# Kinetic and Mechanistic Studies on the Oxidation of Nitrogen(III) ($HNO_2$/$NO_2^-$) by the Tris(biguanide)manganese(IV) Ion in Aqueous Acidic Media

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The kinetics of a net two-electron transfer between an authentic $Mn^{IV}$ complex, $[Mn(bigH)_3]^{4+}$ (*Fig. 1*; bigH = biguanide = $C_2N_5H_7$), and nitrite in aqueous solution in the pH interval 2.00–3.60 is described. Stoichiometric data for the reaction clearly indicates $\Delta[Mn^{IV}]/\Delta[N^{III}]_T = 1.07 \pm 0.10$, and $NO_3^-$ is detected as the oxidized product of nitrite ($[N^{III}]_T = [HNO_2] + [NO_2^-]$). Though both $HNO_2$ and $NO_2^-$ are found to be reactive, the latter is kinetically superior in reducing the fully protonated $Mn^{IV}$ complex. Proton-coupled electron transfer (PCET; 1e, $1H^+$) reduces the activation barrier for the thermodynamically unfavorable reaction of weakly oxidizing $Mn^{IV}$ species. At the end of the redox process, the ligand bigH is released, and the high protonation constants of the ligand carry the overall reaction to completion.

**Introduction.** – In aqueous solution, quite a few oxo-bridged multinuclear $Mn^{IV}$ complexes are known to be stable enough for the successful study of their solution chemistry [1]. In contrast, only one well-characterized mononuclear $Mn^{IV}$ complex has recently been synthesized from aqueous media [2], being stable in aqueous solution over a wide acidity range ($10^{-6}$ to 2M). The paucity of available aqueous-chemistry data of mononuclear $Mn^{IV}$ complexes, which are key species in photosystem II (PS II), is alarming; until recently, only a few kinetic studies on the reduction of the tris(biguanide)manganese(IV) ion ($[Mn(bigH)_3]^{4+}$, bigH = biguanide, $C_2N_5H_7$; see *Fig. 1*) in aqueous solution have been published [3–6]. Solution studies of mononuclear $Mn^{IV}$ complexes, the basic unit of the tetrameric manganese cluster of the oxygen-evolving complex (OEC) of PS II [7], are of potential importance for a better understanding of the rather unexplored polynuclear higher-valent manganese chemistry.

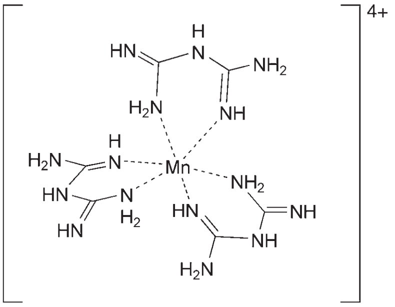

Fig. 1. *Structure of the tris(biguanide)manganese(IV) ion $[Mn(bigH)_3]^{4+}$*

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In this contribution, we report the redox interaction between the authentic two-electron $Mn^{IV}$ oxidant $[Mn(bigH)_3]^{4+}$ and nitrite in aqueous media (pH 2.00–3.60). The $N^{III}$-atom in the form of $HNO_2$ and $NO_2^-$ has a rich redox chemistry [8] both as an oxidant or reductant. The gross reactivity of $N^{III}$ in aqueous solution not only results from $NO_2^-$ and $HNO_2$, but, depending on media acidity and $[N^{III}]$ $(=[HNO_2]+[NO_2^-])$, also $NO^+$ or even different redox species like NO, $NO_2$, or $N_2O_3$ with interesting acid-base chemistry contribute significantly to the reactivity. The study of the $N^{III}$ chemistry in aqueous solution thus remains a fertile endeavor.

Recently, we demonstrated that protonated hydrazine, $N_2H_5^+$, reduces the $[Mn(bigH)_3]^{4+}$ complex [6] and its conjugate base by mechanistically different electron-transfer processes, the latter reduction being associated with a proton coupling. Whether a proton transfer is an essential prerequisite for the $Mn^{IV}$ reduction by nitrogenous reducing agents is now investigated in the case of the reducing agent nitrite.

Additional interest in this study is due to the fact that the dinuclear $Mn^{IV}$ complex $[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)(H_2O)_2(bipy)_2]^{3+}$ oxidizes nitrite probably by a two-electron transfer mechanism [9], whereas the mixed-valent $[(L)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(L)_2]^{3+}$ (L = 1,10-phenanthroline or 2,2'-bipyridine) oxidants prefer one-electron paths [10]. We thus thought it worthwhile to compare our results of nitrite oxidation by the mononuclear $Mn^{IV}$ complex $[Mn(bigH)_3]^{4+}$ with those of the oxidation by the above mentioned dinuclear manganese species.

**Results and Discussion.** – *Equilibrium Results.* Known values of the acidity constants $pK_{a1}$ $(=5.30\pm0.20)$ and $pK_{a2}$ $(=7.60\pm0.30)$ [3] for the $[Mn(bigH)_3]^{4+}$ complex, and the $pK_a$ $(=3.00\pm0.10)$ [11] [12] for $HNO_2$ in $H_2O$ were used in calculating rate constants. For interpreting rate data in deuterated media, these acidity constants were determined at 25.0° in 95% $D_2O$: $pK_{a1}$ and $pK_{a2}$ were found to be unchanged within experimental uncertainty, but $pK_a$ was increased to $3.80\pm0.10$. These values are averages of at least ten results obtained from the built-in programme of the autotitrator.

*Stoichiometry and Reaction Products.* The results of several stoichiometric measurements yielded an average $\Delta[Mn^{IV}]/\Delta[N^{III}]_T$ of $1.07\pm0.10$, which indicates $NO_3^-$ as the $N^{III}$ oxidation product. $NO_3^-$ in the product solution was also determined by analysis with chromotropic acid. The product solution displayed a typical six-line EPR spectrum of $Mn^{II}$ $(I=5/2)$. The overall stoichiometric redox process is, thus, described by *Eqn. 1*.

$$Mn^{IV} + NO_2^- + H_2O \rightarrow Mn^{II} + NO_3^- + 2\,H^+ \quad (1)$$

Iodometric determination of $Cu^{II}$ in the bis(biguanide)copper(II) species precipitated from the product solution indicated release of more than 90% biguanide.

*Kinetics.* The absorbance *vs.* time data followed excellent first-order kinetics as evidenced from good linear plots $(r\geq0.98)$ of $\ln(A_t-A_\alpha)$ *vs.* time for more than 95% completion of reactions. In all kinetic runs, $A_\alpha$ values were less than 0.01. The observed first-order rate constants $k_0$ (*Eqn. 2*) were evaluated from the least-squares slopes of these plots, and are presented in *Table 1.* We also verified that a tenfold variation in the initial $Mn^{IV}$ concentration (0.02–0.20 mM) resulted in almost similar (1–5%) $k_0$ values, which again confirms a first-order decay of $[Mn^{IV}]$. Averages of $k_0$ values from at least three

Table 1. *Some Representative First-Order Rate Constants for the Oxidation of $N^{III}$ by the Tris(biguanide)manganese(IV) Complex.* At 25.0°, $I = 1.0$ M ($NaClO_4$), $\lambda$ 433 nm, $[Mn^{IV}] = 0.10$ mM. The values in the parentheses are calculated from *Eqn. 6*.

| pH | $[N^{III}]_T$ [M] | $10^4\ k_0$ [$s^{-1}$] |
|---|---|---|
| 2.00 | 0.04 | 1.80 (1.81) |
| 2.67 | 0.04 | 2.42 (2.30) |
| 3.02 | 0.04 | 2.65 (2.72)[a] |
| 3.51 | 0.04 | 3.00 (3.27)[b] |
| 2.01 | 0.08 | 3.52 (3.62)[c] |
| 3.00 | 0.02 | 1.35 (1.35)[d] |
| 3.31 | 0.02 | 1.45 (1.53)[e] |
| 3.00 | 0.12 | 8.22 (8.10) |
| 2.25 | 0.08 | 4.13 (3.88) |
| 3.60 | 0.08 | 6.60 (6.70) |
| 3.59 | 0.12 | 9.81 (10.03) |
| 2.02 | 0.06 | 2.63 (2.72)[f] |

[a]) $10^4 k_0 = 2.71\ s^{-1}$ in presence of 0.50 mM added biguanide. [b]) $10^4 k_0 = 3.05 \pm 0.20\ s^{-1}$ in presence of 0.1–1.0M added chloride, $I = 1.0$M ($NaClO_4 + NaCl$). [c]) $10^4 k_0 = 3.59\ s^{-1}$ at $I = 1.0$M ($NaNO_3$). [d]) $10^4 k_0 = 1.30\ s^{-1}$ when the reaction medium was purged with purified $N_2$. [e]) $10^4 k_0 = 3.50\ s^{-1}$ at $I = 0.5$M ($NaClO_4$) and 11.0 $s^{-1}$ at $I = 0.1$M ($NaClO_4$), resp.. [f]) $10^4 k_0 = 2.79\ s^{-1}$ at $I = 0.5$M ($NaClO_4$) and 3.11 $s^{-1}$ at $I = 0.1$M ($NaClO_4$), resp.

independent runs were taken, and the average coefficient of variation (CV) [13] for these measurements was within 3%.

$$-\mathrm{d}[Mn^{IV}]/\mathrm{d}t = k_0[Mn^{IV}] \tag{2}$$

The reaction was found to be first-order in $[N^{III}]_T$, and there is no $[N^{III}]_T$-independent term even at the highest $[N^{III}]_T$ studied. The following changes of the reaction conditions had, within the limits of experimental uncertainties, no influence on the values of $k_0$: the presence of 0.50 mM biguanide, whether the medium is purged with $N_2$ or not, the presence or absence of diffused light, and a variation in the monitoring wavelength in the range 410–440 nm.

No polymer was visually detected when 6% (*v*/*v*) acrylonitrile was added to the reaction mixture, indicating that free radicals do not accumulate in the reaction media in sufficient concentrations for initiation of acrylonitrile polymerization.

We observed a modest increase in $k_0$ with decrease in $[H^+]$ of the reaction media at a fixed $[N^{III}]_T$ (*Fig. 2*). The $Mn^{IV}$ complex is a mild dibasic acid ($pK_{a1} = 5.30 \pm 0.20$, $pK_{a2} = 7.60 \pm 0.30$) [3], and in the pH range investigated, it suffers only a little or no deprotonation, however, the acid–base equilibrium of $N^{III}$ is of importance ($pK_a$ of $HNO_2 = 3.00 \pm 0.10$ at 25.0°, $I = 1.0$M) [11][12]. Progressive generation of more $NO_2^-$ may be a likely cause for the increased rate at higher pH. This is not unexpected from the known kinetic behavior of the $NO_2^-/HNO_2$ couple [11][14] and the well-accepted view that anionic forms of protolytic reductants are much more reactive than the uncharged molecular species, *viz.* their conjugate acids [15]. *Eqns. 3–5* accommodate the observed rate dependence on $[H^+]$ and $[N^{III}]_T$, and the resulting rate law is given by *Eqn. 6*.

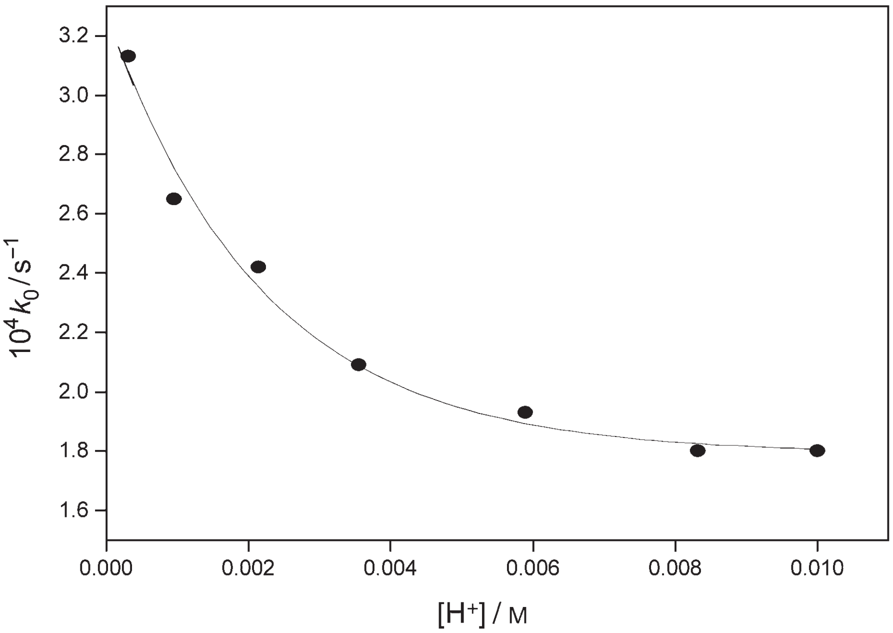

Fig. 2. *Dependence of* $k_0$ *on [H$^+$] at [N$^{III}$]$_T$=0.04*M. At 25.0°, $I$=1.0M (NaClO$_4$), [Mn$^{IV}$]=0.10 mM.

$$\mathrm{HNO_2} \overset{K_a}{\rightleftharpoons} \mathrm{NO_2^-} + \mathrm{H^+} \tag{3}$$

$$[\mathrm{Mn(bigH)_3}]^{4+} + \mathrm{HNO_2} \xrightarrow{k_1} \mathrm{products, Mn^{II}, NO_3^-, bigH} \tag{4}$$

$$[\mathrm{Mn(bigH)_3}]^{4+} + \mathrm{NO_2^-} \xrightarrow{k_2} \mathrm{products, Mn^{II}, NO_3^-, bigH} \tag{5}$$

$$k_0(K_a + [\mathrm{H^+}])/[\mathrm{N^{III}}]_T = k_1[\mathrm{H^+}] + k_2K_a \tag{6}$$

A plot of the left-hand side of *Eqn. 6 vs.* [H$^+$] was found to provide an excellent straight line (*Fig. 3*; $r$=0.99) and yielded the rate constants (in $10^3$ M$^{-1}$ s$^{-1}$) $k_1$=4.03±0.20 and $k_2$=9.48±0.30 from the slope and intercept of the plot by using the known value of $K_a$. These second-order rate constants regenerate all the experimental $k_0$ values quite satisfactorily (*Table 1*).

*Mechanism.* The order $k_2 > k_1$ reminds us that the deprotonated reductants are more reactive in reducing higher-valent metal complexes than their parent acids [15], and the [Mn(bigH)$_3$]$^{4+}$ oxidant is not an exception so far [3] [4]. We also observed a substantial increase in $k_0$ with decrease in ionic strength (*Table 1*) of the reaction media in the higher-pH region, which again supports the increased contribution of the cation–anion reaction to the overall rate. Again, the increase in rate with decreasing ionic strength of the reaction media in the lower-pH region of the pH interval studied was only marginal, and is indicative of a reaction with an uncharged species, predominant at higher acidity. A few kinetic runs were performed in the presence of added chloride ($I$=1.0M NaCl/NaClO$_4$); the observed $k_0$ values were nearly independent on [Cl$^-$] in the range

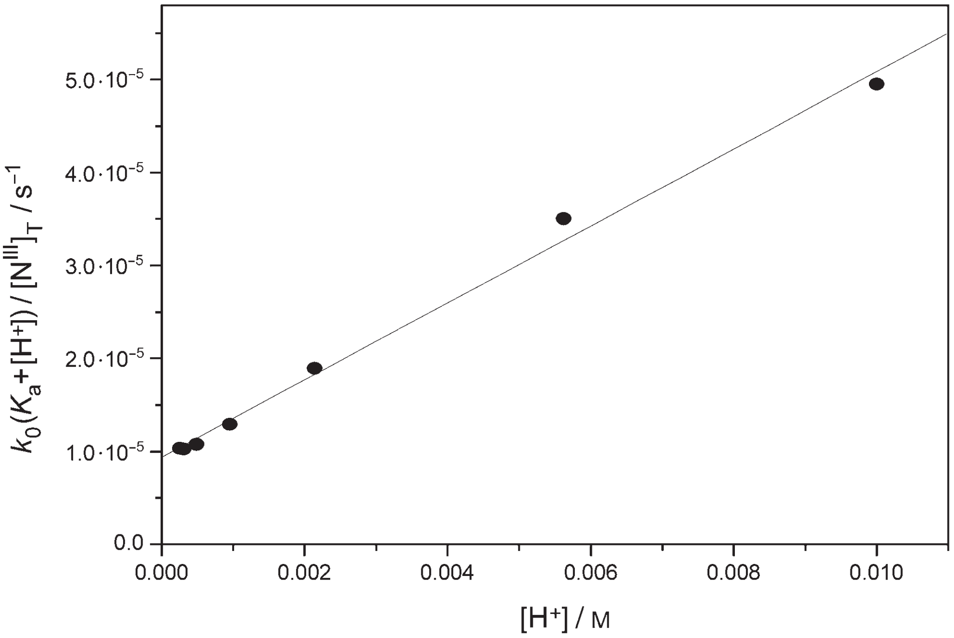

Fig. 3. *Plot of left-hand-side of* Eqn. 6 vs. *[$H^+$]*. At 25.0°, $I = 1.0$M ($NaClO_4$), [$Mn^{IV}$] = 0.10 mM.

0.1–1.0M (*Table 1*), probably indicating that no cationic species is involved in reducing the $[Mn(bigH)_3]^{4+}$ complex. A remarkable rate enhancement by added $Cl^-$ was reported in the oxidation of $Fe^{2+}$ by this $Mn^{IV}$ complex; the increase in rate was due to the conventional medium effect by the polarizable $Cl^-$ anion, as observed by *Gould et al.* in their cation–cation redox reaction [5].

The overall redox process in this study is a net two-electron transfer. However, it is extremely unlikely that the $Mn^{IV}$ reduction at hand proceeds in a single step. The $Mn^{IV}$ is coordinatively saturated, and we found no change in $k_0$ values in presence of added ligand (biguanide) in the entire pH range investigated. This confirms that no pre-equilibrium ligand dissociation exists. Also, we observed no immediate spectral changes on mixing nitrite with the oxidant in the entire pH range, and the absorbance values gradually decayed to less than 0.01, with no generation of isosbestic points. All these (possibly) lend support to an outer-sphere electron transfer. But an outer-sphere two-electron transfer must be considered to be unusually slow (mirroring a prohibitive *Franck–Condon* barrier). Moreover, the $Mn^{IV}$ oxidant is devoid of oxo or halo groups, which supports a two unit bridged transfer at a time. However, besides these oxidant specifications, a direct removal of two electrons from $NO_2^-$ to produce $NO_3^-$ *via* the fast hydrolysis of $NO_2^+$ though is thermodynamically almost as unfavorable ($E°(NO_2^-/NO_3^-) = -0.94$ V) [16] as a one-electron oxidation to $NO_2$ ($E°(NO_2^-/NO_2) = -1.04$ V) [17]; such a two-electron transfer is expected to be much slower than the one-electron transfer as it involves a considerable reorganization of the electronic structure of the species concerned [18] ($NO_2^-$: $C_{2v}$, O–N–O = 115°, O–N = 1.24 Å; $NO_2$: $C_{2v}$, O–N–O = 134.1°, O–N = 1.19 Å; $NO_2^+$: $D_{\alpha h}$, O–N–O = 180°, O–N = 1.15 Å). Though we observed no polymerization of acrylonitrile, it does not confirm a two-electron process because the radicals generated by a one-electron transfer may quickly react before diffusing into the bulk solvent, thus evading detection by the polymerization experiments. Thus, we conclude that we are dealing with sequences of single-electron steps in which only the initial act, *Eqn. 7*, is reflected in the rate law of *Eqn. 6*. The possible routes for the $N^{IV}$ (in the form of $NO_2$) oxidation leading to the product $N^V$ (in the form of $NO_3^-$) may be considered in two distinct ways by *Eqns. 8* and *9*, or by a direct one-electron transfer to the $Mn^{III}$ generated according to *Eqn. 7*.

$$Mn^{IV} + N^{III} \rightarrow Mn^{III} + N^{IV} \qquad (7)$$

$$2\ N^{IV} \rightarrow N^{III} + N^{V} \qquad (8)$$

$$2\ Mn^{III} + N^{III} \rightarrow 2\ Mn^{II} + N^{V} \qquad (9)$$

All the steps of *Eqns. 7–9* are believed to be kinetically silent. Both alternatives are compatible with the overall stoichiometry of *Eqn. 1*. Note here that the reaction of *Eqn. 9* may again be considered as disproportionation of $N^{IV}$ (*Eqn. 8*) or $N^{IV}$ oxidation by $Mn^{III}$. Of the two alternatives for the removal of $N^{IV}$ generated by the rate-limiting one-electron reduction of $Mn^{IV}$ by nitrite (*Eqn. 7*), we are unable to conclude the actual route of $N^{IV}$ decay to produce $N^V$. On the one hand, $N^{IV}$ ($NO_2$) disproportionation to $NO_2^-$ and $NO_3^-$ is almost diffusion controlled ($k = 1 \cdot 10^8\ \text{M}^{-1}\ \text{s}^{-1}$) [19], and no slow non-complementary steps are invoked in this way to reach the overall stoichiometry, on the other hand, the $Mn^{III}$ reduction by $N^{III}$ is expected to be fast also as $d^4$ $Mn^{III}$ is labile [20], which renders the aquation of the $Mn^{III}$ complex spontaneous, resulting in a high reactivity of the partially or fully aquated $Mn^{III}$ species thus formed. Moreover, under the acidic condition used in the present study, ligand opening from the metal center ($Mn^{III}$) is facilitated. Labile $[Mn(acac)_3]$ (ligand exchange rate = 1 $s^{-1}$) [21] rapidly aquates in acidic media to form much more reactive diaqua species $[Mn(acac)_2(H_2O)_2]^+$ (Hacac = acetylacetone = pentane-2,4-dione), which swamps the kinetic activity of $[Mn(acac)_3]$ with its own while reacting with $S^{IV}$ [22], glyoxylate [23], oxalate [24], and $H_2PO_2^-$ [25]. Though it is unexpected that $NO_2$ does survive long enough for consumption by the $Mn^{III}$, the possibility cannot be ruled out. A direct electron transfer from $NO_2$ to $Mn^{3+}_{aq}$, $Mn(OH)^{2+}_{aq}$, and bis(2-ethyl-2-hydroxybutanoato)oxochromate(V) or its $Cr^{IV}$ analogue has been proposed earlier [14] [26].

At the highest pH (3.60) studied in this reaction, the contribution of the $k_1$ path to the overall rate is negligible. Considering any pre-equilibrium association of $NO_2^-$ with the $Mn^{IV}$ complex and subsequent electron transfer as in *Eqn. 10*, where $A_2$ represents the adduct, the rate-law of *Eqn. 11* is obtained.

$$Mn^{IV} + NO_2^- \underset{}{\overset{K_2}{\rightleftharpoons}} A_2 \xrightarrow{k_2} \text{products} \qquad (10)$$

$$k_0 = k_2K_2[NO_2^-]/(K_2[NO_2^-] + 1) \qquad (11)$$

As no rate saturation was obtained even at the maximum $[N^{III}]_T$ studied, $K_2[NO_2^-]$ is $\ll 1$, which requires that the maximum value of $K_2$ should be around 1, with no obvious lower limit. $Mn^{IV}$–$HNO_2$ association ($A_1$, formation constant being $K_1$) is expected to be even less tight than this. This low value for pre-equilibrium adduct formation clearly removes any possibility of strong inner-sphere attachment by increasing the coordination number of $Mn^{IV}$ to seven. Electrostriction [27–30], or some kind of it, aided by H-bonding [31] [32] involving the free amino or imino groups of the ligand with the reducing agents, is thus a finite possibility. Such interactions were previously proposed for this $Mn^{IV}$ oxidant with substrates like $Fe^{2+}$ [3], $In^{I}$ [5], and glyoxylic and pyruvic acids [4].

It may be noted here that a strong pre-equilibrium adduct formation between $Mn^{IV}$ and $NO_2^-$, producing the intermediate $A_2$ (*cf. Eqn. 10*), which reacts with another $NO_2^-$ in a rate-limiting step, would lead to observed kinetics only if $K_2[NO_2^-] \gg 1$. The rate law for this scheme appears to be $k_0 = k_2K_2[NO_2^-]^2/(K_2[NO_2^-] + 1)$. It appears from this restriction that $(K_2)_{min}$ is of the order of $10^4$. However, this high value for $K_2$ seems unlikely in the present system because the $Mn^{IV}$ is coordinatively saturated, and even with oxidizing $Mn^{IV}$ species like $[(L)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(L)_2]^{3+}$ (L = 1,10-phenanthroline or 2,2′-bipyridine) and $[Mn_2^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)(H_2O)_2(bipy)_2]^{3+}$, the association constants with $NO_2^-$ are reported to be much lower, of the order of $10^1$ (or even less) [9] [10].

In some $N^{III}$ reduction of higher-valent metal complexes, NO or $NO^+$ paths have been proposed [33] [34], though we found no such evidence in the present study. A reaction path involving NO would require a $[HNO_2]^2$ term in the rate law, (*cf. Eqn. 12*), and $NO^+$ requires a third-order rate law, $[Mn^{IV}][HNO_2][H^+]$ (*cf. Eqn. 13*). A likely reason for not obtaining the reactivities of these species may be due to the small equlibrium constants of these reaction [33a] [34a].

$$2\ HNO_2 \rightleftharpoons NO + NO_2 + H_2O \quad K = 6.0 \cdot 10^{-6} \quad [33a] \tag{12}$$

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O \quad K = 3.0 \cdot 10^{-7} \quad [34a] \tag{13}$$

The $Mn^{IV}$ is coordinatively saturated by the strong chelating ligand biguanide and is thus expected to be not a too strong oxidant. Cyclic-voltammetry studies of an aqueous solution (deaerated by purging $N_2$ for a long time) of 0.1 mM $[Mn(bigH)_3]^{4+}$ in the presence of 0.1M $(Et_4N)ClO_4$ at pH 3.8 revealed an irreversible reduction (attributed to $Mn^{IV}/Mn^{III}$, *vide infra*) at 0.4 V (*vs.* Ag/AgCl) [4] at a scan rate of 20– 200 mV $s^{-1}$. Free biguanide or $(Et_4N)ClO_4$ is not redox-sensitive at this potential. The irreversible reduction is characterized by no clearly observable re-oxidation of $Mn^{III}$ at 0–0.8 V, which might indicate that the labile $Mn^{III}$ formed from $Mn^{IV}$ quickly depletes. Release of ligand from labile $Mn^{III}$ is, perhaps, a distinct possibility making $Mn^{III}$ a powerful oxidant. We had no direct evidence for any intermediate formation of $Mn^{III}$, even when the $[Mn(bigH)_3]^{4+}$ oxidant reacts with the one-elecctron reducing agent $Fe^{2+}_{aq}$ [3], though the rate data were consistent with the steady-state formation of $Mn^{III}$. This clearly indicates the kinetic instability of $Mn^{III}$, and all attempts to prepare a biguanide-manganese(III) complex failed so far. The reduction at 0.4 V (*vs.* Ag/AgCl) is thus assignable to the $Mn^{IV}/Mn^{III}$ couple.

To get further insight into the reaction mechanism, we performed some kinetic runs in 95% $D_2O$ media. The first-order rate constants obtained were substantially lower than those obtained in $H_2O$, though the rate retardation is relatively more pronounced in the lower-pH region (*Table 2*). Moreover, a plot of first-order rate constants *vs.* mol-% of

$D_2O$ was linear (*Fig. 4*; $r = 0.98$) indicating one-proton one-electron transfer in the rate-limiting step of the $[Mn(bigH)_3]^{4+}$ redox reaction [35a][1]). Proton-coupled electron transfer (PCET) as proposed in this process, thus, is a key step that reduces the activation barrier for the quite endothermic one-electron oxidation of $NO_2^-$ ($E°(NO_2^-/NO_2) = -1.04$ V) [17]. At the higher pH, the more reactive $NO_2^-$ (than $HNO_2$) contributives more to the overall rate. At lower pH, protonation on the free imino[2]) or amino group of the metal-bound ligand exerts a pull on the bonded electrons, and the effect is relayed through the molecule that renders the Mn–N bonds weaker and facilitates the electron acceptance of $Mn^{IV}$. A similar mechanism for acid-catalyzed aquation of the hexacoordinated complexes of $Cr^{III}$ and $Co^{III}$ with biguanide and substituted biguanide ligands was proposed earlier [37], and the rate was found to decrease with decreasing basicity of the biguanide ligands. Above pH 3.0, the protonation was, as found, not much effective compared to that at low pH (*Table 2*), though detectably finite, as evidenced from rate lowering (albeit small) in $D_2O$ at pH > 3.0. To our support, we recall the extreme inertness of $[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine) even in 1M $HClO_4$, as protonation of the ligand cannot take place, unless a metal–ligand bond breaks first [38]. Protonation of the free biguanides [39] released at the completion of $Mn^{IV}$ reduction is another driving force for the thermodynamically apparently unfavorable reaction to go to completion.

Contrary to the observation we report herein, the oxidation of $N_2H_5^+$ by $[Mn(bigH)_3]^{4+}$ is also associated with a remarkable PCET pathway only at higher pH [6]. Probably, at higher pH, where the deprotonated form of $[Mn(bigH)_3]^{4+}$, *i.e.*, $[Mn(bigH)_2(big)]^{3+}$, was found to be more reactive, it is expected to be much more proton accepting due to the lower positive charge, which favors the observed PCET. Though we are at present unable to rationalize the observed PCET difference with $N_2H_5^+$ (at higher pH) and $NO_2^-$ (particularly at lower pH), we note that only $N_2H_5^+$ (and not $N_2H_4$) was reactive, but both $HNO_2$ and $NO_2^-$ are reactive in reducing the $Mn^{IV}$. The $NO_2^-$ path is only 2.35 times more contributing to the overall rate than the $HNO_2$ path. Normally, in redox reactions, the reactivity of $NO_2^-$ is far higher than that of $HNO_2$, and in many reactions, only $NO_2^-$ but not $HNO_2$ reacts, even when the latter is present in considerable concentrations [33b]. The similar $k_2$ values in $H_2O$ and $D_2O$ (in $D_2O$: $10^3k_1 = 1.38 \pm 0.10$ and $10^3k_2 = 8.8 \pm 0.20$; in $H_2O$: $10^3k_1 = 4.03 \pm 0.20$ and $10^3k_2 = 9.48 \pm 0.30$; all in $M^{-1} s^{-1}$) and the only marginally higher reactivity of $NO_2^-$ over $HNO_2$ in the present study may be the result of several factors and their fortuitous cancellations: both $HNO_2$ and $NO_2^-$, but only $N_2H_5^+$, react(s) with $Mn^{IV}$, $[Mn(bigH)_2(big)]^{3+}$ though being potentially more proton-accepting than its parent acid $[Mn(bigH)_3]^{4+}$, but the higher acidity is expected to weaken the Mn–N bonds, and possibly a change in mechanism in the two different paths occurs, both for $N_2H_5^+$ and $N^{III}$. An absolute answer to the problem remains to be found.

It is known that mixed-valent $Mn^{III,IV}$ or isovalent $Mn_2^{III}$ complexes oxidize $NO_2^-$ by one-electron pathways [10], whereas $Mn_2^{IV}$ reduction is two-electron rate-limiting [9]. The proposal for the two-electron step for $Mn_2^{IV}$ reduction [9] originated from the known slower kinetics of $Mn_2^{III,IV}$ or $Mn_2^{III}$ reduction by $NO_2^-$ in comparison to $Mn_2^{IV}$

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[1]) Substantial rate retardations would be observed when $H_2O$ is substituted by $D_2O$; see, *e.g.*, [35b].

[2]) *Ab initio* and semiempirical calculations established the high proton affinities of imino groups of biguanides and related ligands; see, *e.g.*, [36].

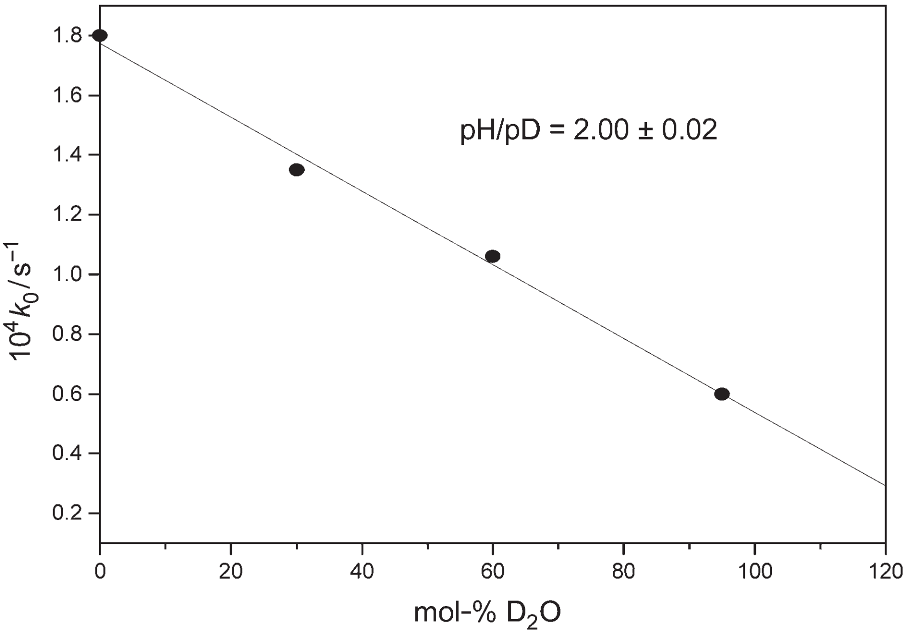

Fig. 4. *Effect of* $D_2O$ *on* $k_0$ *at* $[N^{III}]_T = 0.04$M. $T = 25.0°$, $I = 1.0$M ($NaClO_4$), $[Mn^{IV}] = 0.10$ mM.

Table 2. *Comparison of Observed First-Order Rate Constants in* $H_2O$ *and in* $H_2O/D_2O$ *5:95.* $[Mn^{IV}] = 0.10$ mM, $[N^{III}]_T = 0.04$M, $T = 25.0°$, $I = 1.0$M ($NaClO_4$), $\lambda$ 433 nm.

| Medium | pH or pD | $10^4\ k_0\ [s^{-1}]$ | $k_{H_2O}/k_{H_2O} - k_{D_2O}$ |
|---|---|---|---|
| $H_2O$ | 2.00 | 1.80 | |
| 95% $D_2O$ | $2.00 \pm 0.02$ | 0.60 | 3.0 |
| $H_2O$ | 3.02 | 2.65 | |
| 95% $D_2O$ | $3.00 \pm 0.01$ | 0.98 | 2.7 |
| $H_2O$ | 3.51 | 3.00 | |
| 95% $D_2O$ | $3.50 \pm 0.02$ | 1.56 | 1.9 |

reduction. The mixed-valent $Mn_2^{III,IV}$ or $Mn_2^{III}$ complexes instead prefer one-electron paths as it is firmly established that electrochemical and chemical reduction of several $Mn_2^{III,IV}$ complexes produce a $Mn_2^{III}$ dimer and then a mixture of $Mn^{III}$ and $Mn^{II}$ species. In the present study, however, we did not experience any spectral changes, besides lowered absorptions, during the reaction or formation of new peaks, even when less than stoichiometric amounts of $N^{III}$ were employed in the reaction with the $Mn^{IV}$ complex over the entire pH range studied. This possibly indicates that the $Mn^{III}$ generated by one-electron oxidation of $N^{III}$ quickly depletes to the final product, $Mn^{II}$, as the $Mn^{III}$ is labile, or $NO_2$, the one-electron-oxidized product of $N^{III}$, instantaneously reacts with $Mn^{III}$. Would the $Mn^{III}$ intermediate be stable, spectral assignment might have been possible [1n] [40].

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## Experimental Part

*Materials.* The complex salt tris(biguanide)manganese(IV) ($[Mn(bigH)_3]^{4+}$; bigH = biguanide = imidocarbonimidic diamide = $C_2N_5H_7$), was prepared by a known procedure [2]. Biguanide sulfate ($C_2N_5H_7 \cdot H_2SO_4$) was prepared by a known method reported previously [41]. Stock solns. of $NaNO_2$, $NaClO_4$, and $NaNO_3$ (all of G. R. grade; *E. Merck*) were standardized as described earlier [11]. $D_2O$ (99.9%; *E. Merck*) was used for the preparation of all the solns. when the kinetic isotope effects were measured. Naphthalen-1-amine (*Caution*: the amine should not contain napthalen-2-amine, which is carcinogenic) and sulfanilic acid were from *E. Merck* (G. R. grade), and the disodium salt of 1,8-hydroxynaphthalene-3,6-disulfonic acid (= chromotropic acid; reagent grade; *Sigma*) was used as received. Chromium(II)-scrubbed $N_2$ gas and doubly distilled deionized $H_2O$ were used.

*Equilibrium Measurements.* The acid dissociation constant of the title complex and nitrous acid were determined by pH-metric titration with a *Metrohm (736 GP Titrino)* autotitrator in 95% $D_2O$ at $I = 1.0$M ($NaNO_3$) at 25.0°. To avoid nitrous acid decomposition in acidic media, solns. of $NaNO_2$ in $D_2O$ were titrated with $DNO_3$.

*Stoichiometry and Product Analysis.* The stoichiometry of the reaction was determined under kinetic conditions by reacting $Mn^{IV}$ in the concentration range 0.05–0.50 mM with $[N^{III}]_T$ $(= [HNO_2] + [NO_2^-])$ in 2–4 times of $[Mn^{IV}]$ at pH 3.30–3.60. After completion of the reactions as indicated by the soln. absorption decrease to less than 0.01 at 433 nm, excess nitrite was determined spectrophotometrically [42]. For this purpose, the product mixture was appropriately diluted, and treated with sulfanilic acid and naphthalen-1-amine to form the characteristic red dye. The absorbance of this dye was measured at 520 nm, and the concentration of unreacted $N^{III}$ was obtained from a calibration curve (exper. $\varepsilon^{520} = 4.1 \cdot 10^4$ M$^{-1}$ cm$^{-1}$, in close agreement with the reported $\varepsilon^{520} = 4.0 \cdot 10^4$ M$^{-1}$ cm$^{-1}$) [42] [1n]. We verified that neither $Mn^{2+}$ nor biguanide or $SO_4^{2-}$ interfered in this determination. We also tested that biguanide alone did not respond to this test.

For the EPR experiment, a reaction mixture containing 2 mM $[Mn(bigH)_3]^{4+}$ complex and 100 mM $[N^{III}]_T$ was stored at pH 3.5 until colorless (absorption < 0.01 at 433 nm). The pH of the resulting soln. was lowered to *ca.* 1 (to avoid the complexation of biguanide with $Mn^{2+}$), and an EPR spectrum was recorded.

The released biguanide in the product from $[Mn(bigH)_3]^{4+}$ and $N^{III}$ was quantitatively isolated as $[Cu(bigH)_2]SO_4$ by the addition of ammoniacal $CuSO_4$ in the usual manner [41] [43]. The amount of $Cu^{II}$ thus consumed was determined iodometrically after decomposing the copper complex.

The $NO_3^-$ ion produced in the redox reaction of $[Mn(bigH)_3]^{4+}$ was qualitatively determined by analysis with chromotropic acid [44]. For this purpose, the perchlorate salt of the complex (prepared by using perchloric acid instead of nitric acid in its synthetic procedure)[3]) was treated with excess $NO_2^-$. After completion of the reaction, excess nitrite was removed by sulfite/urea soln. The chromotropic acid reagent was then added to the product mixture, followed by conc. $H_2SO_4$ soln. A yellow color developed, establishing the presence of $NO_3^-$; biguanide and $Mn^{II}$ do not interfere.

*Kinetics and Physical Measurements.* The kinetics of the reaction was followed at 433 nm for one of the absorption peaks [3] of the $Mn^{IV}$ complex in aq. soln., where all other reaction components are transparent. $NaNO_2$ solns. were directly injected into the spectrophotometer cell containing other components of the mixture. The final concentration of the $Mn^{IV}$ complex and the reducing agent were achieved after mixing. Redox decomposition of $HNO_2$ to NO and $NO_2$ in acid media strongly depends on the NO escape rate [45]. The total $N^{III}$ used in our experiments was low, and we used capped quartz cells with minimum vacant space left that minimized $HNO_2$ loss. The pH values of the resulting solns. were measured by separately preparing solns. of desired compositions. A *Shimadzu (1601 PC)* spectrophotometer, with electrically controlled thermostated (25.0 ± 0.1°) cell-housing *(CPS-240A)* and 1.00-cm quartz cells, was used for kinetic-data recording as well as for spectral observations.

The ionic strength of the reaction media was generally maintained at 1.0M by $NaClO_4$. The soln. pH values were adjusted with an *Orion* pH meter (model *710A*), and the calibration of pH electrodes has been described earlier in detail [46]. For reactions in $D_2O$, the pD was calculated as pD = pH + 0.40 [47]. Nitric acid (99 atom-

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[3]) The monomeric structure of the perchlorate salt of the complex $[Mn(bigH)_3]^{4+}$ was determined by single-crystal X-ray analysis ($[Mn(bigH)_3](ClO_4)_4 \cdot H_2O$; manuscript in preparation.

% D; *Aldrich*) and solid NaOH were dissolved in $D_2O$ for this purpose. Excess reducing agent, $[N^{III}]_T$ ($=[HNO_2]+[NO_2^-]$), 0.02–0.12M, over the complex (0.05 mM as solid $Mn^{IV}$ complex)⁴) was maintained in all the kinetic runs. Electrochemical measurements were recorded with an electrochemical analyzer (*model 600A*; *CH Instruments*, USA) by using a three-component electrode system consisting of Pt-wire working and counter electrodes and an Ag/AgCl reference electrode.

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⁴) The solid complex $[Mn(bigH)_3]_2SO_4(NO_3)_6 \cdot 3\,H_2O$ used in the kinetic studies is dimeric. In aq. soln., the $[Mn^{IV}]$ is thus twice that of the calculated concentration based on the molar mass of the solid.

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