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Kinetics of Manganese(III) Acetate in Acetic Acid: Generation of Mn(III) with Co(III), Ce(IV), and Dibromide Radicals; Reactions of Mn(III) with Mn(II), Co(II), Hydrogen Bromide, and Alkali Bromides

Xiang-Dong Jiao and James H. Espenson*

Ames Laboratory and Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50011

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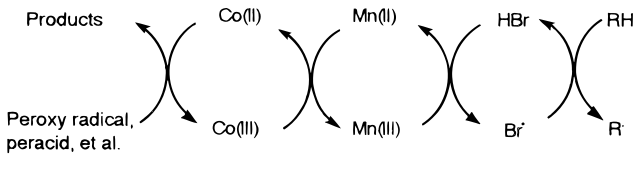
The reaction of cobalt(III) acetate with excess manganese(II) acetate in acetic acid occurs in two stages, since the two forms Co(IIIc) and Co(IIIs) are not rapidly equilibrated and thus react independently. The rate constants at 24.5 °C are $k_c = 37.1 \pm 0.6$ L mol^{-1} s^{-1} and $k_s = 6.8 \pm 0.2$ L mol^{-1} s^{-1} at 24.5 °C in glacial acetic acid. The Mn(III) produced forms a dinuclear complex with the excess of Mn(II). This was studied independently and is characterized by the rate constant $(3.43 \pm 0.01) \times 10^2$ L mol^{-1} s^{-1} at 24.5 °C. A similar interaction between Mn(III) and Co(II) is substantially slower, with $k = (3.73 \pm 0.05) \times 10^{-1}$ L mol^{-1} s^{-1} at 24.5 °C. Mn(II) is also oxidized by Ce(IV), according to the rate law $-d[\text{Ce(IV)}]/dt = k[\text{Mn(II)}]^2[\text{Ce(IV)}]$, where $k = (6.0 \pm 0.2) \times 10^4$ L^2 mol^{-2} s^{-1}. The reaction between Mn(II) and $HBr_2^\bullet$, believed to be involved in the mechanism by which Mn(III) oxidizes HBr, was studied by laser photolysis; the rate constant is $(1.48 \pm 0.04) \times 10^8$ L mol^{-1} s^{-1} at ∼23 °C in HOAc. Oxidation of Co(II) by $HBr_2^\bullet$ has the rate constant $(3.0 \pm 0.1) \times 10^7$ L mol^{-1} s^{-1}. The oxidation of HBr by Mn(III) is second order with respect to [HBr]; $k = (4.10 \pm 0.08) \times 10^5$ L^2 mol^{-2} s^{-1} at 4.5 °C in 10% aqueous HOAc. Similar reactions with alkali metal bromides were studied; their rate constants are 17−23 times smaller. This noncomplementary reaction is believed to follow that rate law so that $HBr_2^\bullet$ and not $Br^\bullet$ (higher in Gibbs energy by 0.3 V) can serve as the intermediate. The analysis of the reaction steps then requires that the oxidation of $HBr_2^\bullet$ to Br_2 by Mn(III) be diffusion controlled, which is consistent with the driving force and seemingly minor reorganization.

Introduction

The oxidation of *p*-xylene to terephthalic acid, and of other methylarenes to their aromatic carboxylic acids, thrives as a large-scale industrial process because of efficient catalysis by cobalt(II) and manganese(II) acetates and hydrobromic acid or other bromide sources.[1,2] Either metal will function alone, but great rate accelerations are realized when both metals are used in the presence of HBr. Manganese is oxidized to Mn(III) by Co(III), whereupon Mn(III) oxidizes the bromide ion to a species that reacts with the methylarene.[3] This might be $Br^\bullet$, $Br_2^{\bullet-}$, or an M(III)−Br complex that mimics the reactivity of a bromine atom. The resultant is a chain reaction with a rate that far exceeds the rate of Co(III) generation in the system.[4,5] The literature in this field is extensive and has recently been reviewed.[1] The chemical steps of the overall process are shown in the following diagram:



Despite investigations of Co/Mn/Br catalysts for the autoxidation of methylarenes,[6−9] the exact roles of the species leading to the synergistic effects have not been fully defined. In this study, we report experimental studies of the kinetics and mechanisms of the reactions between these pairs: Mn(II) with Co(III), $Br_2^{\bullet-}$, and Ce(IV); Mn(III) with HBr (and alkali bromides), Mn(II), and Co(II).

Experimental Section

The following reagents were used as obtained commercially without further purification: manganese(II) acetate, cobalt(II) acetate tetrahydrate, cerium(IV) perchlorate, hydrobromic acid (48%), glacial acetic acid, alkali metal bromides, and bromine.

Solutions of cobalt(III) acetate in glacial acetic acid were prepared from $Co(OAc)_2{\cdot}4H_2O$ with a stream of ozone (80%:20% O_3:O_2) through the solution for 30−50 min.[10] Two molecular forms of Co(III) are known to be formed in comparable amounts from ozonation: Co(IIIs) and Co(IIIc). The structural formulas suggested for these species are shown in Chart 1. The reaction undoubtedly forms Co(IIIa) as well, but its lifetime is too short for it to remain in the cobalt(III) solutions.[11] This point is key to the interpretation of our data, as taken up in the next section.[10,12] The excess ozone was purged from the solution with

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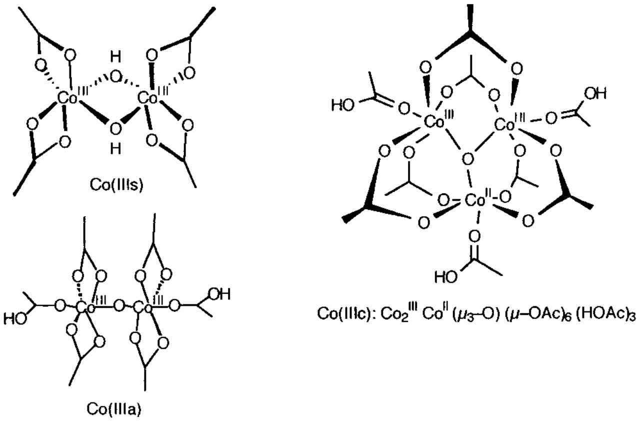
Chart 1



a stream of argon saturated with acetic acid. Solutions of manganese(III) acetate were prepared by oxidation of manganese(II) acetate with a deficiency of cerium(IV) perchlorate in acetic acid.

Reactions were followed spectrophotometrically. A Shimadzu UV-3101PC or Shimadzu Multispec-1501 instrument was used for conventional reactions, and a BioSequential DX-17MW stopped-flow instrument was used for more rapid ones. Certain reactions of $Br_2^{\bullet -}$ (more likely $HBr_2^{\bullet}$; note that HBr is a weak acid, $pK_a = 6.7$ in acetic acid[13]) were studied directly by laser flash photolysis using an Applied Photophysics laser kinetic spectrometer. In this case, the radical of interest was obtained by photolysis of solutions containing Br_3^- (more likely, HBr_3), HBr, and Br_2 at 355 nm. The procedure used for studies in aqueous solutions was followed here.[14] The reaction was monitored at 365 nm; in aqueous solution, $Br_2^{\bullet -}$ has λ_{max} at 360 nm (ϵ 9.9 × 10^4 L mol^{-1} cm^{-1}).[15]

Electrochemical measurements were performed using a BAS-100 electrochemical analyzer. A three-electrode system was used, consisting of a platinum disk working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The reference electrode was separated from the bulk of the solution by a fritted-glass bridge of low porosity which contained the solvent and supporting electrolyte. Measurements were carried out at room temperature in $HOAc-H_2O$ (95:5, v/v) using 0.1 M KNO_3 or 0.1 M $[Bun_4N]BF_4$ as the supporting electrolyte. The half-wave potentials for the oxidation of $Mn(OAc)_2 \cdot 4H_2O$ and NaBr were determined by cyclic voltammetry (CV) (at a scan rate of 30−100 mV/s) or by differential pulse voltammetry (scan rate 5 mV/s). Both methods gave identical results. In the case of Co(OAc)2·4H2O, the Co(III)/Co(II) electrode reaction could not be seen with CV, possibly due to electron transfer being too slow relative to the CV time scale. However, differential pulse voltammetry, which operates on a slower time scale, resulted in a distinctive peak which we assigned to the Co(III)/Co(II) couple.

Results

Oxidation of Manganese(II) by Cobalt(III). The final absorbance of Co(III) attained in each reaction was recorded at 610 nm, a maximum wavelength of Co(III) (ϵ 3.93 × 10^2 L mol^{-1} cm^{-1}); this value is applicable to Co(III) prepared by ozonation.[16] The results, depicted in Figure 1, establish that the end point occurs at a 2:1 ratio of manganese(II) to cobalt(III). In keeping with that, the net reaction can be written as

$$2Mn(II) + Co(III) = Mn(III) \cdot Mn(II) + Co(II) \quad (1)$$

The mixed-valent manganese product in this equation has also been indicated in earlier work.[17] We return to this point later and present direct evidence for the existence of Mn(III)·Mn(II). Clearly, however, Mn(III)·Mn(II) is an inactive form. It is not oxidized by Co(III) or (later) by Ce(IV).

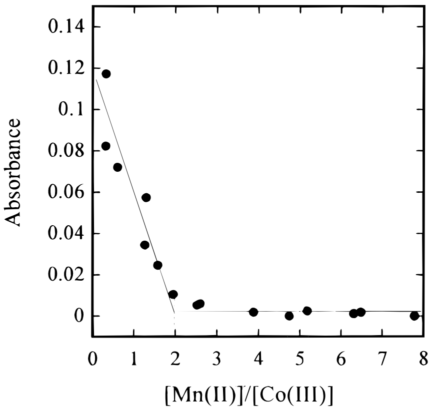


Figure 1. Absorbance at 610 nm after completion of the Mn(II)−Co(III) reaction in acetic acid. Concentration ranges: 0.1−5 mM Mn(II), 0.3−0.6 mM Co(III). Data were taken in a cuvette with a 1 cm optical path; ϵ(Co(III)) = 3.93 × 10^2 L mol^{-1} cm^{-1} at 610 nm.

Kinetics data for the reaction between cobalt(III) and manganese(II) acetates in glacial acetic acid were obtained at 610 nm. A typical experiment is shown in Figure S-1, Supporting Information. In these experiments $[Mn(II)] \gg [Co(III)]$; the ranges of concentrations were 4.5−21 mM Mn(II) and 0.17−1.7 mM Co(III). The concentration of the excess reagent was nearly constant during any experiment. Despite that, a simple kinetics equation was not followed. Instead, the data in each experiment were accurately fit by the biexponential expression

$$Abs_t = Abs_\infty + A_s e^{-k^s_\psi t} + A_c e^{-k^c_\psi t} \quad (2)$$

in terms of the amplitudes of each stage of the absorbance change (A_s, A_c) and the rate constants of the two components. The two terms represent the independent reactions of the species Co(IIIs) and Co(IIIc). This treatment of two parallel reactions is consistent with data in the literature, compiled and interpreted by Jones, who showed that some previously eccentric kinetic patterns could be explained simply in terms of the coexistence of this pair of nonequilibrating Co(III) species.[18] For further analysis of the data, the average concentration of Mn(II) was used, not the initial value, because the excess was not too large; thus $[Mn(II)]_{av} = [Mn(II)]_0 - [Co(III)]_0/2$. Each of the pseudo-first-order rate constants from eq 2 is directly proportional to the concentration of manganese(II); plots of k_ψ against $[Mn(II)]_{av}$ are presented in Figure 2. The slopes of the two lines relate to the reactions

$$Co(IIIc) + Mn(II) \rightarrow Co(II) + Mn(III) \qquad k_c \quad (3)$$

$$Co(IIIs) + Mn(II) \rightarrow Co(II) + Mn(III) \qquad k_s \quad (4)$$

This scheme implies that each Co(III) species reacts independently with manganese(II), the rate equation being

$$\frac{d[Mn(III)]}{dt} = \{k_c[Co(IIIc)] + k_s[Co(IIIs)]\}[Mn(II)] \quad (5)$$

The values of the rate constants are $k_c = 37.1 \pm 0.6$ L mol^{-1} s^{-1} and $k_s = 6.8 \pm 0.2$ L mol^{-1} s^{-1} at 24.5 °C in glacial acetic

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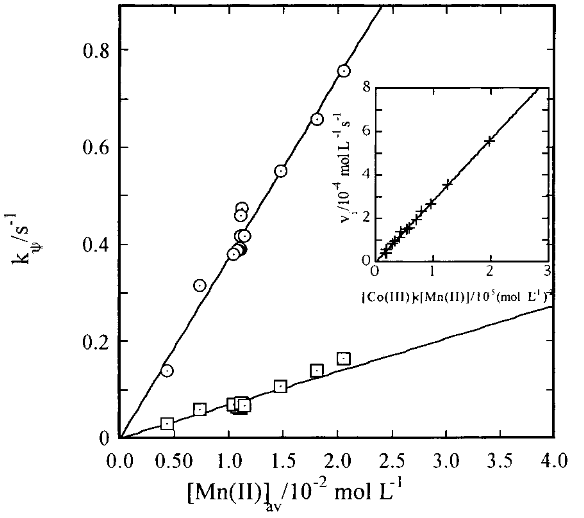

Figure 2. Kinetic data for the reaction of Co(III) with Mn(II) in glacial acetic acid at 24.5 °C, showing the variation of each of the pseudo-first-order rate constants (k_ψ^c, circles; k_ψ^s, squares) determined by biexponential curve fitting with the average concentration of manganese(II) during the experiment. The initial reaction rate is directly proportional to [Co(III)] at constant [Mn(II)], and vice versa; the inset shows that the variation of the initial rate with the product of the initial concentrations is a straight line through the origin.

acid. From the amplitudes determined in each experiment from the fits to eq 2, the proportion of the two cobalt(III) complexes can be determined. These fractions were determined from 13 kinetic experiments, each conducted in triplicate. From these, $f_c = 0.69 \pm 0.05$ and $f_s = 0.31 \pm 0.05$. An assumption made in this calculation is that both Co(IIIs) and Co(IIIc) have the same molar absorptivity per mole of Co(III) at 610 nm. Further, the assignment of the faster component to Co(IIIc) was made on the basis of Jones' data.[8,18]

It proved worthwhile to analyze the kinetic data by a second method, to confirm independently the model embodied in eqs 3−5. The absorbances in each experiment were converted to concentrations of cobalt(III). The concentration−time data were then analyzed by the method of initial rates. The decrease in [Co(III)] with time can be expressed as a polynomial:

$$C_t = C_0 - a_1 t - a_2 t^2 - a_3 t^3 - ... \qquad (6)$$

Least-squares fitting affords the parameter values, the one of interest being a_1, which is equal to v_i, the total initial rate of Co(III) disappearance. Figure 2 (inset) displays the linear plot of v_i against the product of the initial concentrations, $[Co(III)]_0[Mn(II)]_0$. The slope of this line is $k_w = 28.2 \pm 0.2$ L mol^{-1} s^{-1}. This apparent rate constant from the initial-rate method is the concentration-weighted sum of k_s and k_c. From the parameter values given above, the expected value is $k_w = 0.69 \times 37.2 + 0.31 \times 6.8 = 27.8$ L mol^{-1} s^{-1}. The agreement between the two methods supports the reaction scheme.

No effect on the reaction rate was noted when Co(II) (1.1 mM) or NaOAc (2.2 mM) was added. A modest decrease in the value of k_c was caused by the addition of NaCl, ~15% at 1.5 mM to ~38% at 5.9 mM. In the same experiments, k_s was unaffected by NaCl.

Reactions of Mn(III) with Mn(II) and Co(II). To complete the net reaction in eq 1, a reaction between Mn(III) and Mn(II), more rapid than those in eqs 3 and 4, must take place. A rapid interaction occurs between Mn(III), used as $Mn(OAc)_3 \cdot 2H_2O$, and Mn(II), corresponding to

$$Mn(III) + Mn(II) \rightarrow Mn(III) \cdot Mn(II) \qquad (7)$$

The stopped-flow technique was used for kinetic studies with Mn(II) in large excess over Mn(III). Data were collected for product buildup at 405 nm. (A typical experiment is shown in Figure S-2, Supporting Information). The reaction followed first-order kinetics, and the plot of k_ψ against $[Mn(II)]_{av}$ was a straight line through the origin (Figure S-3, Supporting Information). The second-order rate constant in acetic acid is $k_7 = (3.43 \pm 0.01) \times 10^2$ L mol^{-1} s^{-1} at 24.5 °C.

The overall reaction represented in eq 1 comprises reactions 3 and 4 in parallel. To account for the net shoichiometry, however, it is necessary to postulate that reaction 7 follows thereafter. The rate constants independently evaluated for these three reactions can be used to show that, under the conditions used, reaction 7 proceeds rapidly enough so as not to interfere with the kinetic studies of reactions 3 and 4.

Having found reaction 7, a process that inevitably involves acetate bridges between the two Mn centers, it was only logical to ask whether a similar reaction would occur between Mn(III) and Co(II). This reaction does occur, leading to substantial changes in the UV−visible spectrum (Figure S-4a,b). It is, however, ca. 10^3-times slower than reaction 7. The kinetic analysis (Figure S-5, Supporting Information) gives $k_8 = (3.73 \pm 0.05) \times 10^{-1}$ L mol^{-1} s^{-1} at 24.5 °C in acetic acid for this reaction:

$$Mn(III) + Co(II) \rightarrow Mn(III) \cdot Co(II) \qquad (8)$$

Oxidation of Manganese(II) by Cerium(IV). A brief study of this reaction was conducted to confirm that this oxidation occurred more rapidly than the reaction between cerium(IV) and HBr. The manganese oxidation (data in Figures S-8 and S-9, Supporting Information) follows the rate law

$$\frac{d[Mn(III)]}{dt} = k_9[Ce(IV)][Mn(II)]^2 \qquad (9)$$

with $k_9 = (6.0 \pm 0.2) \times 10^4$ L^2 mol^{-2} s^{-1} at 4.5 °C in 10% aqueous acetic acid.

Reactions of Mn(II) and Co(II) with $HBr_2^\bullet$. In light of the possible intermediacy of this radical, experiments were carried out in glacial acetic acid at ~23 °C to establish the kinetics of its oxidation of these divalent metal acetates. The radical was formed by photodissociation:

$$HBr_3 \xrightarrow{h\nu} Br^\bullet + HBr_2^\bullet; \qquad Br^\bullet + HBr \rightarrow HBr_2^\bullet \qquad (10)$$

The solution contained $Mn(OAc)_2$, HBr, and Br_2 in glacial acetic acid. Radical formation occurred in the time of the 355 nm laser flash (~10 ns), accompanied by the buildup of the absorbance from the bromine-containing free radical. Aqueous $Br_2^{\bullet -}$ has λ_{max} 360 nm (ϵ 9.9×10^4 L mol^{-1} cm^{-1}). A similar spectrum was assumed in acetic acid. The subsequent reaction for the loss of $HBr_2^\bullet$ was essentially that of oxidation, eq 11; radical disproportionation, eq 12, accounted for a negligible component

$$M(II) + HBr_2^\bullet + HOAc \rightarrow M(III) + 2HBr + OAc^- \qquad (M = Mn, Co) \quad (11)$$

$$2HBr_2^\bullet \rightarrow Br_2 + 2HBr \qquad (12)$$

under these conditions. The loss of $HBr_2^\bullet$ was monitored at 365 nm; the value of the molar absorptivity does not enter the analysis of the kinetic data because the reaction followed first-order kinetics. The plots of k_ψ against the concentration of $M(OAc)_2$ (M = Mn, Co) were linear, as shown in Figure S-6 (Supporting Information) confirming an overall second-order rate law. The rate constants are as follows: Mn, $k_{11,Mn} = (1.48 \pm 0.04) \times 10^8$ L mol^{-1} s^{-1}; Co, $k_{11,Co} = (3.0 \pm 0.1) \times 10^7$ L mol^{-1} s^{-1}.

Reactions of Monomeric Manganese(III) with Bromides. The following points must be noted at the outset. First, as commented upon earlier, hydrogen bromide is a weak acid[19,20] in acetic acid; the pK_a of HBr is 6.7[13] in this solvent of low dielectric constant (6.18). The alkali metal bromides in acetic acid are ionized only to a minor extent; the pK_d values are 6.1 for Li, 6.9 for Na, and 6.96 for K in glacial acetic acid at 30 °C.[21] Our interpretation is based on the assumption that ions are not the predominant forms, even in 10% aqueous acetic acid. Second, the aggregation of two or more manganese atoms into polymetallic species takes some time, inferentially because the constructions of acetate bridges in reaction 7 and others like it are not instantaneous. A newly formed and presumably monomeric Mn(III) was needed for these studies, so that the results would have direct bearing on the reactivity of low-concentration and short-lived Mn(III) intermediates in industrial practice. Thus, commercial "$Mn(OAc)_3$" was avoided, as were any aged solutions of Mn(III). We have taken advantage of the rapid oxidation of Mn(II) with cerium(IV), described in the immediately preceding section, to prepare the solutions of manganese(III) used for the bromide oxidations. Third, these reactions were studied at 4.5 °C in 10% water−acetic acid (v/v). The low temperature was needed to lower the rate; the addition of water, to prevent freezing. The dielectric constant of the mixed solvent is 13,[22] much closer to the dielectric constant of anhydrous acetic acid, 6.18, than that of water, 78.3. We therefore presume that HBr exists primarily in the molecular form.

The rapidity of the bromide reactions required that the stopped-flow technique be used. Manganese(II) acetate and HBr or MBr were placed in one of the reservoirs; cerium(IV) was placed in the other. The Mn(II)−Ce(IV) reaction, described in the preceding section, was so rapid that it was complete before the process under study began. The reaction progress was monitored by recording the decrease in absorbance of Mn(III) at 461 nm (ϵ 50 L mol^{-1} cm^{-1}). In the case of HBr, the initial concentrations were 2.0 mM Mn(III) and 12−35 mM HBr. The data were fit to first-order kinetics. The variation of k_ψ with [HBr] is depicted in Figure 3, which shows the parabolic dependence on [HBr] and the linear dependence on [HBr]^2; the correlation coefficient is 0.991. This is the best single-parameter model that describes the data, and a more complex model is not warranted. Similar data, presented in Figure S-7 (Supporting Information), show that the same kinetic equations are followed by the alkali metal bromides. The rate law under these conditions can be written as

$$-\frac{d[\mathrm{Mn(III)}]}{dt} = k_{13}[\mathrm{Mn(III)}][\mathrm{HBr}]^2 \qquad (13)$$

with $k_{13} = (4.10 \pm 0.08) \times 10^5$ L^2 mol^{-2} s^{-1} at 4.5 °C. For the alkali metal halides, the analogous rate constants, with dimensions 10^4 L^2 mol^{-2} s^{-1}, are 1.78 ± 0.08 (LiBr), 1.86 ± 0.06 (NaBr), and 2.45 ± 0.09 (KBr). The alkali metal halides all react with nearly the same rate constant and are some 20 times less reactive than HBr. At the completion of the reaction, bromine was clearly evident in the reaction. (See Table 2.)

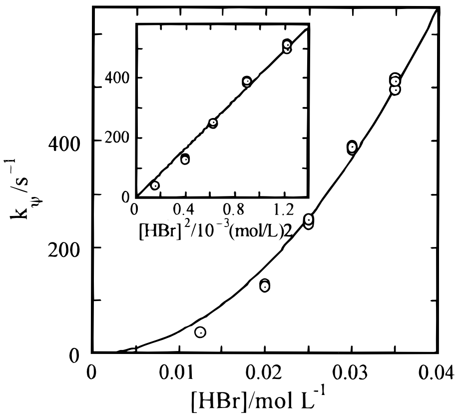

Figure 3. Rate constants for the oxidation of excess HBr by mononuclear Mn(III) in acetic acid with 10 vol % water at 4.5 °C, showing that the pseudo-first-order rate constant shows a second-order dependence on [HBr], as in eq 13.

The functional dependences on [HBr]^2 and [MBr]^2 suggest that the dibromide radical anion (or, as explained previously, its protonated analogue $HBr_2^\bullet$) may be an intermediate in the oxidation. This mechanism avoids the higher-energy $Br^\bullet$; in aqueous solution, atomic bromine is 0.3 V higher in Gibbs energy than $Br_2^{\bullet-}$. These comments are made in advance of a full consideration of the scheme but in recognition that Mn(III) is limited to single-electron reactions.

Inhibiting Effect of Manganese(II) on the Mn(III)−HBr and −MBr Reactions. The reductions in rate upon addition of manganous acetate to the reaction were quite pronounced. This effect was traced to the coordination of bromide and Mn(II), sharply reducing the concentration of free HBr. Again assuming that ionic species are disfavored, species such as Mn(OAc)Br and $MnBr_2$, each solvated, can be used to account for this effect. Their analogues are well-known for cobalt; coordination of Co(II) and LiBr has been studied by electrochemical and spectrophotometric techniques.[23] The Co(II) complexes with ≥2 bromides are tetrahedral, with strong, long-wavelength absorptions. Given that the bromomanganese(II) complexes do not perceptibly absorb visible light, the spectra of $Co(OAc)_2$−LiBr solutions were recorded without and with added $Mn(OAc)_2$. The formation constants of the bromomanganese(II) complexes were determined from the multiwavelength absorbance data by use of the program PSEQUAD;[24] known parameters for the bromocobalt complexes were fixed in this determination. The results are log $\beta_1 = 3.84$, log $\beta_2 \leq 6.3$, and log $\beta_3 = 9.4$. The stepwise formation constants thus fall in the order $K_1 > K_3 > K_2$. The same order was found for Co(II)−bromide coordination.[23]

Standard Reduction Potentials. Values of $E_{1/2}$ were determined[25] in glacial acetic acid for Co(III)/Co(II), Mn(III)/Mn(II), and Br_2/Br^- couples. The results are given in Table 1, along with aqueous values[26,27] for purposes of comparison. Other work

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Table 1. Standard Electrode Potentials (V) in Acetic Acid and Aqueous Solutions vs NHE

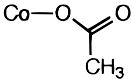
couple	$E_{1/2}$(HOAc)[a]	$E°(H_2O)$
$Br_2(l)/2Br^-$	1.07	1.06[b]
Mn(III)/Mn(II)	1.77	∼1.5[b]
Co(III)/Co(II)	2.0	1.8[b]
$Br_2/Br_2^{\bullet -}$		0.4_6[c]
$Br_2^{\bullet -}/2Br^-$	(1.9_4)[d]	1.6_6[c] (1.62)[e]
$Br^{\bullet}/Br^-$		∼2 (1.92)[e]

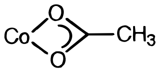
[a] Reference 25; values determined vs SCE were converted to NHE by the addition of 0.22 V. [b] Reference 27. [c] Reference 26. [d] Deduced from kinetics data for opposing reactions; see text. [e] Reference 37.

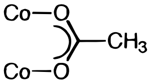
in 10% aqueoius HOAc has been reported, giving for Mn(III)/Mn(II) $E° = 1.04$ V.[22,28]

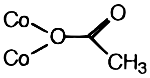
Discussion

Metal acetates in acetic acid adopt complex structures owing to the different modes of coordination of acetate ions and acetic acid.[29] Chart 1 depicts the suggested structural formulas for the two forms of cobalt(III) encountered in this work. In addition, several other forms include the "active" species Co(IIIa) (likely a (μ-oxo)dicobalt complex)[18,30] as well as tri-,[31−33] tetra-, and octacobalt[34,35] forms. In these species, it is possible to recognize several modes of acetate coordination (these structural formulas ignore the roles of OH, OH_2, and HOAc in many compounds):









For the most part, the different molecular forms do not equilibrate rapidly among themselves, not only because of the intrinsic inertness of cobalt(III) toward ligand substitution but also because of the activation energy needed for ligand reconfiguration.

Manganese(III) structures have been less well studied. When $Mn(OAc)_3{\cdot}2H_2O$ was dehydrated, crystals of anhydrous manganese(III) acetate were obtained, with the formula $[Mn_3O(OAc)_6(HOAc)(OAc)]_n$. The three metal atoms form an oxo-centered equilateral triangle connected by three pairs of acetate bridges; such units are further linked by acetic acid and acetate ion bridges;[36] cf. Co(IIIc) in Chart 1. Some structural complexity of $Mn(OAc)_3{\cdot}2H_2O$ in acetic acid is suggested by the kinetic studies of the reactions between commercial $Mn(OAc)_3{\cdot}2H_2O$ and M(II) acetates. Indeed, the occurrence of these interactions in itself suggests that (at least) dinuclear species can be formed.

We decided for two reasons not to use these manganese(III) acetate solutions further. First, the structure of the solution species is complex and its structure is not known. Second, a monomeric manganese(III) species can be first-formed from Co(III). The Mn(III) intermediate in the oxidation of *p*-xylene to terephthalic acid will be the same; it is so reactive that oligomerization seems unlikely. Thus we turned for the balance of the studies to Mn(III) prepared in situ with Ce(IV) and used immediately by a second reagent already present, such as HBr.

The principal matter to discuss is the mechanism by which Mn(III) oxidizes HBr and alkali bromides. A combination such as this has been termed noncomplementary, often but not necessarily meaning that an uncommon or metastable oxidation state of one element or the other intervenes in the reaction scheme. In this system, such an entity would be zerovalent bromine. The second-order dependence of the rate on the HBr concentration provides a key piece of evidence, from which we argue that the intermediate is $HBr_2^{\bullet}$, not $Br^{\bullet}$. The thermodynamics of the activation process, from the reduction potentials in Table 1, shows why that is further plausible. The lack of the radical potentials in acetic acid precludes a numerical estimate of $\Delta G°$ for $Mn(III) + HBr \rightarrow Mn(II) + Br^{\bullet}$. In water, at least, >0.3 V separates the potentials of $Br_2^{\bullet -}$ and $Br^{\bullet}$.[26,37] The higher-potential bromine atom would be difficult if not impossible to form with Mn(III).[28] Previously, others concluded that $Br^{\bullet}$ formation from Mn(III) and Br^- is thermodynamically favorable. In other words, we further argue that $HBr_2^{\bullet}$ results directly, not from the reaction between HBr and $Br^{\bullet}$. On the basis of the kinetics and thermochemical data, we suggest this happens by way of reductive elimination of dibromide from an unstable dibromomanganese(III) species:

$$Mn(OAc)_3 + 2HBr \rightarrow 2HOAc + Mn^{III}(OAc)Br_2 \rightarrow Mn^{II}(OAc)_2 + HBr_2^{\bullet} \quad (14)$$

The overall process in eq 14 is nearly thermoneutral, $\Delta G_{14}°$ being −0.1 V in H_2O (Table 1) and perhaps[38] +0.1 V in HOAc. The point may, however, be moot, in that the rate constants have been determined for both directions of this reaction (see eqs 11 and 13), and from their quotient, given that $k_{11} = k_{-14}$ and $k_{14} = k_{13}/2$, we have $K_{14} = k_{14}/k_{11} = 1.4 \times 10^{-3}$ and $\Delta G_{14}° = -0.1_7$ V.

The fate of the dibromide radical may be any of these: to oxidize Mn(II) back to Mn(III) by the reverse of eq 14, to disproportionate (eq 12), or to *reduce* Mn(III):

$$Mn(OAc)_3 + HBr_2^{\bullet} \rightarrow Mn(OAc)_2 + HOAc + Br_2 \quad (15)$$

The third option is certainly correct. Were Mn(II) principally reoxidized, no net reaction would have been noted. Were $HBr_2^{\bullet}$ lost by disproportionation, reaction 11 would not have been seen and the rate law in eq 13 would not hold. As to the plausibility of reaction 15 itself, one must first examine the rate law expected if reactions 14 and 15 occur in sequence. The equation is

$$-\frac{d[Mn(III)]}{dt} = \frac{k_{14}k_{15}[Mn(III)]^2[HBr]^2}{k_{-14}[Mn(II)] + k_{15}[Mn(III)]} \quad (16)$$

For conformity to the experimental rate equation, eq 13, it is required that

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(38) One sees in Table 1 that the $E°$ values for the metallic reagents become more positive than those in water, whereas $E°$ of the $Br_2/2Br^-$ couple does not change at all. The metallic species are entirely changed in coordination shell and structure, whereas the bromine compounds differ only in secondary solvation. One can surmise that the bromine radical couples have about the same $E°$ values in acetic acid as they do in water, but such determinations have not been reported.

Table 2. Summary of Reactions and Rate Constants in Acetic Acid and Aqueous Acetic Acid

reaction	rate const[a]	T, °C	solvent
$2Mn(II) + Co(III) = Mn(III){\cdot}Mn(II) + Co(II)$ $-d[Mn(III)]/dt = k[Mn(II)][Co(III)]$	Co(IIIc): 37.1 Co(IIIs): 6.8	24.5	HOAc
$Mn(III) + Mn(II) \rightarrow Mn(III){\cdot}Mn(II)$	343	24.5	HOAc
$Mn(III) + Co(II) \rightarrow Mn(III){\cdot}Co(II)$	0.373	24.5	HOAc
$2Mn(II) + Ce(IV) \rightarrow Mn(III){\cdot}Mn(II) + Ce(III)$ $-d[Ce(IV)]/dt = k[Mn(II)]^2[Ce(IV)]$	6.0×10^4	4.5	10% aq HOAc
$Mn(II) + HBr_2^{\bullet} \rightarrow Mn(III) + 2HBr$	1.48×10^8	~23	HOAc
$Co(II) + HBr_2^{\bullet} \rightarrow Co(III) + 2HBr$	3.0×10^7	~23	HOAc
$Mn(III) + 2HBr \rightarrow Mn(II) + {}^1/_2Br_2$ $-d[Mn(III)/]/dt = k[Mn(III)][HBr]^2$	4.10×10^5	4.5	10% aq HOAc
$Mn(III) + 2MBr \rightarrow Mn(II) + {}^1/_2Br_2$ $-d[Mn(III)/]/dt = k[Mn(III)][MBr]^2$	1.78×10^4 (Li) 1.86×10^4 (Na) 2.45×10^4 (K)	4.5	10% aq HOAc

[a] With concentration expressed as mol L^{-1} and time as s.

$$k_{15}[Mn(III)] \gg k_{-14}[Mn(II)] \qquad (17)$$

Is this plausible? At the midpoint of any kinetics experiment, the two oxidation states are present at equal concentrations. In effect, then, this asks for a comparison between k_{-14} (a measured value, 1.5×10^8 L mol^{-1} s^{-1}) and k_{15}. Now reaction 15 occurs with a much greater driving force, $\Delta G_{15}° \sim +1$ V. Furthermore, the changes in molecular structure in reaction 15 appear to be minimal, in that a Br−Br bond already exists and Mn−Br coordination appears unnecessary. Thus, contributions from inner-shell reorganization appear to be minimal. For these reasons, it does appear logical to suggest that the value of k_{15} is near the diffusion-controlled limit, which then provides a consistent interpretation.

The oxidation of Mn(II) with Ce(IV) proceeds according to the rate law in eq 9. In keeping with this, the following reaction scheme can be suggested:

$$Mn^{II} + Ce^{IV} \rightleftarrows \{Mn{\cdot}Ce\} \quad (k_1, k_{-1}) \qquad (18a)$$

$$\{Mn{\cdot}Ce\} + Mn^{II} \rightarrow Ce^{III} + \{Mn^{II}{\cdot}Mn^{III}\} \quad (k_2) \qquad (18b)$$

The chemical sense of the proposed mechanism features the intermingling of electron-transfer and acetate-bridging events. The form of the general steady-state rate equation is

$$-\frac{d[Ce(IV)]}{dt} = \frac{k_1k_2[Ce(IV)][Mn(II)]^2}{k_{-1} + k_2[Mn(II)]} \qquad (19)$$

in the limit in which the first step is slower than the second, that is, when the second step is rate controlling. In this event, $k_{-1} \gg k_2[Mn(II)]$, and the reaction rate in the limit is given by

$$-\frac{d[Ce(IV)]}{dt} = \frac{k_1k_2}{k_{-1}}[Ce(IV)][Mn(II)]^2 \qquad (20)$$

This rate equation is in agreement with the experimental form. This formulation parallels that in eq 16, which represents the rate equation for the two steps for Br$^-$ oxidation by Mn(III), eqs 14 and 15. The experimental rate law requires the first oxidation step for Br$^-$ to be rate controlling but the second step for Ce(IV) to be so. The relative rates of the two stages in eq 18 are reasonable, in view of the more extensive molecular rearrangements that appear to be required by bridging acetates in the second reaction.

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Supporting Information Available: Plots for the analysis of kinetic data and for the evaluation of numerical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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