an electrically controlled thermostatted (25.0 ± 0.1 °C) cell housing (CPS-240A). For faster reactions, Fe^{2+} solution was injected directly into the spectrophotometer cell containing the other components of the reaction mixture. The desired concentration of the complex and the reducing agent was achieved after mixing. All kinetics were monitored in the presence of excess Fe^{2+} over **1** at an ionic strength 1.0 M ($NaClO_4$).

Stoichiometry and Reaction Products: The stoichiometry was measured by estimating unchanged Fe^{2+} spectrophotometrically. Reaction mixtures containing 4−10 times Fe^{2+} over **1** were allowed to react completely under an N_2 atmosphere until the solution turned colourless. Excess 1,10-phenanthroline was then added along with potassium hydrogen phthalate (pH ≈ 4). The red colour of $[Fe(phen)_3]^{2+}$ was then measured at 510 nm (ε = 11100 $M^{-1}cm^{-1}$).[11,13] In another aliquot of product solution, the Fe^{3+} produced was quantified by adding NH_4SCN and measuring the absorbance of $[Fe(SCN)]_{aq}^{2+}$ so formed at 460 nm.[11,12] A reaction mixture, initially containing 2.5 mM [Mn^{IV}], 100 mM [Fe^{2+}] and 10 mM [Fe^{3+}], stored till colourless (absorption < 0.01 at 433 nm), was treated with NaOH solution at about 50 °C with constant stirring. The pH was thus raised to about 5 and the solution was kept for about 24 hours, after which all the iron had precipitated as iron(III) hydroxide. This was removed by filtration. The pH of the resulting solution was lowered to about 1 to avoid the complexation of biguanide with Mn^{2+} and an EPR spectrum was recorded. The biguanide ligand in the product was quantitatively isolated as $[Cu(LH_2)_2]SO_4$ by the addition of $CuSO_4$. The amount of Cu^{II} thus held was determined iodometrically after decomposing the copper complex.[14]

Equilibrium Measurements: A 15 mL mixture of 1.00 mM complex and 3.00 mM $HClO_4$ was titrated with a standard NaOH solution to determine the acid dissociation constants of the title complex. The titration was carried out at 25.0 °C and I = 1.0 M ($NaClO_4$) with a Metrohm 736 GP Titrino autotitrator.

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