Inorg. Chem. **2004**, *43*, 1779–1783

Inorganic Chemistry
Article

Electron Transfer. 157. Reactions of Hypervalent Manganese Species with s^2 Metal-Ion Reductants[1]

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Received October 29, 2003

Solutions of the complexes of hypervalent manganese, $[Mn^{III}(C_2O_4)_3]^{3-}$ (in oxalate buffers), $[Mn^{IV}(bigH)_3]^{4+}$ (in biguanide buffers), and $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ (in bipyridyl buffers) may be reduced by s^2 center reductants In(I), Sn(II), and Ge(II), yielding Mn(II) quantitatively. In all cases, rates are determined by the initial act of electron transfer, giving an s^1 transient (In^{II}, Sn^{III}, or Ge^{III}); subsequent steps are rapid and kinetically silent. The In^{I}–Mn^{III} and Ge^{II}–Mn^{III} reactions are inhibited by added oxalate, whereas the Sn^{II}–($Mn^{III}Mn^{IV}$) reaction is strongly accelerated by Cl^-. The In^{I}–Mn^{IV} reaction is complicated by formation of a 1:1 addition compound $In^{I}\cdot Mn^{IV}$. We find no evidence for two-unit steps in any of these systems.

Introduction

The various functions assumed by manganese in biological systems[2] fall into two broad classes. In nonredox structural roles, such as the action of metallohydrolases, coordination to Mn(II) serves to hold an enzyme in a specific conformation necessary for its reactivity.[3] In contrast, redox transformations such as the catalyzed photolysis of water (photosystem II), or the catalyzed disproportionation of H_2O_2, feature changes in the oxidation state of catalytic manganese and require interconversions involving Mn(III), Mn(IV), di- or polynuclear Mn(III,IV) derivatives,[4a,b] and, possibly, a Mn(V) species.[4c]

Despite the importance of these intermediate states, relatively few mechanistic studies of their redox reactions have been described, particularly with $2e^-$ reductants. The recent availability of the s^2-ions, indium(I)[5] and germanium(II),[6] in workable concentrations allows us to examine reactions with soluble strongly reducing $2e^-$ reductants. A number of these conversions utilized, as buffers, oxalate (pH 3.7−5.3), biguanide (pH 2.0−3.8), or 2,2′-bipyridyl (pH 4.5−5.3), thus narrowing the pH gap between biorelated systems and the very acidic media most often used for Sn(II,IV), Ge(II,IV), and In(I,III) interconversions. We have also included some parallel experiments with Fe(II) for comparisons between this d^6 and our s^2 donors.

Experimental Section

Materials. The following reagents (Aldrich products) were used without further purification: manganese(II) sulfate monohydrate ($MnSO_4\cdot H_2O$), manganese acetate tetrahydrate ($Mn(OAc)_2\cdot 4H_2O$), potassium permanganate, 2,2′-dipyridyl, hydrogen peroxide (30% in water), sodium oxalate, oxalic acid, indium metal powder, germanium(IV) oxide, tin(II) chloride, iron(II) perchlorate ($Fe(ClO_4)_2\cdot xH_2O$), cyanoguanidine, $H_2N{-}C({=}NH){-}NH{-}CN$, and CF_3SO_3H (triflic acid). Solutions were prepared with Millipore-Q water and purged with pure argon to remove traces of O_2. Solutions of Ge(II) and In(I) were prepared and standardized as described.[5,6]

Potassium tris(oxalato)manganate(III), $K_3Mn(C_2O_4)_3\cdot 3H_2O$, was prepared from MnO(OH) as described by Chaudhuri[7,8] ($\epsilon_{516} = 230$ M^{-1} cm^{-1} in oxalate buffer, pH 5.3).

Biguanide sulfate, $H_2N{-}C({=}NH){-}NH{-}C({=}NH){-}NH_2\cdot H_2SO_4$, “$bigH\cdot H_2SO_4$”, was prepared by the ammoniation of cyanoguani-

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[1] Sponsorship of this work by the National Science Foundation (Grant CHE-0090865) is gratefully acknowledged.

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[3] Dismukes, G. C. *Chem. Rev.* **1996**, *96*, 2909.

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[7] Bhattacharjee, M. N.; Chaudhuri, M. K.; Purkayastha, R. N. D. *Inorg. Chem.* **1985**, *24*, 447. Results in this synthesis depended markedly on the mode of preparation of the MnO(OH) used. Material resulting from the procedure of Giovanoli[8a] gave excellent yields of the complex, whereas the hydroxide prepared by the method of Brauer[8b] gave a highly impure complex.

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10.1021/ic030307+ CCC: $27.50

Table 1. Stoichiometry of Reductions of Complexes of Hypervalent Manganese

oxidant (ox.)	reductant (red.)	conditions	λ, nm	[red.]/[ox.]
$[Mn^{III}(C_2O_4)_3]^{3-}$	Ge(II)	0.10 M oxalate buffer, pH 5.2	516	0.49 ± 0.01
	In(I)			0.48 ± 0.01
	Fe(II)			1.00 ± 0.04
$[Mn^{IV}(bigH)_3]^{4+}$	Ge(II)	0.3 M HCl + 0.7 M NaCl	437	1.06 ± 0.01
	Sn(II)			1.00 ± 0.04
	In(I)	0.3 M HCl		0.98 ± 0.06
	Fe(II)	2.5 M HCl		1.95 ± 0.05
$[(bipy)_2Mn^{III}(O)_2\text{-}Mn^{IV}(bipy)_2]^{3+}$	Ge(II)	0.01 M bipy buffer, pH 4.6	685	1.47 ± 0.03
	Sn(II)			1.54 ± 0.03
	In(I)			1.50 ± 0.03

dine[9] and converted to the free base by treatment with NaOH.[10] The water-stable manganese(IV) complex, $[Mn(bigH)_3]_2SO_4(NO_3)_6 \cdot 3H_2O$, was synthesized by the procedure of Banerjee.[11] The stock solution of the $[Mn^{IV}(bigH)_3]^{4+}$ complex was prepared in aqueous triflic acid at pH 1.0; λ_{max} 352 nm ($\epsilon = 9300\ M^{-1}\ cm^{-1}$), 435 nm ($8040\ M^{-1}\ cm^{-1}$).[12]

The mixed-valence $Mn^{III}Mn^{IV}$ complex, $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$, was prepared as its perchlorate salt as described by Cooper and Calvin[13] ($\epsilon_{685} = 560\ M^{-1}\ cm^{-1}$ in bipyridyl buffers). Note that this complex, and $Mn(C_2O_4)_3^{3-}$ as well, are stable only in solutions buffered by the respective chelating ligands.

Stoichiometric Studies. Stoichiometries of the redox reactions were carried out under argon with the oxidant in excess and were monitored at λ_{max} of the oxidant. Measured deficient quantities of each reductant were added to a known excess of oxidant, and absorbance decreases were compared to those resulting from addition of excess reductant. Decreases for the $Ge(II)-Mn(C_2O_4)_3^{3-}$ and $Sn(II)-Mn(C_2O_4)_3^{3-}$ systems were corrected for the slow self-decomposition of the oxidant. Results are summarized in Table 1.

Kinetic Studies. All reactions were carried out under argon. Rates were evaluated by measurements of absorbance decreases associated with the loss of hypervalent manganese, using a Durrum-Gibson stopped flow spectrophotometer interfaced with an OLIS computer system or a Shimadzu 1601 UV−vis spectrophotometer. Temperatures were 22.5 ± 0.5 °C. Ionic strength was maintained with $NaClO_4$. Concentrations were most often adjusted so that no more than 12% of the reagent in excess was consumed in a given run. Since stock solutions of $[Mn(C_2O_4)_3]^{3-}$ in oxalate buffer decompose slowly on standing, solutions of this oxidant were prepared fresh for each set of kinetic runs. Aside from the In(I) reductions of $[Mn^{IV}(bigH)_3]^{4+}$ at high $[Cl^-]$ (which yielded profiles with prominent zero-order components),[14] kinetic curves were exponential, and rate constants were calculated by nonlinear least-squares fitting to the relationship describing first-order decay.

Results

The close approach to 1:2 stoichiometry noted for the reactions of the s^2 cations with the Mn^{III} complex, to 1:1 stoichiometry found for the Mn^{IV} derivative, and to 3:2 determined for the $Mn^{III}Mn^{IV}$ species (Table 1) indicates that the predominant reduction product is Mn^{II} in each case:

$$Ge^{II} + 2Mn^{III} \rightarrow Ge^{IV} + 2Mn^{II} \tag{1}$$

$$Sn^{II} + Mn^{IV} \rightarrow Sn^{IV} + Mn^{II} \tag{2}$$

$$3In^{I} + 2Mn^{III}Mn^{IV} \rightarrow 3In^{III} + 4Mn^{II} \tag{3}$$

The observed uniphasic decay curves rule out the formation and loss of intermediate species on a time scale comparable to that of the primary reaction, in contrast to the $Mn^{III}Mn^{IV}$ reactions with organic reductants and with sulfite.[15] Note also that the use of biguanide, oxalate, and bipyridyl buffers extends the pH range over which s^2 reductants can be used without immediate precipitation of their hydroxides or the hydroxides of the reaction products.

Reductions of Mn(III) and Mn(III,IV). Kinetic data for the $In(I)-Mn(C_2O_4)_3^{3-}$ reaction in oxalate buffers appear in Table S-1 (Supporting Information). The reduction is first order in both redox partners and is inhibited by added oxalate, and, less steeply, by increases in acidity. Rates are correlated by expression 4. Refinement yields $k = (82 \pm 3)\ s^{-1}$ and $k' = (4.9 \pm 0.1) \times 10^{-3}\ M\ s^{-1}$. Calculated and observed rates are compared in the right-hand column of this table.

$$\text{rate} = -d[Mn^{III}]/dt = (k + k'/[H^+])\frac{[Mn^{III}][In^{I}]}{[C_2O_4{}^{2-}]} \tag{4}$$

The $Ge(II)-Mn(C_2O_4)_3^{3-}$ reaction (Table S-2) showed an even sharper inverse oxalate dependence. The rate law 4 features both 1/[ox] and $1/[ox]^2$ terms:

$$\text{rate} = -d[Mn^{III}]/dt = \frac{[Mn^{III}][Ge^{II}]}{[H^+]}\left(\frac{k_1}{[C_2O_4{}^{2-}]} + \frac{k_2}{[C_2O_4{}^{2-}]^2}\right) \tag{5}$$

Refinement yields $k_1 = (1.13 \pm 0.03) \times 10^{-5}\ M\ s^{-1}$ and $k_2 = (2.6 \pm 0.2) \times 10^{-7}\ M^2\ s^{-1}$. In contrast, Fe^{II} exhibited straightforward second-order behavior ($k_{Fe} = (9.7 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1}$). Only an upper limit ($3\ M^{-1}\ s^{-1}$ in 0.05 M oxalate buffer) was estimated for the slow Sn^{II} reduction, reflecting competition with the ongoing unimolecular decay of the oxidant under our reaction conditions.

The reductions of the mixed valence binuclear complex $[(bipy)_2Mn^{III}(O)_2Mn^{IV}(bipy)_2]^{3+}$ by In^{I} and Ge^{II} in 2,2′-bipyridyl buffers also obeyed simple monomial rate laws, with rate constants for these $3e^-$ transactions [$k_{In(I)} = (2.6 \pm 0.1) \times 10^5$, $k_{Ge(II)}$ $(2.5 \pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$] considerably greater than values for the $1e^-$ reduction of Mn^{III}. No distortions of decay cures, attributable to transformations of intervening states, are apparent.

Reductions by Sn(II) in aqueous chloride media should take into account the partition of this reductant into four ligation levels:[16]

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[9] Karpides, D.; Fernelius, W. C.; Joeston, M. D. *Inorg. Synth.* **1963**, *IX*, 56.

[10] Holter, S. N.; Fernelius, W. C.; Meek, D. *Inorg. Synth.* **1963**, *IX*, 58.

[11] Das, G.; Bharadwaj, P. K.; Ghosh, D.; Chaudhuri, B.; Banerjee, R. *Chem. Commun.* **2001**, 323.

[12] When this solution was made basic, both peaks diminished reversibly, and a new maximum appeared at 395 nm. Variation, with $[H^+]$, of the ratio Abs_{352}/Abs_{395} allowed an estimate of a pK_A 8.3.

[13] Cooper, S. R.; Calvin, M. *J. Am. Chem. Soc.* **1977**, *99*, 6623.

[14] Further study of these kinetically more complex systems is in progress.

[15] Ghosh, M. C.; Reed, J. W.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1994**, *33*, 73.

[16] Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1976; Vol. 4, pp 10, 109.

$$Sn^{2+} + Cl^- \rightleftharpoons SnCl^+ \; (K_1 = 12) \tag{6}$$

$$Sn^{2+} + 2Cl^- \rightleftharpoons SnCl_2(aq) \; (K_2 = 53) \tag{7}$$

$$Sn^{2+} + 3Cl^- \rightleftharpoons SnCl_3^- \; (K_3 = 32) \tag{8}$$

Rates for Sn^{II}−Mn(III,IV) (Table S-3) conform to expression 9 in which the denominator reflects the partial conversions of Sn(II) into chloro complexes.

$$k_{obs} = \frac{[Sn^{II}](k_0 + k_1K_1[Cl^-] + k_2K_2[Cl^-]^2)}{1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3} \tag{9}$$

The numerator indicates partition of the reaction into contributing paths. Refinements of data in terms of eq 9 yield rate constants for these paths: $k_0 = (6.5 \pm 0.2) \times 10^2$ M^{-1} s^{-1}, $k_1 = (6 \pm 2) \times 10^2$ M^{-1} s^{-1}, and $k_2 = (1.10 \pm 0.07) \times 10^4$ M^{-1} s^{-1}. The relatively high uncertainty associated with k_1 suggests that the monochloro path is marginal.

Reductions of $Mn(bigH)_3^{4+}$ Complex. The reaction of this Mn(IV) cation with In(I) in 0.10 M $HClO_4$ is slow (k_2 = 0.30 M^{-1} s^{-1}) but is accelerated markedly by chloride. The kinetic picture in Cl^--containing media at low pH is complicated by mixed order profiles and is treated in a separate contribution.

Reproducible In(I)−Mn(IV) data (Table S-4A) were obtained in biguanide buffers. Rates are subject to kinetic saturation and conform to a rate law (eq 10).

$$k_{obs} = \frac{-d[Mn^{IV}]/dt}{[Mn^{IV}]} = \frac{k_{lim}K[In^I]}{1 + K[In^I]} \tag{10}$$

Refinement in terms of eq 10 yields $k_{lim} = (0.148 \pm 0.007)$ s^{-1} (a limiting value at high $[In^I]/[Mn^{IV}]$ ratios) and an association constant, $K = (6.5 \pm 0.8) \times 10^3$ M^{-1}, pertaining to a 1:1 complex formed by the redox partners.

The Ge(II)−$Mn^{IV}(bigH)_3^{4+}$ reaction, examined in a similar buffer (Table S-4B), exhibits no evidence of kinetic saturation involving the metal centers. It is, however, modestly sensitive to acidity; a 70-fold increase in $[H^+]$ retards the reaction by half. In this case, rates are correlated by eq 11:

$$rate = [Ge^{II}][Mn^{IV}](k + k'[H^+]^{-1}) \tag{11}$$

Refinement yields $k = (5.9 \pm 0.2) \times 10^2$ M^{-1} s^{-1} and $k' = (0.11 \pm 0.01)$ s^{-1}. Rates are independent of [buffer] within the range 0.03−0.15 M.

The Fe(II)−$Mn^{IV}(bigH)_3^{4+}$ reaction in 1 M H^+ is imperceptibly slow in the absence of chloride but, like the In(I)−Mn(IV) couple, is strikingly accelerated by this anion. Kinetic data for the catalyzed conversion (Table S-5) are satisfactorily reproducible and generate the binomial rate law (eq 12):

$$rate = -d[Mn^{IV}]/dt = [Fe^{II}][Mn^{IV}](k_1[Cl^-] + k_2[Cl^-]^2) \tag{12}$$

Refinement yields $k_1 = 17.1 \pm 0.7$ M^{-2} s^{-1} and $k_2 = 17.8 \pm 0.5$ M^{-3} s^{-1}.[16]

Rate laws and kinetic parameters for all systems are summarized in Table 2.

Discussion

The oxidation of an s^2 center ($s^2 \rightarrow s^0$) by $Mn(C_2O_4)_3^{3-}$ must occur by a pair of single electron transfers to successive Mn(III) units. The kinetic profiles for the In(I)−$Mn(C_2O_4)_3^{3-}$ and the Ge(II)−$Mn(C_2O_4)_3^{3-}$ reactions show no rapid change immediately after mixing, nor are there departures from exponential curves pointing to the growth and decay of an s^1 intermediate. We then conclude that, in both conversions, the initial transfer is rate-determining and that the follow-up step is much more rapid, hence kinetically silent. Such sequences, e.g., eqs 13−14, are in accord with those previously assigned to oxidations of s^2 ions by Co(III) and Fe(III) species[5,6] and remind us that the s^1 intermediate in such cases is much more strongly reducing than its s^2 parent.[18]

$$Mn^{III} + Ge^{II} \rightarrow Mn^{II} + Ge^{III} \text{ (slow)} \tag{13}$$

$$Mn^{III} + Ge^{III} \rightarrow Mn^{II} + Ge^{IV} \text{ (rapid)} \tag{14}$$

The very high rate for the Fe(II)−$Mn(C_2O_4)_3^{3-}$ reaction (10^5 M^{-1} s^{-1}) suggests (although it does not prove) the employment of an inner-sphere route involving an oxalato bridge, and an analogous path is reasonable for the initial step in the In^I−Mn^{III} couple since In^+, alone among the s^2 centers, has been shown to utilize oxalato-bridging in redox.[5] The much slower reductions by Ge^{II} and Sn^{II}, the latter marginally detectable, reflect the recognized[19] reluctance of these centers to utilize inner-sphere routes for single electron transactions.

The $[oxalate]^{-1}$ proportionality observed for the In^I reduction (rate law 4) denotes an activated complex formed from the principal redox couple with one unit of oxalate removed. Although kinetics does not tell us whether this is lost from $[Mn(C_2O_4)_3]^{3-}$ or an In^I−$C_2O_4^{2-}$ complex, it most probably arises from the oxidant, for loss of a negative fragment most generally enhances the effectiveness of an oxidant but mutes the effectiveness of the reductant. Measurements by Taube[20] yield the dissociation quotient 1.4 × 10^{-3} M for eq 15.

$$[Mn^{III}(C_2O_4)_3]^{3-} \rightleftarrows [Mn^{III}(C_2O_4)_2]^- + C_2O_4^{2-} \qquad K = 1.4 \times 10^{-3} \; (\mu = 2.0 \text{ M}) \tag{15}$$

The ratio k_4/K_{15} (where k_4 pertains to the predominant path contributing to rate law 4) gives an estimated bimolecular constant 6 × 10^4 M^1s^{-1} for the reduction of the bis-chelated oxidant by the predominant In(I) species (its aqua ion or an oxalate complex) in this solution. Analogous interpretation

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(17) Attempted kinetic examination of the Sn(II)−$Mn^{IV}(biguanide)_3^{4+}$ reactions in biguanide buffer was frustrated by the precipitation of SnO_2. Although the 1:1 stoichiometry of this reaction was established in HCl solution (Table 1), decay curves taken in the latter medium have not yet been disentangled.

(18) (a) Schwarz, H. A.; Comstock, D.; Yandell, J. K.; Dodson, H. W. *J. Phys. Chem.* **1974**, *78*, 488. (b) Al-Ajlouni, A. M.; Gould, E. S. *Res. Chem. Intermed.* **1998**, *24*, 843.

(19) Babich, O. A.; Gould, E. S. *Inorg. Chem. Acta* **2002**, *336*, 80.

(20) Taube, H. *J. Am. Chem. Soc.* **1948**, *70*, 3928.

Table 2. Rate Laws and Kinetic Parameters for the Reductions of Mn(III), Mn(IV), and Mn(III,IV) Species with Metal Reducing Centers[a]

oxidant	reductant	rate law	eq	params
$[Mn^{III}(C_2O_4)_3]^{3-}$	In(I)[b]	$(k + k'/[H^+])\dfrac{[Mn^{III}][In^I]}{[C_2O_4^{\ 2-}]}$	4	$k = (82 \pm 3)\ s^{-1}$ $k' = (4.9 \pm 0.1) \times 10^{-3}\ M\ s^{-1}$
	Ge(II)[b]	$\dfrac{[Mn^{III}][Ge^{II}]}{[H^+]}\left(\dfrac{k_1}{[C_2O_4^{\ 2-}]} + \dfrac{k_2}{[C_2O_4^{\ 2-}]^2}\right)$	5	$k_1 = (1.13 \pm 0.03) \times 10^{-5}\ M\ s^{-1}$ $k_2 = (2.6 \pm 0.2) \times 10^{-7}\ M^2\ s^{-1}$
	Fe(II)[b]	$k[Mn^{III}][Fe^{II}]$		$k = (9.7 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1}$
$[Mn^{IV}(bigH)_3]^{4+}$	Ge(II)[c]	$[Mn^{IV}][Ge^{II}](k + k'[H^+]^{-1})$	11	$k = (5.9 \pm 0.2) \times 10^2\ M^{-1}\ s^{-1}$ $k' = 0.11 \pm 0.01\ s^{-1}$
	Fe(II)[d]	$[Mn^{IV}][Fe^{II}](k_1[Cl^-] + k_2[Cl^-]^{2-})$	12	$k_1 = 17.1 \pm 0.7\ M^{-2}\ s^{-1}$ $k_2 = 17.8 \pm 0.5\ M^{-3}\ s^{-1}$
	In(I)[e]	$\dfrac{[Mn^{IV}]k_{lim}K[In^I]}{1 + K[In^I]}$	10	$k_{lim} = 0.148 \pm 0.007\ s^{-1}$ $K = (6.5 \pm 0.8) \times 10^3\ M^{-1}$
$[(bipy)_2Mn^{III}(O)_2\text{-}Mn^{IV}(bipy)_2]^{3+}$	Ge(II)[f]	$k[Mn^{III,IV}][red]$		$k = (2.5 \pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$
	In(I)[f]			$k = (2.6 \pm 0.1) \times 10^5\ M^{-1}\ s^{-1}$
	Sn(II)[f]	$\dfrac{[Mn^{III,IV}][Sn^{II}](k_0 + k_1K_1[Cl^-]) + k_2K_2[Cl^-]^2}{1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3}$	9	$k_0 = (6.5 \pm 0.2) \times 10^2\ M^{-1}\ s^{-1}$ $k_1 = (6 \pm 2) \times 10^2\ M^{-1}\ s^{-1}$ $k_2 = (1.10 \pm 0.07)10^4\ M^{-1}\ s^{-1}$ $K_1 = 12; K_2 = 52.5; K_3 = 32$[g]

[a] Reactions carried out at 22.5 ± 0.5 °C. [b] Oxalate buffers, pH 3.6−5.1, $\mu = 0.20$ M. [c] Reactions in biguanide buffers, pH 1.98−3.82, $\mu = 0.20$ M. [d] Reactions in 1.0 M H^+; $\mu = 2.0$ (Cl^-/ClO_4^-). [e] Biguanide buffers, pH 3.2; $\mu = 0.60$ M. [f] Reactions in bipyridyl buffers; [buffer] = 0.010−0.015 M; pH 4.5−5.3; $\mu = 0.10-0.15$ M. [g] Reference 16.

of the minor k' path in eq 4 awaits knowledge of the pK_A value of the principal reductant.

The $[oxalate]^{-2}$-proportional term in eq 5, pertaining to the $Ge(II)-Mn(C_2O_4)_3^{3-}$ reaction, indicates that a second site also subject to oxalato inhibition has come into play. This very probably lies at the Ge(II) center, for this small dipositive cation would be expected to bind oxalate more effectively than the larger unicharged In(I) donor.

The reduction of $[Mn^{IV}(bigH)_3]^{4+}$ to Mn(II) and the oxidation of an s^2 center to s^0 are both net $2e^-$ transactions. Nevertheless, it is extremely unlikely that the Mn^{IV} reductions at hand proceed in a single step. Outer-sphere two-unit transfers must be considered to be unusually slow (mirroring a prohibitive Franck−Condon barrier).[21] Moreover, our Mn^{IV} oxidant is devoid of groups (oxo or halo) that can support a two unit bridged transfer.

We are thus dealing with sequences of single electron transfers, e.g., eqs 16−19, in which only the initial act is reflected in the rate law(s):

$$Mn^{IV} + Ge^{II} \rightarrow Mn^{III} + Ge^{III}\ \text{(rate determining)} \quad (16)$$

$$Mn^{III} + Ge^{III} \rightarrow Mn^{II} + Ge^{IV}\ \text{(rapid)} \quad (17)$$

$$Mn^{IV} + Ge^{III} \rightarrow Mn^{III} + Ge^{IV}\ \text{(rapid)} \quad (18)$$

$$Mn^{III} + Ge^{II} \rightarrow Mn^{II} + Ge^{III}\ \text{(rapid)} \quad (19)$$

Our experiments give no information as to the relative importance of the rapid steps 17, 18, and 19 despite the relatively low rate found here for the $Mn^{III}-Ge^{II}$ reaction 5 in oxalate buffer.

The two-term rate law, eq 11, for the $Ge^{II}-[Mn^{IV}(bigH)_3]^{4+}$ reaction points to the operation of two initiation paths. If the inverse-$[H^+]$ term is taken to reflect action of the deprotonated reductant $[Ge^{II}OH]^+$, the ratio k'/K_A $(0.11/10^{-3})$[16,22] yields an estimated bimolecular value near $10^2\ M^{-1}\ s^{-1}$ for this component.

Among the redox systems considered, only the $In^I-[Mn^{IV}(bigH)_3]^{4+}$ reaction is subject to kinetic saturation, i.e., an approach to a limiting rate ($k_{lim} = 0.15\ s^{-1}$) at high concentrations of the reductant. The resulting rate law (eq 10) points to formation of a 1:1 complex ($Mn^{IV}{\cdot}In^I$) with the redox rate proportional to the concentration of this adduct. The association constant ($K = 6 \times 10^3$) of this complex, resulting from data refinement, is unexpectedly great for two positively charged components, but we are not dealing with “bare” ions. The oxidant, and probably the reductant as well, are wrapped in sheaths featuring outer-NH fragments that allow associative interionic hydrogen bonding. This picture is in accord with the relatively low rate for redox, suggesting that interaction of the 5s electrons of In^I with an outside coreagent is disfavored by this shielding.

The notable feature of the $Fe^{II}-[Mn^{IV}(bigH)_3]^{4+}$ reaction is its sensitivity to added chloride. Examined here in 1.0 M H^+, it exhibits kinetic terms proportional to $[Cl^-]$ and $[Cl^-]^2$. This effect cannot be attributed to partial conversion of the oxidant to a more reactive chloro complex ($Cl^- + Mn^{IV}(bigH) \rightleftarrows Mn^{IV}-Cl + bigH$), since the Cl^--enhancement is not reversed by addition of external biguanide. Involvement of an $Fe^{2+}(Cl^-)$ complex is equally unlikely in view of its very low stability constant (0.35 M).[23] We suspect that we are instead seeing another example of a medium effect in which redox reactions of positive metal centers are accelerated by polarizable anions,[24] but we are astonished at the magnitude in this case.

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(21) Lappin, A. G. *Redox Mechanisms in Inorganic Chemistry*; Ellis Harwood: New York, 1994; Chapter 3.

(22) Ge(II) is assumed to be about 0.5 pK units more acidic than Sn^{2+}(aq).

(23) Moodley, K. G.; Nicol, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 933.

The binuclear mixed valence cation, $[(bipy)_2Mn^{IV}(O)_2Mn^{III}(bipy)_2]^{3+}$, which has been taken as a simple model of the manganese-containing reactive center in photosystem II,[25] is reduced by our s^2 centers to 2 Mn^{II}, a net $3e^-$ change. As with $[Mn^{IV}(bigH)_3]^{4+}$, the structure of the oxidant rules out both (2e + 1e) and (1e + 2e) paths. Once again we are dealing with single electron sequences, in accord with the multistep routes proposed to accommodate the complex profiles observed for the reductions of the same $Mn^{III}Mn^{IV}$ cation by HSO_3^- and by hydroquinone.[15] In the present case, rate determination by the initial step results in much simpler curves but yields much less information. As in most earlier series,[26] reductions by In^I are, in the absence of complicating effects, at least 10^2 times as rapid as those by the weaker reductant, Ge^{II}.

The striking catalysis by chloride of the $Sn^{II}-(Mn^{III}Mn^{IV})$ reduction (eq 9) resembles similar accelerations of reactions of Sn(II) with Co(III) species[27] and with the le^- oxidant nitrosodisulfonate.[26a] In each instance, attachment of additional chloro ligand(s) to the reductant makes the Sn^{II} center more like the le^- oxidation intermediate (presumably $SnCl_2^+$), and the resulting structural similarity would be expected to lower the Franck−Condon barrier to the initial electron transfer act.

Conclusions

The nine redox systems summarized in Table 2 present us with no fewer than seven different rate laws. This array (reflecting, in part, differing speciation behavior of the reductants and differences in reaction media) should not obscure the connecting thread in this narrative. Despite variations in detail, each hypervalent Mn oxidant is reduced cleanly to Mn(II). In all cases, rates are determined by the initial step, and intervening states are not observed. In acidic media, our manganese species thus behave unlike hypervalent chromium[28] and vanadium,[29] both of which may be reduced in discernible steps under favorable conditions.

Acknowledgment. We are grateful to Dr. James Espenson for valuable discussions and to Mrs. Arla Dee McPherson for technical assistance.

Supporting Information Available: Tabulated kinetic data for the following redox reactions: (S-l) $Mn^{III}(C_2O_4)_3^{3-}$ + In(I); (S-2) $Mn^{III}(C_2O_4)_3^{3-}$ + Ge(II); (S-3) $[(bipy)_2Mn^{III}\text{-}(O)_2Mn^{IV}(bipy)_2]^{3+}$ + Sn(II); (S-4A) $[Mn^{IV}(bigH)_3]^{4+}$ + In(I); (S-4B) $[Mn^{IV}(bigH)_3]^{4+}$ + Ge(II); (S-5) $[Mn^{IV}(bigH)_3]^{4+}$ + Fe(II). This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) See, for example: (a) Carlyle, D. W.; Espenson, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 599. (b) Przystas, T. J.; Sutin, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 5545.

(25) (a) See, for example: Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153. (b) Carrell and co-workers[4a] have presented detailed evidence against the applicability of this and related Mn(III)Mn(IV) cations as satisfactory models for the reactive center in photosytem II.

(26) See, for example: (a) Yang, Z.; Gould, E. S. *J. Chem. Soc., Dalton Trans.* **2003**, 2219. (b) Yang, Z.; Gould, E. S. *Res. Chem. Intermed.* **2003**, *29*, 181.

(27) Wetton, E. A. M.; Higginson, W. C. E. *J. Chem. Soc.* **1965**, 5890.

(28) Babich, O. A.; Gould, E. S. *Inorg. Chem.* **2001**, *40*, 5708.

(29) Yang, E.; Gould, E. S. *J. Chem. Soc., Dalton Trans.* **2003**, 3963.