Equilibrium and Kinetics Studies of Reactions of Manganese Acetate, Cobalt Acetate, and Bromide Salts in Acetic Acid Solutions

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The oxidation of hydrogen bromide and alkali metal bromide salts to bromine in acetic acid by cobalt(III) acetate has been studied. The oxidation is inhibited by $Mn(OAc)_2$ and $Co(OAc)_2$, which lower the bromide concentration through complexation. Stability constants for $Co^{II}Br_n$ were redetermined in acetic acid containing 0.1% water as a function of temperature. This amount of water lowers the stability constant values as compared to glacial acetic acid. $Mn^{II}Br_n$ complexes were identified by UV−visible spectroscopy, and the stability constants for $Mn^{II}Br_n$ were determined by electrochemical methods. The kinetics of HBr oxidation shows that there is a new pathway in the presence of $M^{II}Br_n$. Analysis of the concentration dependences shows that $CoBr_2$ and $MnBr_2$ are the principal and perhaps sole forms of the divalent metals that react with Co(III) and Mn(III). The interpretation of these data is in terms of this step (M, N = Mn or Co): $M(OAc)_3 + N^{II}Br_2 + HOAc \rightarrow M(OAc)_2 + N^{III}Br_2OAc$. The second-order rate constants (L mol^{-1} s^{-1}) for different M, N pairs in glacial acetic acid are 4.8 (Co, Co at 40 °C), 0.96 (Mn, Co at 20 °C), 0.15 (Mn(III)•Co(II), Co at 20 °C), and 0.07 (Mn, Mn at 20 °C). Following that, reductive elimination of the dibromide radical is proposed to occur: $N^{III}Br_2OAc + HOAc \rightarrow N(OAc)_2 + HBr_2^{\bullet}$. This finding implicates the dibromide radical as a key intermediate in this chemistry, and indeed in the cobalt−bromide catalyzed autoxidation of methylarenes, for which some form of zerovalent bromine has been identified. The selectivity for $CoBr_2$ and $MnBr_2$ is consistent with a pathway that forms this radical rather than bromine atoms which are at a considerably higher Gibbs energy. $Mn(OAc)_3$ oxidizes $PhCH_2Br$, $k = 1.3$ L mol^{-1} s^{-1} at 50.0 °C in HOAc.

Introduction

A complex set of equilibrium and kinetics steps governs the reactions between cobalt, manganese, and bromide in acetic acid solutions.[1−6] Interest in these issues derives from the success of the cobalt−manganese−bromide system in catalyzing the autoxidation of methylarenes.[3,6,7] In this report, the oxidation of HBr to bromine by cobalt(III) and manganese(III) in acetic acid, especially the decelerating role of cobalt(II), is reported. Also, data for the coordination equilibria for bromocobalt(II) complexes have now been extended to conditions other than those originally employed.[8]

The industial oxidation of *p*-xylene to terephthalic acid using cobalt(II) and bromide as cocatalysts is carried out with the stoichiometric cobalt concentration equal to that of bromide, which has been suggested to mean that the monobromide, CoBrOAc, is the most active form.[9−13] The rate constant for the reduction of Co(III) in Co(II)/NaBr/*p*-xylene solutions was found to be approximately proportional to the total bromide concentration when $[NaBr]_{tot}$ is nearly equal to [CoBrOAc].[14] We have undertaken a study of the reactions between cobalt(III) and cobalt(II) in the presence of bromide to determine rate constants for the different bromocobalt(II) species present. We find that $CoBr_2$ is the principal and likely sole reactant for Co(III), suggesting a key role for the dibromide radical anion, $Br_2^{\bullet-}$, in the catalytic cycle. The effect of Co(II) on the Mn(III)−HBr reaction gives concordant results, providing further proof for the previously implied involvement of $Br_2^{\bullet-}$.[1]

Experimental Section

Reagents. Certain compounds were obtained commercially, including cobalt(II) acetate tetrahydrate, manganese(II) acetate (anhydrous), cerium(IV) perchlorate as a solution in 6 M perchloric acid, hydrobromic acid (48% aqueous solution), lithium and sodium bromides, *p*-xylene, benzyl bromide and several of its derivatives, and glacial acetic acid. Manganese(III) acetate was used both as the oxo-centered trinuclear commercial material[15] and as the mononuclear form prepared in situ by oxidation of $Mn(OAc)_2$ with cerium(IV).[1]

Cobalt(III) was prepared by bubbling ozone into a solution of cobalt(II) acetate. This converts the pink Co(II) by way of the metastable apple-green species Co(IIIa) to the olive-green forms Co(IIIc) and Co(IIIs) in a 69:31 ratio. Suggested structures are shown in Chart 1.[1,16−20] Other solutions of Co(III) were prepared by Zakharov's method, which

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(1) Jiao, X.-D.; Espenson, J. H. *Inorg. Chem.* **2000**, *39*, 1549.
(2) Metelski, P. D.; Adamian, V. A.; Espenson, J. H. *Inorg. Chem.* **2000**, *39*, 2434.
(3) Partenheimer, W. *Catal. Today* **1995**, *23*, 69.
(4) Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry*, 3rd ed.; VCH Publishers: New York, 1997; p 393.
(5) Kamiya, Y. *Tetrahedron* **1966**, *22*, 2029.
(6) Partenheimer, W.; Gipe, R. K. *ACS Symp. Ser.* **1993**, *523*, 81−88.
(7) Walling, C. *J. Am. Chem. Soc.* **1969**, *91*, 7590.
(8) Sawada, K.; Tanaka, M. *J. Inorg. Nucl. Chem* **1977**, *39*, 339.
(9) Hay, A. S.; Blanchard, H. S. *Can. J. Chem.* **1965**, *43*, 1306.
(10) Kamiya, Y.; Nakajima, T.; Sakoda, K. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2211.
(11) Kamiya, Y. *J. Catal.* **1974**, *33*, 480.
(12) Zakharov, I. V.; Kumpan, Y. V. *Kinet. Catal.* **1993**, *34*, 922−927.
(13) Partenheimer, W. In *Catalysis of Organic Reactions*; Blackburn, D. W., Ed.; Marcel Dekker: New York, 1990; pp 321−345.
(14) Geletii, Y. V.; Zakharov, I. V.; Strizhak, P. E. *Kinet. Catal.* **1985**, *26*, 736−741.
(15) Hessel, L. W.; Romers, C. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 545.
(16) Lande, S. S.; Falk, C. D.; Kochi, J. K. *J. Inorg. Nucl. Chem* **1971**, *33*, 4101.
(17) Jones, G. H. *J. Chem. Res.* **1982**, 207.
(18) Babushkin, D. E.; Talsi, E. P. *J. Mol. Catal.* **1998**, *130*, 131.
(19) Blake, A. B.; Chipperfield, J. R.; Lau, S.; Webster, D. E. *J. Chem. Soc., Dalton Trans.* **1990**, 3719−3724.
(20) Chipperfield, J. R.; Lau, S.; Webster, D. E. *J. Mol. Catal.* **1992**, *75*, 123.

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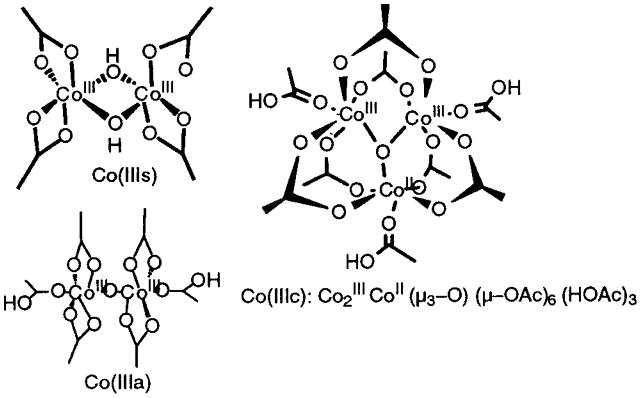
Chart 1



employs an in situ oxidation procedure based upon the oxidation of Co(II) by $ArCH_2OO^\bullet$.[14] In it, oxygen is introduced into a solution of $Co(OAc)_2$, *p*-xylene, and sodium bromide; the cobalt(III) concentration builds up until the oxygen has been depleted, whereupon [Co(III)] diminishes as it oxidizes $Co^{II}Br_n$ complexes. Further addition of oxygen can be repeated, so that the rise and fall of the cobalt(III) absorbance can be made to recur. The falling stage of this transformation, representing the oxidation of HBr by Co(III) in the presence of Co(II), was the portion of interest to us in this study.

Equilibrium mixtures of bromocobalt(II) and bromomanganese(II) complexes were prepared from $Co(OAc)_2$ or $Mn(OAc)_2$ in glacial acetic acid with a stoichiometric deficiency of NaBr or LiBr. The distribution of $Co^{II}Br_n$ was calculated from the stepwise formation constants.[8] Under the conditions chosen, the monobromocobalt(II) complex is the predominant species, but as we shall see it is the concentration of dibromocobalt(II) that is most important in the reaction chemistry. Water is known to affect the extent to which given species of bromide−cobalt(II) are formed, and so the stability constants were redetermined at the water concentrations used here using the electrochemical method described by Sawada and Tanaka.[8]

Acetic acid is not an ionizing medium; hydrobromic acid is a weak acid with pK_a 6.7. Cobalt(II) acetate can be crystallized from water as the six-coordinate complex $Co(OAc)_2\cdot(H_2O)_4$ with four waters coordinated to $Co(OAc)_2$.[22,23] Slow crystallization of 0.12 M $Co(OAc)_2(H_2O)_4$ from acetic acid afforded a different structure of hydrated cobalt(II) acetate with an infinite chain structure, *catena*-poly-[monoaquadiacetatocobalt(II) monohydrate], $[Co^{II}(CH_3COO)_2(H_2O)\cdot H_2O]_n$.[24] Cobalt(II) acetate forms a pink solution in wet acetic acid, consistent with six-coordinate $Co(HOAc)_n(H_2O)_m(OAc)_2$; in chemical equations it will be written simply as $Co(OAc)_2$. The monobromocobalt(II) complex is also pink, whereas the dibromo and higher complexes are deep blue, thus tetrahedral complexes. Similarly, the bromo complexes will be designated CoBrOAc and $CoBr_2$.

Trivalent Mn(III) and Co(III) exist in di- and trinuclear forms in acetic acid, as well as transient mononuclear species. This point is particularly pertinent for Co(III), the kinetic inertness of which ensures that such forms will not likely equilibrate with one another in the reaction time. We have recently commented upon the Mn(III) and Co(III) species.[1,16−20] Except when speciation itself becomes an issue, the notation $M(OAc)_3$ will be used.

Kinetics. Most of the reactions were examined with UV−visible methods, for which Shimadzu 2101 and 3101 and Shimadzu MultiSpec 1501 instruments were used. The reaction cuvettes were maintained at constant temperature (5−80 °C, as desired) by an electronically controlled cell holder. Faster reactions were studied by the stopped-flow method with a Bio-Sequential DX-17MW instrument from Applied Photophysics. The pseudo-first-order rate constant, k_ψ, was evaluated by the nonlinear least-squares fitting to the absorbance−time values to the equation

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + (\mathrm{Abs}_0 - \mathrm{Abs}_\infty) \times e^{-k_\psi t}$$

Results

Bromide−Co(II) Complexation Equilibria. Equilibrium constants are known for the stepwise formation of bromocobalt(II) complexes in glacial acetic acid at 25.0 °C.[8] Spectrophotometric and electrochemical determinations were carried out in solutions containing 48.5 mmol/L H_2O (0.1 wt %) in acetic acid over a range of LiBr concentrations (3.15−100 mmol/L) at temperatures of 25.0−60.0 °C and a cobalt(II) concentration of 12.3 mmol/L as described by Sawada and Tanaka.[8] Spectral scans were recorded over the range 400−800 nm at intervals of 1.0 nm for at least 20 bromide concentrations at each selected temperature. Figure S-1[25] shows representative results. The data at each temperature were analyzed simultaneously at all wavelengths and bromide concentrations using the program PSEQUAD. [21] In addition, these solutions were analyzed for free bromide by the electrochemical method described by Sawada and Tanaka.[8] The equilibrium constants so determined, presented in Table 1, indicate the diminution of the binding constants caused by even this low water concentration. Table 1 also includes the values of $\Delta H°$ and $\Delta S°$ from the fits to the van't Hoff equation, Figure S-2.[25] One form in which the temperature-dependent equilibria will be used in this research rests on the quotient K_2/K_1, which represents K_D, a ligand distribution equilibrium; it shows but a small temperature effect.

Bromide−Mn(II) Complexation Equilibria. None of the bromomanganese(II) species exhibit an absorption band of useful intensity. Three bromomanganese(II) species were identified in ternary mixtures of $Mn(OAc)_2$, $Co(OAc)_2$, and LiBr. Addition of the manganese salt lowers the absorbance of the solution by competitively lowering the concentrations of the $Co(II)Br_n$ species responsible for light absorption. Using the PSEQUAD program,[21] three bromomanganese(II) species were identified. The stability constants of $Mn^{II}Br_n$ were determined by the electrochemical method described by Sawada and Tanaka.[8] These experiments used 2.20 mmol L^{-1} $Mn(OAc)_2$ and 0−21.8 mmol L^{-1} LiBr in glacial acetic acid at 25 °C. These formation constants were calculated for $MnBr_n$: $K_1 = 701 \pm 8$, $K_2 = 91 \pm 10$, and $K_3 = 18 \pm 8$. When expressed as overall formation constants, the values become $\log \beta_1 = 2.84$, $\log \beta_2 = 4.80$, and $\log \beta_3 = 6.06$. At 50 °C, $K_1 = 415 \pm 13$, $K_2 = 19 \pm 3$, and $K_3 \sim 0$. No association between Co(II) and Mn(II) could be detected spectrophotometrically.

The formation constants K_n for both cobalt and manganese decrease markedly with the water content. This becomes an important point in the practical autoxidation chemistry, as water is a byproduct. For that reason, autoxidation becomes ineffective once water reaches a certain level. This depends on the hydrocarbon used, but it is about 10% water in the case of terephthalic acid.

Manganese(III) Oxidation of Bromide in the Presence of Mn(II). We have reported the oxidation of HBr and MBr (M = alkali metal) by Mn(III).[1] When $Mn^{II}Br_n$ complexes are also present in solution, a new pathway opens that arises from direct oxidation of $Mn^{II}Br_n$. The net reaction remains as before:

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(21) Zékány, L.; Nagypál, I. In *Computational methods for the determination of formation constants*; Leggett, D., Ed.; Plenum Press: New York, 1985. We are grateful to Gábor Lente for assistance in its implementation.

(22) Kaduk, J. A.; Partenheimer, W. *Powder Diffr.* **1997**, *12*, 27−39.

(23) Niekerk, J. N. V.; Schoening, F. R. *Acta Crystallogr.* **1953**, *6*, 609−612.

(24) Jiao, X.-D.; Guzei, I. A.; Espenson, J. H. *Z. Kristallogr.*−*New Cryst. Struct.* **2000**, *215*, 173.

(25) See the Supporting Information.

Table 1. Equilibrium Constants and Other Thermodynamic Parameters for the Stepwise Formation of Bromocobalt(II) Complexes in Acetic Acid[a,b]

	glacial HOAc	HOAc (0.1% H_2O)						
K_n	25.0 °C	25.0 °C	40.0 °C	50.0 °C	60.0 °C	$\Delta H°$/kJ	$\Delta S°$/J K^{-1}	$\Delta G_{298}°$/kJ
K_1	850	491	330	297	271	−14.0 (20)	4.0 (70)	−15.2 (20)
K_2	300	116	84	67	71	−12.7 (34)	−3.5 (100)	−13.7 (50)
K_3	680	63	28	24	19	−27.9 (48)	−59.9 (150)	−45.7 (100)
K_4	2.5							
K_D[c]	0.35	0.24	0.25	0.23	0.26			

[a] Values in glacial HOAc from ref 8. [b] With 12.0 mmol L^{-1} Co(II), 0−100 mmol L^{-1} NaBr. [c] $K_D = K_2/K_1$.

$$2Mn(OAc)_3 + 2HBr \rightarrow 2Mn(OAc)_2 + 2HOAc + Br_2 \quad (1)$$

The kinetics of HBr oxidation by $Mn(OAc)_3$ in the presence of $Mn(OAc)_2$ was studied by monitoring the decrease in the Mn(III) absorption at λ 461 nm (ϵ 308 L mol^{-1} cm^{-1}) with 34−90 mM Mn(II), 0.07−0.15 mM Mn(III), and 14−53 mM HBr. Representative kinetics experiments are shown in Figures S-3 and S-4.[25] The data from each experiment were analyzed by pseudo-first-order kinetics (see Table S-1[25]). The resulting values of k_ψ were then correlated with the concentrations of the species present in solution. This rate law was found to fit the concentration dependences:

$$\frac{d[Mn(OAc)_3]}{dt} = k_\psi[Mn(OAc)_3] = k'\frac{[Mn(OAc)_3][Mn(OAc)Br]^2}{[Mn(OAc)_2]} \quad (2)$$

with $k' = (8.6 \pm 0.7) \times 10^{-3}$ L mol^{-1} s^{-1} in glacial acetic acid at 20.0 °C. Figure S-5[25] shows the plot of k_ψ against the quotient $[Mn(OAc)Br]^2/[Mn(OAc)_2]$ for the data at 20 °C in HOAc. The linearity of this plot, although imperfect, covers a substantial variation of each concentration, which we take to mean that eq 2 represents the "best" single-term rate law. Doubtless, were one to introduce additional parameters, such as a contribution from the tribromomanganese complex, a better statistical fit could have been obtained, but that procedure appears to be unjustified from the precision of the data. From eq 2 one can infer that the reaction occurs mainly by way of a bimolecular reaction between $Mn(OAc)_3$ and the minor species $MnBr_2$, formed in a ligand-distribution equilibrium. It is independently known that Mn(II) and Mn(III) undergo an extensive and rapid association in a 1:1 ratio to give an acetate-bridged species[1] written as $Mn^{II}{\cdot}Mn^{III}$. This is the reaction scheme suggested by these results:

$$2Mn(OAc)Br = MnBr_2 + Mn(OAc)_2 \quad (\text{fast}, K_D = K_2/K_1 = 0.13) \quad (3)$$

$$Mn^{III} + Mn^{II} \rightarrow Mn^{II}{\cdot}Mn^{III} \quad (k_4 = 3.4 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1})^1 \quad (4)$$

$$Mn^{II}{\cdot}Mn^{III} + MnBr_2 \rightarrow 2Mn^{II} + Mn^{III}Br_2^{+} \quad (k_5) \quad (5)$$

Since $K_D = 0.13$, $k_5 = (6.6 \pm 0.5) \times 10^{-2}$ L mol^{-1} s^{-1} (20 °C, glacial acetic acid).

Is it reasonable to suggest that only the species $MnBr_2$ reacts? This is the simplest inference one might draw from the form of the rate equation. We return to this point following the presentation of data referring to the study of the effect of cobalt(II) on bromide oxidation by Mn(III) and Co(III) in the next two sections, since the same subject arises there as well.

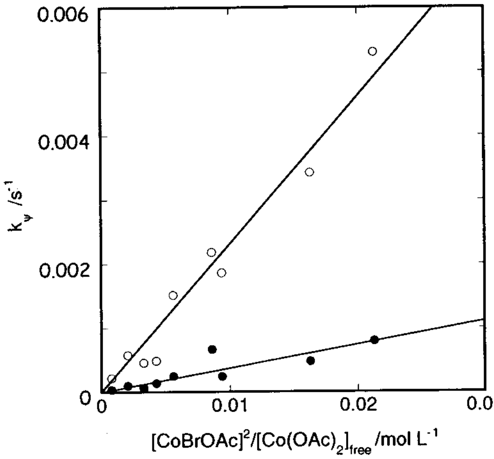


Figure 1. Kinetics of the reaction of Mn(III) (open circles) and $Mn^{III}{\cdot}Mn^{II}$ (filled circles) with $Co^{II}Br_n$ as a function of the X-variable, which is proportional to $[CoBr_2]$, as in eq 7.

Manganese(III) Oxidation of Bromide in the Presence of Co(II). $Co(OAc)_2$ affects the oxidation of LiBr by $Mn(OAc)_3$ much as $Mn(OAc)_2$ does, but this system is complicated by the slowness, compared to eq 4, of the analogous trivalent−divalent interaction:

$$Mn^{III} + Co^{II} \rightarrow Co^{II}{\cdot}Mn^{III} \quad (k_6 = 0.37 \text{ L mol}^{-1} \text{ s}^{-1})^1 \quad (6)$$

As a consequence, the separate reactions of Mn^{III} and $Co^{II}{\cdot}Mn^{III}$ could be resolved from the biexponential kinetics. Figure S-6[25] shows a representative kinetics experiment and its resolution into two components. This treatment gives for each experiment two pseudo-first-order-rate constants, labeled as the large and small components, $k_\psi{}^l$ and $k_\psi{}^s$, which are functions of the concentrations present. Both $k_\psi{}^l$ and $k_\psi{}^s$ vary linearly with the quotient $[CoBrOAc]^2/[Co(OAc)_2]$, Figure 1. Thus the rate law is analogous to eq 2. The reaction scheme allows for a ligand-distribution equilibrium among the bromocobalt(II) species, which is followed by parallel oxidation steps in which $CoBr_2$ reacts with $Mn(OAc)_3$ and $Co^{II}{\cdot}Mn^{III}$. The derived rate constant at 20.0 °C in glacial acid for $Mn(OAc)_3$ is $k' = 0.13 \pm 0.01$ L mol^{-1} s^{-1}; for $Co^{II}{\cdot}Mn^{III}$, $k' = 0.021 \pm 0.002$ L mol^{-1} s^{-1}, according to this reaction scheme:

$$2CoBrOAc = CoBr_2 + Co(OAc)_2 \quad (K_D = K_2/K_1 = 0.24) \quad (7)$$

$$Mn(OAc)_3 + CoBr_2 \rightarrow Mn(OAc)_2 + Co^{III}(OAc)Br_2 \quad (k_8) \quad (8)$$

$$Co^{II}{\cdot}Mn^{III} + CoBr_2 \rightarrow Co^{II} + Mn^{III} + Co^{III}Br_2 \quad (k_9) \quad (9)$$

The rate constants determined from this treatment are $k_8 = 0.96$ L mol^{-1} s^{-1} and $k_9 = 0.15$ L mol^{-1} s^{-1}, each known to ca. ±10−15%.

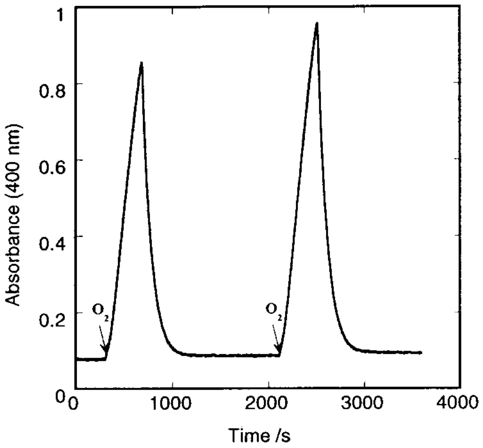


Figure 2. The Co(III) absorbance at 400 nm rises when oxygen is introduced into a solution of *p*-xylene (1.6 mol L^{-1}) containing 80 mM Co(OAc)$_2$ and 30 mM NaBr at 40 °C, until the supply of oxygen has been exhausted, whereupon the net oxidation of HBr by Co(III) occurs with the effects of Co(II), particularly CoBr$_2$, described herein. Addition of more O$_2$, simply by momentarily opening the sealed cuvette, allows the cycle to repeat; the phenomenon can be repeated many times.

Cobalt(III) Oxidation of Bromide in the Presence of Cobalt(II). This reaction at 40.0 °C in glacial acetic acid was monitored by following the absorbance of Co(III) at 335 or 400 nm, where the respective molar absorptivities are 1500 and 640 L mol^{-1} cm^{-1}. One set of experiments was conducted using the method devised by Zakharov and co-workers,[12,14] described in the Experimental Section; $[\mathrm{Br}_{\mathrm{total}}] = 4-30$ mM, $[\mathrm{Co^{II}}_{\mathrm{total}}] = 80$ mM, [*p*-xylene] = 0.3 mol L^{-1}, $[\mathrm{O_2}] \approx 1$ mM. The rise and fall with the addition and depletion of oxygen make an informative display, as given in Figure 2. In the second group, with ozone-generated Co(III), the concentrations were 2−9 mM $\mathrm{Br_{total}}$ and 19−117 mM $\mathrm{Co^{II}}_{\mathrm{total}}$. The distribution among the $\mathrm{Co^{II}}$-Br_n species at 20.0 °C in glacial acetic acid was calculated from the equilibrium constants reported earlier in this paper (25 °C, 0.1% H$_2$O). Given $[\mathrm{Co^{II}}]_{\mathrm{T}} \gg [\mathrm{Co(III)}]$ (=0.06−0.4 mM), the reactions followed first-order kinetics and the distribution among the $\mathrm{Co^{II}Br}_n$ species remained constant throughout each experiment. The pseudo-first-order rate constants are a *quadratic* function of [CoBrOAc] in experiments at constant [Co(OAc)$_2$]; see Figure S-7;[25] they are a linear function of [CoBrOAc]^2/[Co(OAc)$_2$]. This shows that the reaction rate is described by this equation:

$$-\frac{\mathrm{d[Co(OAc)_3]}}{\mathrm{d}t} = k'\frac{\mathrm{[Co(OAc)_3][CoBrOAc]^2}}{\mathrm{[Co(OAc)_2]}} \qquad (10)$$

Table S-1[25] provides the concentrations and rate constants. Precisely equivalent to this data analysis is one in which the rate constant is expressed as a function of [CoBr$_2$]. The concentration of the dibromocobalt(II) species is related to the others by the equilibrium constant for the ligand redistribution equilibrium shown in eq 7. As a result the following reaction is implicated and its second-order rate constant can be obtained as the quotient $k_{11} = k'/K_{\mathrm{D}}$:

$$\mathrm{Co(OAc)_3 + CoBr_2 \rightarrow Co(OAc)_2 + CoBr_2(OAc)} \qquad (k_{11}) \qquad (11)$$

Figure 3 presents a plot of k_ψ against the concentration of CoBr$_2$ calculated from the equilibrium constant expressions. It proved to be immaterial whether Co(III) was prepared from ozone or generated in situ according to Zakharov's method; the two experimental methods gave consistent data. The slope in Figure 3 provides the value of the second-order rate constant for the reaction between CoBr$_2$ and Co(III) as 4.8 ± 0.2 L mol^{-1} s^{-1} at 313 K. This reaction was studied as a function of temperature. The values of k (eq 11) were analyzed by the Eyring equation, Figure S-8,[25] giving these activation parameters: $\Delta H^\ddagger = 95.2 \pm 4.9$ kJ mol^{-1} and $\Delta S^\ddagger = 74 \pm 16$ J K^{-1} mol^{-1}.

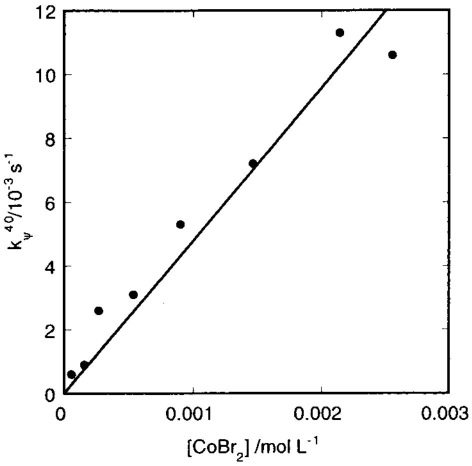


Figure 3. A plot the pseudo-first-order rate constant for the oxidation of HBr by Co(OAc)$_3$, showing that CoBr$_2$ is the active form of cobalt(II). Agreement is illustrated by the inclusion of data for the two methods of preparing Co(III), prior ozonolysis and in situ catalytic generation with oxygen according to ref 14.

Table 2. Rate Constants for the Oxidation of Aralkyl Bromides by Monomeric Manganese(III) at 25.0 °C in Glacial Acetic Acid

$\mathrm{XC_6H_4CH_2Br}$	$k/10^{-2}$ L mol^{-1} s^{-1}
H	9.8
o-Me	7.1
p-Br	7.0
m-Br	6.4
p-Me	1.4_6
m-Me	1.3

Cobalt(III) Oxidation of Bromide. The oxidation of bromide by cobalt(III), studied with a ≥10-fold excess of bromide over cobalt(III), was studied at 35.0 °C in 10% aqueous HOAc. The decrease in the absorbance of Co(III) could be fit to biexponential kinetics, consistent with the existence of the two species shown in Chart 1.[1,16−20] The resolved rate constants, when plotted against bromide, each gave a linear plot, confirming that both Co(IIIc) and Co(IIIs) follow second-order kinetics overall. The rate constants (L mol^{-1} s^{-1}) for Co(IIIc) are 9.9 (HBr) and 0.20 (NaBr); the corresponding rate constants for Co(IIIs) are 1.4 (HBr) and 0.036 (NaBr).

Reaction of Manganese(III) with Benzyl Bromide. Our earlier work reported on the reaction of PhCH$_2$Br with cobalt(III),[2] and we have now turned to the more reactive Mn(III). To avoid oligomeric species, such as the commercial Mn(OAc)$_3$ which is an oxo-centered trinuclear compound, the Mn(III) used in this research was the mononuclear species prepared in situ by cerium(IV) oxidation as detailed previously.[1] The reaction was studied under argon with pseudo-first-order conditions, $\mathrm{ArCH_2Br} \geq 10 \times [\mathrm{Mn(III)}]_0$, at 25.0 °C in glacial acetic acid; see Figure S-9.[25] The plot of k_ψ against [ArCH$_2$Br] is a straight line through the origin, see Figure S-10.[25] The slope gives the rate constants presented in Table 2 for six different aryl groups. Kinetic data for benzyl bromide were also determined at 35.0 and 50.0 °C, Figure S-11,[25] from which $\Delta H^\ddagger = 76 \pm 14$ kJ mol^{-1} and $\Delta S^\ddagger = -22 \pm 45$ J K^{-1} mol^{-1}.

Table 3. Summary of Reactions and Rate Constants

reaction, rate law[a]	k/L mol^{-1} s^{-1}	temp/°C	solvent
A. Co(III) Oxidation of HBr, NaBr			
$v = k$[Co(IIIc)][bromide]	9.9 (HBr) 0.20 (NaBr)	35.0	10% aq HOAc
$v =$ k[Co(IIIs)][bromide]	1.4 (HBr) 0.036 (NaBr)	35.0	10% aq HOAc
B. Co(III) Oxidation of HBr or NaBr, in the Presence of Co(II)			
$v = k\frac{[Co(OAc)_3][Co(OAc)Br]^2}{[Co(OAc)_2]}$	$k' = 1.8$ (HBr)	40.0	HOAc
$= k[Co(OAc)_3][CoBr_2]$	$k = 3.6$ $k = 4.8$ (NaBr)	40.0	0.1% aq HOAc 0.1% aq HOAc
C. Mn(III) Oxidation of HBr in the Presence of Mn(II) or Co(II)			
$v = k\frac{[Mn(OAc)_3][MnBrOAc]^2}{[Mn(OAc)_2]}$	$k' = 8.6 \times 10^{-3}$	20.0	HOAc
$= k[Mn(OAc)_3][MnBr_2]$	$k = 6.6 \times 10^{-2}$		
$v = k\frac{[Mn(III)][CoBrOAc]^2}{[Co(OAc)_2]}$		20.0	HOAc
$= k_8[Mn(OAc)_3][CoBr_2]$	$k_8 = 0.96$		
$+ k_9[Mn^{III}\cdot Co^{II}][CoBr_2]$	$k_9 = 0.15$		
D. Mn(III) and Co(III) Oxidation of Benzyl Bromide			
$v = k[M(OAc)_3][PhCH_2Br]$	1.5 [Mn][b] 0.9 [Co(IIIa)][c]	50.0	HOAc

[a] $v = -d[M(III)]/dt$. [b] Values for other $ArCH_2Br$ are given in Table 2. [c] From ref 2.

Discussion

Table 3 summarizes the kinetic data for the reactions encountered in this study. All of these data and those given in the previous study[1] point to this scheme: the $M^{II}Br_2$ species, M = Co or Mn, is oxidized by $Mn(OAc)_3$ and $Co(OAc)_3$ in the rate-controlling step. This pathway for the oxidation of HBr or NaBr occurs to the exclusion, for example, of the oxidation of $M(OAc)_2$ or MBrOAc, and is much faster than the oxidation of HBr or NaBr. We propose that this pattern signals a key feature of the mechanism. When MBr_2 is oxidized, the resulting dibromometal(III) complex has a favorable pathway for unimolecular reductive elimination. This yields the dibromide radical, which is then converted to molecular bromine by subsequent oxidation. These are the proposed reactions, where M in either oxidation state may be Co or Mn:

$$M^{II}Br_2 + M'(OAc)_3 \rightarrow M^{III}Br_2(OAc) + M'(OAc)_2 \quad (12)$$

$$M^{III}Br_2(OAc) + HOAc \rightarrow M(OAc)_2 + HBr_2^{\bullet} \quad (13)$$

$$HBr_2^{\bullet} + M'(OAc)_3 \rightarrow Br_2 + M(OAc)_2 + HOAc \quad (14)$$

According to this scheme, as given in eq 12, only the dibromo complex of M(II) is reactive. It is only logical, however, that $M(OAc)_2$ and MBrOAc could also participate in parallel redox reactions with M(III). Indeed, it is only reasonable that the oxidation reactions of $M(OAc)_2$ and MBrOAc would have rate constants very similar to k_{12}. In this proposal, it is neither necessary nor profitable to propose any special function for coordinated bromide in eq 12: we propose that outer-sphere electron transfer occurs. Therefore, it is logical to suppose that all three species of the divalent metals are participants: $M(OAc)_2$ and MBrOAc, as well as MBr_2. Our findings indicate that only the reaction of MBr_2 is productive; its product is able to undergo reductive elimination of dibromide as in eq 13.

The M(III) products formed by the oxidation of $M(OAc)_2$ and MBrOAc, lacking a suitable low-energy reaction pathway, would revert to the starting materials by the reverse reaction step. Note that eq 12 is nearly thermoneutral, as are the similar reactions of the other M(II) reagents. Thus they are nonproductive insofar as bromine production is concerned. If not quickly consumed by other reactions, dibromide radical produced as by eq 13 can disproportionate forming bromide and bromine:

$$2HBr_2^{\bullet} \rightarrow Br_2 + 2HBr \quad (15)$$

When a methylarene ($ArCH_3$, in general) is present, the dibromide radical is responsible for the reactions that lead to the subsequent oxidation sequence:

$$HBr_2^{\bullet} + ArCH_3 \rightarrow 2HBr + ArCH_2^{\bullet} \quad (16)$$

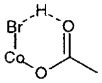
$$ArCH_2^{\bullet} + O_2 \rightarrow ArCH_2OO^{\bullet} \quad (17)$$

The role of the active intermediate is clearly played by the dibromide radical, not (for instance) by atomic bromine in solution. The selectivity for $HBr_2^{\bullet}$ formation has its origin in thermodynamics: $Br^{\bullet}$ is at a considerably higher free energy than $HBr_2^{\bullet}$. In water, for example, $E°$ for $Br^{\bullet}/Br^-$ exceeds $E°$ for $Br_2^{\bullet -}/2Br^-$ by 0.3 V.[26−28] Even in the absence of the divalent metal salt, manganese(III) oxidizes HBr and NaBr in reactions whose kinetics implicates the $MnBr_2(OAc)$ intermediate and reactions 13 and 14. To summarize: the dibromide radical is accessible from reactions of Mn(III) and Co(III), whereas $Br^{\bullet}$ is not.

For both HBr and NaBr, Mn(III)[1] is much more reactive than either of the Co(III) species. Not only that, but the Mn(III) reactions follow a rate law that shows a second-order dependence on [HBr] and [NaBr]. This kinetic form was attributed to the intervention of a dibromomanganese(III) intermediate that underwent reductive elimination to form the dibromide radical. This reaction is given by eq 13, and it is obviously the pertinent reaction, regardless of whether the dibromomanganese(III) species is prepared from electron transfer or ligand substitution.

Given the ubiquitous role that the dibromide radical appears to play in several of the mechanisms reported here and previously,[1,2] we are inclined to suggest by analogy that it plays a role in the Co(III)−HBr reactions also. That claim could not be documented from the kinetics or other data, however, since the *first* substitution reaction between Co(III) and HBr was rate-controlling, no doubt because of the low rate of ligand substitution into the coordination sphere of d^6 Co(III). Inferential evidence for the dibromide radical is nonetheless found, reasoning by analogy from the reactions in which HBr is oxidized by Co(III) or Mn(III) in the presence of Co(II), eqs 12−14.

In the oxidation of bromide by M(III) in the absence of M(II), in both this work on Co(III) and our earlier studies of Mn(III),[1] it was found that HBr reacts much more rapidly than NaBr and other alkali metal bromides do. This effect can be attributed to stabilization of the transition state by formation of a hydrogen bond, as shown in this diagram:



The rate constants for the oxidation of benzyl bromide by Mn(III) and by Co(IIIa)[2] have been determined; at 50 °C, the values of k/L mol^{-1} s^{-1} are similar: 1.5 for Mn(III) and 0.9 for

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(26) Stanbury, D. M. *Adv. Inorg. Chem.* **1989**, *31*, 69−137.
(27) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637−1755.
(28) Field, R. J.; Koros, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.

Co(IIIa). These reactions are believed to occur in three steps: outer-sphere electron transfer to form a radical cation, ionization of the radical cation, and a second redox step. The following equations show the reactions suggested.

$$M(OAc)_3 + ArCH_2Br \rightarrow M(OAc)_2 + ArCH_2Br^{\bullet+}\cdot OAc^- \quad (18)$$

$$ArCH_2Br^{\bullet+}\cdot OAc^- \rightarrow ArCHBr^\bullet + HOAc \quad (19)$$

$$ArCHBr^\bullet + M(OAc)_3 \rightarrow ArCHBrOAc + M(OAc)_2 \quad (20)$$

The result that k_{18} is nearly the same for Mn and Co is consistent with these species having similar reduction potentials in acetic acid, 1.77 and 2.0 V, respectively.[29] Both values are sufficiently high to oxidize benzyl bromide.[29] The organic product of eq 20 will, through additional solvolysis and oxidation, be converted to a carboxylic acid.

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Supporting Information Available: Graphs of kinetic data and their analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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[29] Adamian, V. A., as cited in ref 1.