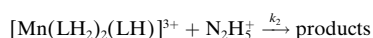
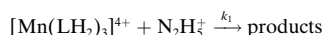


## Mechanistic Studies on the Oxidation of Hydrazine by Tris(biguanide)manganese(IV) in Aqueous Acidic Media

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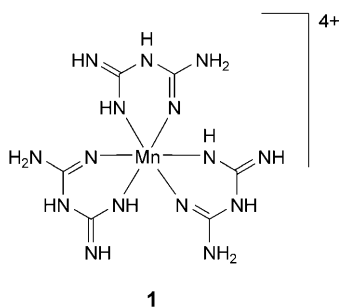
The title Mn<sup>IV</sup> complex, [Mn(LH<sub>2</sub>)<sub>3</sub>]<sup>4+</sup> (LH<sub>2</sub> = biguanide = H<sub>2</sub>NC(=NH)NHC(=NH)NH<sub>2</sub>), an authentic two-electron oxidant, quantitatively oxidizes hydrazine (H<sub>2</sub>NNH<sub>2</sub>) to dinitrogen in the pH interval 2.00–3.50. The net four-electron oxidation of hydrazine is provided by two Mn<sup>IV</sup> as established by stoichiometric studies. The overall reaction is composed of two parallel paths:



The values of  $k_1$  and  $k_2$  (in  $\text{M}^{-1} \text{s}^{-1}$ ) are, respectively,  $(5.50 \pm 0.6) \cdot 10^{-3}$  and  $11.4 \pm 1.5$  at 25.0° and  $I = 1.0\text{M}$  (NaNO<sub>3</sub>). The order  $k_2 \gg k_1$  is unusual as protonated oxidants are generally more reactive than their conjugate bases. The remarkably superior reactivity of the conjugate base of the oxidant in oxidizing N<sub>2</sub>H<sub>5</sub><sup>+</sup> may be at least in part due to an overall positive-charge reduction in [Mn(LH<sub>2</sub>)<sub>2</sub>(LH)]<sup>3+</sup> as compared to [Mn(LH<sub>2</sub>)<sub>3</sub>]<sup>4+</sup> that favors reaction with positively charged N<sub>2</sub>H<sub>5</sub><sup>+</sup>, and more plausibly, a change in the mechanism is responsible for this result as not  $k_1$  but  $k_2$  is substantially lowered in D<sub>2</sub>O media indicating that proton motion is coupled with electron transfer in the  $k_2$  path. The rate-determining step appears to be a one-electron transfer from N<sub>2</sub>H<sub>5</sub><sup>+</sup> to Mn<sup>IV</sup>.

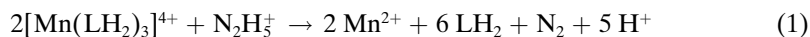
**Introduction.** – Tris(biguanide)manganese(IV) complex **1** ([Mn(LH<sub>2</sub>)<sub>3</sub>]<sup>4+</sup>; LH<sub>2</sub> = biguanide = imidodicarbonimidic diamide = H<sub>2</sub>NC(=NH)NHC(=NH)NH<sub>2</sub>; Fig. 1) is the only mononuclear water-soluble Mn<sup>IV</sup> complex that is quite stable over a wide range of acidity (10<sup>-6</sup> to 2M) and is structurally well characterized [1]. In aqueous solution, complex **1** behaves as a weak dibasic acid ( $\text{p}K_{\text{a}1} = 5.30 \pm 0.20$ ,  $\text{p}K_{\text{a}2} = 7.60 \pm 0.30$ ), and the deprotonations arise from the protons bound to the sp<sup>2</sup> N-atoms of the ligand [2]. The aqueous chemistry of mononuclear Mn<sup>IV</sup> remained uncovered until recently oxidation kinetics of metal ions like Fe<sup>2+</sup> [2][3], In<sup>+</sup> [3], and  $\alpha$ -keto acids like glyoxylic and pyruvic acids [4] were published.

The oxygen-evolving complex (OEC) of photosystem II (PS II) has a tetrameric manganese cluster as its key structural feature [5]. The tetrameric manganese cluster (Mn<sub>4</sub><sup>IV</sup>) catalyzes the four-electron oxidation of H<sub>2</sub>O to O<sub>2</sub> by advancing through five intermediate oxidation states, S<sub>0</sub>–S<sub>4</sub> [6], and in this cycle, proton movement to a tyrosinase radical provides extra driving force relative to a purely outer-sphere electron transfer [7]. Firmly established proton motion coupled to electron transfer in the OEC is the basic mechanism of fundamental importance in bioenergetic conversion. Recently synthesized Mn<sub>4</sub><sup>IV</sup> clusters are believed to be potential structural models of

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

OEC [8]<sup>1)</sup>, and multinuclear higher-valent metal centers are proven oxidants for a variety of reducing agents [9]. To explain in a finer way the mechanistic patterns of reactions and reactivity, studies of their basic unit, the mononuclear  $Mn^{IV}$  complex should play an important role. We report here the kinetics of oxidation of hydrazine by the  $Mn^{IV}$  complex **1** in aqueous acidic media. We also note that the O–H bond energy of tyrosine (86.5 kcal mol<sup>-1</sup>) [10] compares well with the N–H bond dissociation energy of hydrazine (84.0 kcal mol<sup>-1</sup>) [11], and it is interesting to see whether hydrazine may take part in a proton-coupled electron transfer (PCET) as tyrosinase does in PS II.

**Results and Discussion.** – *Stoichiometry and Reaction Products.* Measurements at different pH and different reactant ratios (complex/hydrazine) yielded  $\Delta[\text{hydrazine}]/\Delta[Mn^{IV}] = 0.48 \pm 0.05$ . Dinitrogen was detected by GC analysis. In the product mixture, rendered alkaline, no ammonia could be detected with *Nessler's* reagent. The gas generated in the reaction contained no  $HN_3$  since the outcoming gas produced no characteristic color with an aqueous  $Fe(NO_3)_3$  solution. Iodometric determination of  $Cu^{2+}$  in the bis(biguanide)copper(II) salt precipitated from the product solution indicated release of more than 90% biguanide. These results suggest that we are dealing with the net reaction of *Eqn. 1*.



*Kinetics.* No immediate spectrophotometric change was observed on mixing hydrazine with the  $Mn^{IV}$  complex **1** over the entire range of experimental pH. The whole reaction course followed good first-order kinetics – the  $\log(A_t - A_\infty)$  vs. time plots were found to be linear to more than 90% completion of the reactions. In all kinetic runs,  $A_\infty$  values were essentially zero (less than 0.01). The observed first-order rate constants  $k_0$ , defined by *Eqn. 2*, were obtained from the least-squares slopes of these plots and are presented in *Table 1*. Moreover, a ten-fold variation in the initial  $[Mn^{IV}]$  (0.02–0.20 mM) resulted in no change of the  $k_0$  values within experimental uncertainty ( $\pm 5\%$ ); this also confirmed a first-order  $[Mn^{IV}]$  decay.

$$- d[Mn^{IV}]/dt = 2 k_0[Mn^{IV}] \quad (2)$$

<sup>1)</sup> Recent data strongly suggest that OEC contains a cubane-like  $Mn_3CaO_4$  cluster linked to a fourth Mn by a mono- $\mu$ -oxo bridge; see [5].

Table 1. Some Representative First-Order Rate Constants at 25.0°.  $I = 1.0\text{M}$  ( $\text{NaNO}_3$ ),  $[\text{complex}] = 0.05\text{ mM}$ .

pH	$T_{\text{R}}/\text{mM}$	$10^4 k_0/\text{s}^{-1\text{a}}$	
2.00	2.50	0.55 (0.57)	
2.12		0.68 (0.65)	
2.30		0.85 (0.83)	
2.60		1.45 (1.46)	
2.90		2.63 (2.64)	
3.00		3.25 (3.23)	
3.20	1.00	5.00 (5.04) <sup>b)</sup>	
3.50		9.50 (9.53) <sup>b) c)</sup>	
2.60		0.55 (0.58)	
		2.00	1.07 (1.12)
		3.00	1.68 (1.75)
	3.50	2.00 (2.05)	
	5.00	2.83 (2.93)	
	10.00	5.70 (5.86)	

<sup>a)</sup> Calculated  $k_0$  values by using *Eqn. 9* are given in parentheses. <sup>b)</sup>  $10^4 k_0/\text{s}^{-1}$  values are 4.89 and 9.57 at pH 3.20 and 3.50, respectively, at  $I = 1.0\text{M}$  ( $\text{NaCl}$ ). <sup>c)</sup>  $10^4 k_0/\text{s}^{-1}$  values are 3.25 and 6.31 at  $I = 0.2$  and  $0.5\text{M}$  ( $\text{NaNO}_3$ ), respectively.

Reactions studied in the presence of added biguanide (0.05–0.2 mM) had no effect on the observed rate constants. No polymer was formed when the reactions were carried out in the presence of 6% (v/v) acrylonitrile.

At a fixed  $[\text{H}^+]$ ,  $k_0$  vs.  $T_{\text{R}}$  ( $= [\text{N}_2\text{H}_4] + [\text{N}_2\text{H}_5^+]$ ) plots were straight lines ( $r \geq 0.98$ ) passing through the origin (*Fig. 2*), and there was no indication at all of rate saturation even at the highest  $T_{\text{R}}$  (0.01M) studied.  $k_0$  Values were also found to increase significantly with the pH of the reaction media (*Table 1*). The rate/pH profile clearly indicated progressive generation of more-reactive species at higher pH, *e.g.*, in accord with the expected well-established superior reactivity of deprotonated hydrazine  $\text{N}_2\text{H}_4$  over  $\text{N}_2\text{H}_5^+$  as shown in *Eqns. 3* and *4* which lead to the rate law of *Eqn. 5*.



$$k_0(K_a + [\text{H}^+]) = 2 k_1 K_a T_{\text{R}} \quad (5)$$

However, the left-hand side of *Eqn. 5* is a function of increasing  $[\text{H}^+]$  that is not a demand of the rate law *Eqn. 5* at a particular  $T_{\text{R}}$ , and thus this scheme would not be a valid one. Moreover, the observed rate constants increased significantly with increasing ionic strength of the reaction media (maintained by  $\text{NaNO}_3$  or  $\text{NaClO}_4$ , *Table 1*), which does not correspond to a reaction of an uncharged species such as  $\text{N}_2\text{H}_4$ .

Another reaction scheme takes into account a higher reactivity of deprotonated  $\text{Mn}^{\text{IV}}$  complex **1** with  $\text{N}_2\text{H}_5^+$  as shown in *Eqns. 6–8*; this would lead to the observed kinetics assuming  $T_{\text{R}} \approx [\text{N}_2\text{H}_5^+]$  ( $\text{p}K_a$  of  $\text{N}_2\text{H}_5^+$  is 8.18 [12] at 25.0° and  $I = 1.0\text{M}$ ). Therein, the species  $\text{N}_2\text{H}_6^{2+}$  is not considered since the protonation constant for  $\text{N}_2\text{H}_5^+$  is

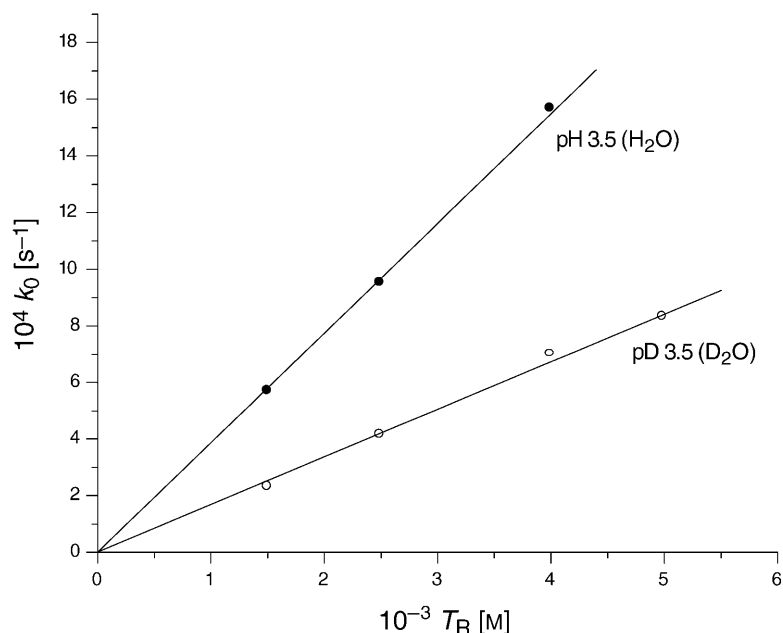
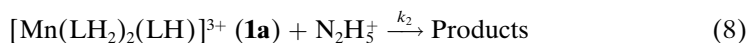
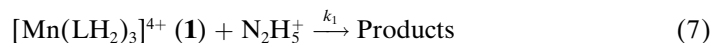
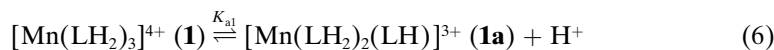


Fig. 2. Plot of  $k_0$  vs.  $T_R$ .  $T = 25.0^\circ$ ,  $I = 1.0\text{M}$  ( $\text{NaNO}_3$ ) and  $[\text{complex}] = 0.05\text{ mM}$  for all experiments; Set  $\circ$ : pH 3.5 ( $\text{H}_2\text{O}$ ),  $T_R = (1.50\text{--}4.00)\text{ mM}$ , pH 3.50; Set  $\bullet$ : pD 3.5 ( $\text{D}_2\text{O}$ );  $T_R = (1.50\text{--}5.00)\text{ mM}$ , pD 3.50,  $\text{D}_2\text{O} = 70\text{ mol-\%}$ .

small ( $K = 1.72$ ) [13], and it is much expected that the doubly protonated species  $\text{N}_2\text{H}_6^{2+}$  will not be reactive even if present in considerable concentration [13][14]. The derived rate law for this scheme is Eqn. 9.



$$k_0([\text{H}^+] + K_{a1})/T_R = 2(k_1[\text{H}^+] + k_2K_{a1}) \quad (9)$$

The left-hand side of Eqn. 9 vs.  $[\text{H}^+]$  produced a good straight line (Fig. 3,  $r \geq 0.99$ ), the slope and intercept yielding  $2k_1 = (1.10 \pm 0.06) \cdot 10^{-2}\text{ M}^{-1}\text{ s}^{-1}$  and  $2k_2 = (22.8 \pm 1.5)\text{ M}^{-1}\text{ s}^{-1}$  (Table 2). These rate constants reproduced the observed  $k_0$  values satisfactorily (Table 1) supporting the proposed scheme given by Eqns. 6–8. Rate enhancement with increasing media ionic strength also qualitatively fitted in with the proposed cation, redox, though it is extremely unusual that a deprotonated oxidant such as  $\mathbf{1a}$  reacts quicker (2000 times) than its protonated conjugate acid  $\mathbf{1}$ .

*Mechanism.* We could not collect any spectral or kinetic evidence for adduct formation between the redox partners in this study. Yet, a purely outer-sphere

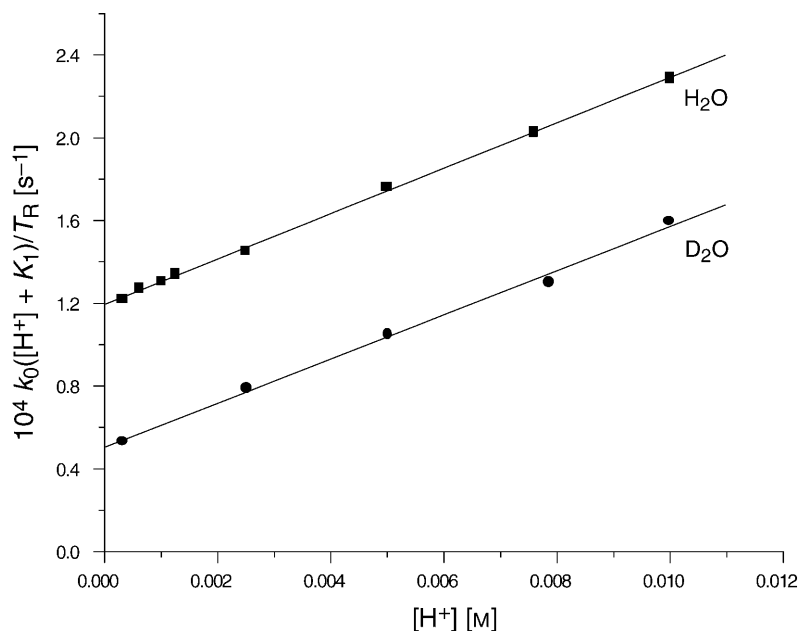


Fig. 3. Plot of left-hand-side of Eqn. 9 vs.  $[H^+]$ .  $T=25.0^\circ$ ,  $I=1.0\text{M}$  ( $\text{NaNO}_3$ ) and  $[\text{complex}]=0.05\text{ mM}$  for all experiments; Set  $\blacksquare$ :  $\text{H}_2\text{O}$   $T_R=2.50\text{ mM}$ ,  $\text{pH } 2.00-3.50$ ; Set  $\bullet$ :  $\text{D}_2\text{O}$ ,  $T_R$  2.50 mM,  $\text{pD } 2.00-3.50$ ,  $\text{D}_2\text{O}=70\text{ mol-\%}$ .

Table 2. Second-Order Rate Constants  $[\text{M}^{-1}\text{ s}^{-1}]^a$  for the Oxidation of Hydrazine by the  $\text{Mn}^{\text{IV}}$  Complex **1** at  $25.0^\circ$ .  $I=1.0\text{M}$  ( $\text{NaNO}_3$ ).

Reaction path	Rate constants <sup>a</sup> ) in $\text{H}_2\text{O}$	Rate constants <sup>a</sup> ) in 70 mol-% $\text{D}_2\text{O}$
$k_1$	$(1.10 \pm 0.06) \cdot 10^{-2}$	$(1.07 \pm 0.06) \cdot 10^{-2}$
$k_2$	$22.8 \pm 1.5$	$9.50 \pm 0.70$

<sup>a</sup>) These values are for the overall reaction and are therefore equal to  $2k$  where  $k$  is the rate constant for the reactions of Eqns. 10 and 11.

mechanism seems unlikely, as the reduction potential for the  $\text{N}_2\text{H}_5^+/\text{N}_2\text{H}_4^+$  ( $-1.17\text{ V}$ )<sup>2)</sup> is thermodynamically very unfavorable.

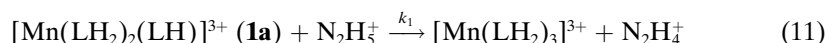
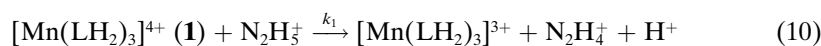
This highly unfavorable potential is the stumbling block for  $\text{N}_2\text{H}_5^+$  entering into an outer-sphere reaction, particularly when the oxidant is not so powerful, like the present  $\text{Mn}^{\text{IV}}$  oxidant [4]. Another barrier for an outer-sphere electron transfer is the small self-exchange rate ( $\leq 0.3\text{ M s}^{-1}$ ) [15] for the one-electron hydrazine redox couple. The octahedral  $\text{Mn}^{\text{IV}}$  coordinatively saturated by the strongly chelating biguanide suffers no ligand dissociation over the investigated pH range, as evidenced by the unchanged observed rate constants in the presence of added biguanide. Formation of a strong

2) The equilibrium constant ( $K = 1.3 \cdot 10^{-20}$ ) for the overall reaction  $\text{N}_2\text{H}_5^+ \rightleftharpoons \text{N}_2\text{H}_4^+ + \text{H}^+ + \text{e}$  which was obtained as a product of two equilibrium constants,  $K_a = 10^{-8.18}$  for the reaction [12],  $\text{N}_2\text{H}_5^+ \rightleftharpoons \text{N}_2\text{H}_4 + \text{H}^+$ , and  $K_1 = 2 \cdot 10^{-12}$  for  $\text{N}_2\text{H}_4 \rightleftharpoons \text{N}_2\text{H}_4^+ + \text{e}$ .

inner-sphere pre-equilibrium adduct between  $\text{Mn}^{\text{IV}}$  and hydrazine is thus not a finite possibility for providing a subsequent low-energy path for electron transfer.

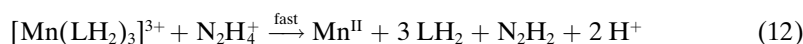
To search for the mechanism, we measured  $k_0$  values in media containing 70 mol-%  $\text{D}_2\text{O}$  (pD 2.0–3.5) and determined the second-order rate constants (*Fig. 3*) in the same way as done in  $\text{H}_2\text{O}$  (*Table 2*). This demonstrated a substantial kinetic isotope effect at higher pH as the  $k_1$  path remained unaffected in  $\text{D}_2\text{O}$ , whereas  $k_2$  was substantially lowered. Variation in rate resulting from replacement of the solvent  $\text{H}_2\text{O}$  by  $\text{D}_2\text{O}$  is expected to be slight for simple electron-transfer reactions. However, dramatic rate retardation is expected when electron transfer is coupled to the movement of a proton which is in equilibrium with solvent protons [16].

The observation clearly revealed the occurrence of a PCET in the  $k_2$  path only. It may be recalled here that the rate retardation in  $\text{D}_2\text{O}$  is also more pronounced at higher pH for oxidation of hydrazine [17] by multinuclear oxo-bridged higher-valent Mn and Fe complexes where the difference in basicities of the oxo bridges in the pH-dependent oxidant species played the key role. The  $\text{Mn}^{\text{IV}}$  complex **1** is devoid of any such oxo bridge but the deprotonated  $\text{sp}^2$  N-atoms<sup>3)</sup> of the ligand in the  $\text{Mn}^{\text{IV}}$  complex **1a** should have much more proton acceptance power than **1** because of one unit decrease in positive charge in **1a** compared to **1**. The rate-determining steps for the one-electron reaction may thus be presented by *Eqns. 10* and *11* where the  $k_2$  step is associated with a proton transfer to the biguanide ligand.



Unambiguous assignment of the mechanistic path for  $k_1$  is difficult. However, for both the pathways,  $k_1$  and  $k_2$ , a pre-equilibrium weak adduct formation through H-bonding involving NH or  $\text{NH}_2$  fragments of the biguanide ligand with the reducing agent or any kind of it aided by electrostriction [21][22] is possible. Such interactions were proposed for the reduction of this  $\text{Mn}^{\text{IV}}$  complex with  $\text{Fe}^{2+}$  [2][3],  $\text{In}^+$  [3], and  $\alpha$ -keto acids [4].

The absence of any polymeric product in the reactions perhaps indicates that radicals which are formed in the one-electron steps ( $k_1$  and  $k_2$ ) quickly react before escaping into bulk. We may thus be able to propose that the  $\text{Mn}^{\text{III}}$  produced in the reactions of *Eqns. 10* and *11* reacts very fast with the hydrazyl radical ( $\text{N}_2\text{H}_4^+$ ) and ultimately leads to the products,  $\text{Mn}^{\text{II}}$  and  $\text{N}_2$  (*Eqns. 12* and *13*).



<sup>3)</sup> The deprotonation sites in the (biguanide)manganese(IV) complex demands some discussion. Reports so far available [18] for complexes of metals in their usual valence states strongly suggest deprotonation from the NH moiety between the two C-atoms of biguanide, whereas kinetics of self-decomposition of  $[\text{Ag}(\text{enbbg})]^{3+}$  (enbbg = ethane-1,2-diylbis(biguanide)) [19] or of its biguanide analogue [20] were interpreted in terms of deprotonation from the formally  $\text{sp}^2$  N-atom (=NH) directly bonded to the high-valent metal center. Unusually high-valent  $\text{Mn}^{\text{IV}}$  oxidant may be another example in this class, though here also deprotonations from the remote NH group cannot be ruled out.

The radical species  $N_2H_4^+$  and the disproportionation reaction (*Eqn. 13*) are well-established facets of hydrazine chemistry [23]. Along with these fast steps, the high protonation constants [24] of the ligand,  $H_2L$ , drag the overall reaction to completion.

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### Experimental Part

**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], and its purity was checked by elemental (C, H, N) analysis as well as by spectral data. Stock solns. of hydrazinium nitrate were prepared by double decomposition of hydrazinium sulfate (G. R., *E. Merck*) with barium nitrate (G. R., *E. Merck*) and estimated by using a standard  $KIO_3$  soln. Such stock solns. were stable at least for a month when kept at *ca.* 10° and in the dark. Solns. of recrystallized  $NaNO_3$  or  $NaClO_4$  (both of G. R., *E. Merck*) were standardized by passing them through a *Dowex 50W-X8* cation-exchange resin (in the strong-acid form) and titrating the liberated acid with standard  $NaOH$  soln. to a phenolphthalein end point. Most of the measurements were made at 25.0° and  $I = 1.0M$  ( $NaNO_3$ ). All the kinetic experiments were done in  $H_2O$  which was deionized and then doubly distilled. A few kinetic runs were also performed in 70 mol-%  $D_2O$  medium.

**Physical Measurements and Kinetics.** All absorbance vs. time data were recorded with a *Shimadzu 1601-PC* spectrophotometer by 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 of complex **1**, in the electrically controlled thermostated ( $25 \pm 0.1$ )° cell housing (*CPS-240*). The soln. pH values (2.00–3.50) were adjusted with  $HNO_3$  or  $NaOH$  and were measured with the *Ag/AgCl* combined glass electrode of the *Metrohm 736-GP-Titrino* autotitrator; the electrode calibration was described earlier [4]. For reactions in  $D_2O$ , the pD was calculated as  $pD = pH_{measured} + 0.40$  [25]. No additional buffer was used in the kinetic experiments as during the reaction, pH drift was within a maximum of 0.05 units.

**Stoichiometry and Reaction Products.** Measurements were done in the pH range 2.0–3.5. Reaction mixtures containing 4–5 mol-equiv. of hydrazine over the complex **1** (at  $I = 2.0M$  ( $NaNO_3$ ) to speed up the reaction; *vide infra*) were allowed to react until completion. The hydrazine content in the spent solns. were determined colorimetrically at 458 nm, after developing a yellow color with 4-(dimethylamino)benzaldehyde (G. R., *E. Merck*; crystallized from alcohol) dissolved in a mixture of  $EtOH$  and conc.  $HCl$  soln. [26];  $Mn^{2+}$  and biguanide do not interfere in this determination. The gaseous product formed during the reaction was collected over a sat.  $NaCl$  soln. and analyzed by GC with a *Chemito(India)-GC-8610* apparatus equipped with *TCD*, a *Porapak Q* and molecular sieve *13X* column as described earlier [27]. The small volume of gas evolved in the kinetic runs had no effect on the measured absorbance, as verified from the unchanged absorbance on shaking the spectrophotometer cell. *Nessler's* reagent (alkaline potassium tetraiodomercurate(II)) was used to test qualitatively for ammonia as a product; the test can detect  $500 \mu g l^{-1}$  of  $NH_3$  [28]. Formation of  $HN_3$ , if any, as a gaseous product of the reaction was tested by using an aq.  $Fe(NO_3)_3$  soln. The ligand, biguanide ( $LH_2$ ), was quantitatively isolated as  $[Cu(LH_2)_2]SO_4$  from the product soln. by adding an ammonical  $CuSO_4$  soln. The amount of  $Cu^{II}$  thus complexed was determined iodometrically after decomposing the copper complex [29].

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