Preparation and characterization of manganese(IV) in aqueous acetic acid[†]

Joo-Eun Jee, Oleg Pestovsky* and Andreja Bakac*

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Mn(IV) acetate was generated in acetic acid solutions and characterized by UV-vis spectroscopy, magnetic susceptibility, and chemical reactivity. All of the data are consistent with a mononuclear manganese(IV) species. Oxidation of several substrates was studied in glacial acetic acid (HOAc) and in 95:5 HOAc–H₂O. The reaction with excess Mn(OAc)₂ produces Mn(OAc)₃ quantitatively with mixed second-order kinetics, $k (25.0 \degree C) = 110 \pm 4 \ M^{-1} \ s^{-1}$ in glacial acetic acid, and $149 \pm 3 \ M^{-1} \ s^{-1}$ in 95% AcOH, $\Delta H^{\ddagger} = 55.0 \pm 1.2 \ kJ \ mol^{-1}$, $\Delta S^{\ddagger} = -18.9 \pm 4.1 \ J \ mol^{-1} \ K^{-1}$. Sodium bromide is oxidized to bromine with mixed second order kinetics in glacial acetic acid, $k = 220 \pm 3 \ M^{-1} \ s^{-1}$ at 25 °C. In 95% HOAc, saturation kinetics were observed.

Introduction

The complex process of oxidation of *p*-xylene to terephthalic acid uses molecular oxygen as oxidant, and salts of cobalt and manganese in the presence of hydrobromic acid/bromide salts as co-catalysts in acetic acid.¹⁻⁴ Decades-long research into the mechanism of this multi step process^{2,5-11} has provided a fair amount of understanding of some of the chemistry involved, but much more remains to be uncovered, and every answer seems to raise new questions. In the current mechanistic picture, the main active species include oxidation states 2+ and 3+ for both cobalt and manganese. Bromide undergoes a number of transformations through radical and non-radical forms, with HBr₂. (as a major hydrogen-atom abstracting agent that generates carbon radicals) and bromometal complexes (as a source of HBr₂.) playing major roles. Brominated hydrocarbons, elemental bromine, and traces of methyl bromide are generated in the process as well.¹

Unlike cobalt, manganese has an accessible 4+ oxidation state, but there is no serious role for such a species in the current mechanistic schemes, even though the highly oxidizing intermediates in the Mid Century $(MC)^1$ and related catalytic autoxidation processes almost certainly have the potential to generate Mn(Iv). In fact, solid MnO_2 is often observed in reaction mixtures when autoxidation of methyl aromatics is carried out with manganese-containing catalysts.^{12,13} A plausible source of MnO_2 is the disproportionation of Mn(III).¹³ These observations seem to suggest a role for the 4+ oxidation state that is not only unproductive in the overall oxidation process, but instead contributes to the loss of the catalyst.

To gain a better understanding of this chemistry, we have generated Mn(IV) in acetic acid and examined its reactivity toward several components of the MC process. Here we describe the oxidation of bromide ions and manganese(II) acetate.

The exact chemical composition of Mn(IV) used in this work has not been established, although one or more acetate ligands are almost certainly present. Numerous synthetic carboxylato complexes of Mn(IV) have been reported in the literature, mostly in the context of oxygen-evolving center in photosystem II. These complexes are either mixed-valence¹⁴ or all-Mn(IV), mononuclear¹⁵⁻¹⁷ or polynuclear,^{18,19} and often contain additional ligands^{14,17,19-21} or oxo-bridges.¹⁹ In other words, the structure and composition of Mn(IV) complexes is not easily predictable, even when they are prepared by well-designed synthetic procedures. Even less structural information can be expected for a solution species. None the less, the kinetics data obtained in this work, see later, strongly support the notion that the same (major) species was generated by four different preparative reactions involving either oxidation of Mn(II) or reduction of KMnO₄.

Experimental

Potassium permanganate, manganese(II) acetate, manganese(III) acetate, meta-chloroperoxybenzoic acid (mcpba), glacial acetic acid, *tert*-butanol, sodium bromide, and bromine, all Aldrich, and CD₃COOD (CIL) were of highest purity available and were used as received. The peroxide content of mcpba was determined by reduction with excess Fe_{aq}^{2+} and spectrophotometric quantitation of Fe_{aq}^{3+} so generated ($\varepsilon_{240} = 4160 \text{ M}^{-1} \text{ cm}^{-1}$).

Preparation of Mn(IV)

Four different methods were used to generate solutions of Mn(IV) in glacial acetic acid (HOAc) and in aqueous HOAc–H₂O (95:5, v/v). Method 1 utilized the reduction of potassium permanganate by HOAc. To 3 mL of HOAc was added 15 µL of 0.010 M KMnO₄ in HOAc, and the absorbance was monitored at 266 nm ($\varepsilon_{\text{Mn(IV)}} = 7.80 \times 10^3 \text{ M}^{-1} \text{ cm}^{1-}$) until stable reading was reached (about 5 min). For work in 95% HOAc, water was added after the formation of Mn(IV) was complete. This method was used most often to generate low concentrations of Mn(IV) for kinetic purposes. Larger concentrations could also be prepared, but the reaction times were significantly longer. An increase in water concentrations during the reaction was not responsible for the slower rates, as shown by similar kinetics in glacial and 95% AcOH.

Oxidation of Mn(II) with mcpba formed the basis of method 2. In agreement with the literature,²² the reaction was autocatalytic,

Ames Laboratory, Iowa State University, Ames, IA 50011, USA. E-mail: bakac@ameslab.gov, prp@ameslab.gov; Fax: +1515-294-5233; Tel: +1515-294-3544; Tel: +1515-294-5826

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reflecting greater reactivity of the initial product, Mn(III), toward mcpba. Fig. S1 (ESI)† shows a typical time course for the formation of Mn(IV) from Mn(II) and a slight excess of mcpba over the theoretical 1:1 stoichiometry.

Method 3 was an attempt to take advantage of the fast Mn(III)/mcpba reaction. Unfortunately, spectrophotometric titrations of Mn(III) acetate with mcpba yielded stable absorbance readings after the addition of much less than stoichiometric amounts of mcpba, suggesting that only a portion of Mn(III)was oxidized. It is possible that this behaviour was caused by polymeric Mn(III) species that did not equilibrate rapidly on the titration time scale. Molar absorptivities and kinetics behaviour of Mn(IV) obtained by this method (once the unusual titration stoichiometry was taken into account) were comparable to those of the samples prepared by methods 1 and 2. None the less, in view of the unexpected titration ratios, no kinetic or product results reported here utilized Mn(IV) prepared by method 3.

Method 4 utilized the reaction of Mn(II) with a slight excess of O₃. The reaction was instantaneous, and generated a species with the same spectrum and lifetime as that obtained by methods 1–3. Because of the additional time required to remove excess ozone by purging with argon or O₂ after the formation of Mn(IV) was complete, this method was not used for precise kinetic experiments for which we used freshly generated samples, see below.

Solutions of Mn(IV), prepared by any of the methods described above decayed, most likely by oxidation of the solvent, to a mixture of Mn(III) and Mn(II) within several hours. All of the kinetic and spectroscopic data were obtained with freshly prepared solutions, no more than ten minutes after the formation of Mn(IV). Independent experiments showed that the age of the solutions had no effect on the kinetics of any of the reactions studied with Mn(IV)as limiting reagent.

Magnetic susceptibility measurements were carried out by the Evans method²³ at room temperature (20 ± 1 °C inside the NMR probe) with the use of a Varian VXR-300 spectrometer. A CD₃COOD solution of the paramagnetic solute and 10.5 mM *tert*-butanol was placed inside a 5 mm × 170 mm NMR tube, and ¹H NMR spectrum was recorded. A 1.6 mm × 100 mm capillary filled with a 105 mM *tert*-butanol solution in CD₃COOD was inserted inside the NMR tube, and the spectrum was recorded again. From the two spectra, the paramagnetic chemical shift of the methyl groups of *tert*-butanol, $\Delta\delta$, was obtained. The solutions were highly paramagnetic but also very dilute, which allowed the use of a simplified form of the magnetic susceptibility equation, eqn (1),²⁴

$$\chi_{mol} = \frac{3\Delta\delta}{400\pi C} \tag{1}$$

where χ_{mol} is the magnetic molar susceptibility of the solute, and *C* the concentration of the solute. The magnetic moment and number of unpaired electrons were calculated as in eqn (2)–(3).²⁵

$$\mu = 2.828 \, (\chi_{\rm mol} T)^{1/2} \, (BM) \tag{2}$$

$$n = (1 + \mu^2)^{1/2} - 1 \tag{3}$$

UV-vis spectra and some kinetic data were obtained with a conventional UV-vis Shimadzu 3101 PC spectrophotometer. Faster spectral changes and kinetic measurements were performed with an OLIS RSM-1000 rapid-scanning and Applied Photophysics DX-17 MV stopped-flow spectrophotometers. The kinetics of oxidation of NaBr with Mn(IV) were monitored at either 266 nm ($\varepsilon = 4.09 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for Br₃⁻, and 7.80 × 10³ M⁻¹ cm⁻¹ for Mn(IV)), or 340 nm (ε for Mn(IV) = 3.35 × 10³ M⁻¹ cm⁻¹). The rate constants obtained at the two wavelengths were identical within the error (< 5%). Kinetic data were fitted to the appropriate expressions with the program Kaleidagraph 4.0.

Attempts to obtain the ESR spectrum of frozen samples of Mn(Iv) at both liquid nitrogen and liquid helium temperatures were unsuccessful. As pointed out by a reviewer, mononuclear Mn(Iv) sometimes gives very broad spectra. The heterogeneity of the samples in acetic acid, which failed to form glass, appears to add to the problem. The only observed signal was that corresponding to Mn(II).

Results

UV-vis spectra of Mn(II), Mn(III) and Mn(IV) in 95% AcOH, Fig. 1, are almost identical to the corresponding spectra obtained in glacial acidic acid. Mn(IV) exhibits no sharp features in the visible region and is characterized only by a broad shoulder at 450–500 nm. At 462 nm, Mn(III) showed a maximum ($\varepsilon = 277$ M⁻¹ cm⁻¹ in glacial AcOH, 232 M⁻¹ cm⁻¹ in 95% AcOH), in good agreement with literature data.^{22,26} At this wavelength, Mn(IV) has $\varepsilon = 617$ M⁻¹ cm⁻¹ in glacial AcOH, and 603 M⁻¹ cm⁻¹ in 95% AcOH.



Fig. 1 UV-vis spectra of $Mn(OAc)_2$, $Mn(OAc)_3$, and Mn(IV) in 95% HOAc.

Magnetic susceptibility

A sample of Mn(IV), prepared by oxidation of 10 mM Mn(OAc)₂ with ~ 11.7 mM mcpba afforded the following values: $\Delta \delta = 0.228$ ppm, $\chi_{mol} = 5.44 \times 10^{-3}$ cm³ mol⁻¹, $\mu = 3.57$ BM, n = 2.71 electrons. A control sample of 10.6 mM Cr(CIO₄)₃·6H₂O (Aldrich), a high-spin d³ ion, yielded $\Delta \delta = 0.305$ ppm, $\chi_{mol} = 6.87 \times 10^{-3}$ cm³ mol⁻¹, $\mu = 4.01$ BM, n = 3.14 electrons. A mononuclear Mn^{IV}(biguanide)₃⁴⁺ ion exhibits $\mu = 3.73$ BM.¹⁷ It therefore seems safe to conclude that our manganese(IV) complex also has a high-spin d³ configuration.

Reaction of Mn(IV) with NaBr

The reaction with excess NaBr in both glacial and 95% AcOH generated an intense absorption band at 266 nm, characteristic of Br_{3}^{-} ($\varepsilon = 4.09 \times 10^{4} M^{-1} cm^{-1}$ in aqueous solution).²⁷ The absorbance changes at 266 nm yielded the stoichiometric ratio $[Br_2]_{tot}/[Mn(IV)] = 1.0$, where $[Br_2]_{tot}$ represents the sum $\{[Br_2] + [Br_3^{-1}]\}$, eqn (4)–5, and $K_{Br} = 53 \pm 2 M^{-1}$ in aqueous acetic acid.^{28,29} This result is consistent with the requirement that Mn(II) must be the final product regardless of the mechanism because any Mn(III) that may be involved as intermediate will be rapidly reduced with additional NaBr, see below. When bromide (0.20–3.0 mM) was present in large excess over Mn(IV) (0.020 mM), so that the ratio $[Br_3^{-}]/[Br_2]$ remained constant throughout the course of each run, greater than 95% of the overall absorbance change took place in a fast, single-step reaction.

$$Mn(IV) + 2Br^{-} \rightarrow Mn(II) + Br_{2}$$
(4)

$$\mathbf{Br}_2 + \mathbf{Br}^- \rightleftharpoons \mathbf{Br}_3 - \mathbf{K}_{\mathbf{Br}}$$
(5)

The kinetics of this step in glacial AcOH were determined with a stopped-flow and yielded pseudo-first-order rate constants that exhibited linear dependence on the concentration of bromide, $k = 217 \pm 3$ M⁻¹ s⁻¹ at 25 °C, Fig. 2. This reaction was followed by an additional small increase in Br₃⁻ that required 100–200 s for completion, indicating that a low concentration of another, less reactive species was also present in our solutions of Mn(IV).



Fig. 2 Plot of k_{obs} against the concentration of NaBr for the reaction with Mn(IV) generated by method 1 (open squares) and method 2 (filled diamonds) in glacial acetic acid.

The kinetics of oxidation of NaBr (0.10–2.0 mM) with mcpba (0.05 mM) was briefly examined under comparable conditions. The reaction obeyed mixed second order kinetics with $k = 148 \pm 3 \text{ M}^{-1} \text{ s}^{-1}$. Thus, Mn(IV) and mcpba have comparable reactivities toward NaBr.

In aqueous 95% AcOH, the Mn(IV)/NaBr reaction exhibited saturation behaviour at higher bromide concentrations, as shown in Fig. 3.



Fig. 3 Plots of k_{obs} vs. [NaBr] for the oxidation of NaBr with Mn(IV) in 95% AcOH in the temperature range $25 \le T \le 45$ °C. The lines are fits to eqn (8).

A reasonable mechanistic interpretation might involve the formation of a bromomanganese complex or ion pair followed by rate-determining electron transfer and hydrolysis, as in eqn (6)-7. The associated rate law is shown in eqn (8). The data in Fig. 3 show systematic deviation from the fits suggesting a more complex mechanism. It appears that in 95% acidic acid and at high bromide concentrations, higher (and less reactive) bromide complexes form, rendering Mn(IV) less oxidizing and thus slowing down the reaction. The absence of the dibromo and higher species in glacial acetic acid can be rationalized by the much lower concentration of free bromide ions in this nonpolar environment. The slopes of k_{obs} vs. [NaBr] at low bromide concentrations in 95% acetic acid, where the dependence on [NaBr] is linear, yielded the rate constants and activation parameters listed in Table 1. These correspond to a limited form of eqn (8), namely $1 > K[Br^{-}]$ and $k_{obs} = kK$. The activation parameters are also composite, $\Delta H^{\dagger}_{obs} = \Delta H^{\dagger} + \Delta H^{0}$ and $\Delta S^{\dagger}_{obs} = \Delta S^{\dagger} + \Delta S^{0}$ as is almost always the case in bimolecular reactions which require some sort of reactant association prior to electron transfer. If the equilibrium constant for the association step is small, the individual steps

Table 1 Kinetic data for the oxidation of NaBr and Mn(II) with Mn(IV) in 95% AcOH" $\,$

T∕°C	$Mn(IV) + Br^{-b}$	Mn(IV) + Mn(II)
	$k_{\rm Br}/{ m M}^{-1}~{ m s}^{-1}$	$k_{\rm Mn}/{ m M}^{-1}~{ m s}^{-1}$
5	_	28 ± 6
10		40 ± 10
15		60 ± 10
20		100 ± 20
25	260 ± 10	150 ± 20
35	567 ± 8	
40	876 ± 33	
45	1174 ± 21	
$\Delta H^{\ddagger}_{obs}/\text{kJ mol}^{-1}$	55.6 ± 3.6	55.0 ± 2.1
$\Delta S^{\dagger}_{obs}/\mathrm{J} \mathrm{mol}^{-1} \mathrm{K}^{-1}$	-11.7 ± 11.5	-4.8 ± 7.1

^{*a*} Mn(IV) prepared from KMnO₄. $\lambda_{mon} = 266$ nm. ^{*b*} Determined at [Br⁻] < 0.60 mM. At higher [Br⁻], saturation kinetics were observed, see text and Fig. 3.

(corresponding to k and K) cannot be resolved and composite values are reported instead.

The value of the rate constant at 25° C (260 M⁻¹ s⁻¹) is comparable to that obtained in glacial acetic acid (217 M⁻¹ s⁻¹), supporting our contention that the behaviour at higher [NaBr] is exceptional and reflects medium effects rather than intrinsic difference in oxidation chemistry. Clearly, the fast steps after electron transfer (eqn (6)) have to be different. In glacial acetic acid (absence of water), the 2 e⁻ oxidized bromide must react directly with Br⁻ without prior hydrolysis first to HOBr.

$$Mn(IV) + Br \xrightarrow{K} (Br \xrightarrow{}) Mn(IV) \xrightarrow{H_2O,k} HOBr + H^{+}$$
(6)

$$HOBr + Br \xrightarrow{H^+} Br_2 + H_2O \quad k \tag{7}$$

$$k_{\rm obs} = \frac{k \ \mathrm{K} \left[\mathrm{Br}^{-} \right]}{1 + \mathrm{K} \left[\mathrm{Br}^{-} \right]} \tag{8}$$

Oxidation of Mn(II) with Mn(IV)

0.8

0.6

0.4

0.2

0.0

200

Absorbance

Upon addition of excess Mn(II) to Mn(IV) (≤ 0.2 mM), the characteristic spectrum of Mn(IV) disappeared and was replaced with that of Mn(III) as shown in Fig. 4. Under our experimental conditions, the reaction in eqn (9) proceeded to completion and generated quantitative amounts of Mn(III).

Final

 $Mn(IV) + Mn(II) \rightarrow 2 Mn(III)$ (9)

Initial

500

600

400

Nnm



300

The kinetics were determined at 266 nm with Mn(II) in large excess over Mn(IV). A plot of pseudo-first order rate constants against the concentration of Mn(II) were linear and yielded a second-order rate constant $k = 110 \pm 4 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0 °C in glacial acetic acid. This value did not change significantly upon addition

of 5% H₂O, $k = 149 \pm 3 \text{ M}^{-1} \text{ s}^{-1}$. The kinetics in 95% AcOH were determined as a function of temperature in the range 5≤ T ≤25 °C. The data, shown in Fig. 5 and Table 1, were fitted to the Eyring equation, and yielded the following activation parameters: $\Delta H^{\ddagger} = 55.0 \pm 1.2 \text{ kJ mol}^{-1}$, $\Delta S^{\ddagger} = -18.9 \pm 4.1 \text{ J mol}^{-1} \text{ K}^{-1}$. The summary of all of the kinetic data in glacial acetic acid is given in Table 2.



Fig. 5 Plot of k_{obs} against the concentration of Mn(II) for the reaction with Mn(IV) in 95% acetic acid in the temperature range $5 \le T \le 25$ °C.



Fig. 6 Second-order dependence of pseudo-first order rate constants on [NaBr] for the reaction with Mn(III) generated from equimolar amounts of Mn(IV) and Mn(II) in glacial AcOH. The line is a fit to eqn (10).

Oxidation of NaBr with Mn(III)

Literature data are available in 90% AcOH for the reaction of NaBr with Mn(III) that was generated by oxidation of Mn(II) acetate with Ce(IV).⁵ This method was suggested to generate monomeric Mn(III), as opposed to commercial samples which are believed to contain dimeric, acetate-bridged Mn(III).^{5,22} We have now examined the oxidation of bromide with a sample of Mn(III) produced in the Mn(IV)/Mn(II) reaction, in part to establish how the reactivity of this Mn(III) compares with that generated by other

 Table 2
 Summary of kinetic data at 25.0° C in glacial acetic acid

Reaction	$k/M^{-1} s^{-1}$
$\overline{NaBr + Mn^{IVa}}$	217 ± 3
$NaBr + Mn^{IVb}$	205 ± 7
$NaBr + Mn^{IVc}$	133 ± 5
$NaBr + Mn^{IIId}$	$(2.40 \pm 0.10) \times 10^{6e}$
$NaBr + Mn^{IIIf}$	$(2.83 \pm 0.21) \times 10^{6e,g}$
	$(4.60 \pm 0.16) \times 10^{5e, l}$
$NaBr + Mn^{IIIi}$	$1.9 \times 10^{4e.j}$
NaBr + mcpba	148 ± 5
$Mn^{IV} + Mn^{II} = 2 Mn^{III}$	110 ± 3
$Mn^{IV} + Mn^{II} = 2 Mn^{III}$	149 ± 20^{k}

^{*a*} Mn(IV) prepared by method 1. ^{*b*} Method 2. ^{*c*} Method 3. ^{*d*} Mn^{III} generated by mixing Mn^{IV} and Mn^{II}. ^{*e*} Units: M⁻² s⁻¹. ^{*f*} Commercial sample. ^{*g*} Faster of two reactions. ^{*h*} Slower of two reactions. ^{*i*} From Mn^{II} + Ce^{IV}, ref. 5. ^{*j*} 4.5 °C, 10 vol% water. ^{*k*} 5 vol% H₂O.

methods. This is an important point, because our data suggest (see later) that at least some Mn(III) in the industrial oxidation process derives from the Mn(IV)/Mn(II) reaction.

Solutions of Mn(III), freshly prepared from equimolar amounts (0.10 mM) of Mn(IV) and Mn(II) in glacial acetic acid, were immediately loaded into the stopped flow, and the kinetic data were collected at 460 nm within several minutes. Within that period of time, the measured rate constants showed no systematic trends, suggesting that the same Mn(III) species persisted throughout the experiment.

The kinetics obeyed the mixed third order rate law of eqn (10), which has the same form as that reported earlier in 90% AcOH.⁵ The second-order dependence on [Br⁻] is illustrated in Fig. 6. The fit to eqn (10) yielded the rate constant $k_{\text{Mn3}} = (2.40 \pm 0.10) \times 10^6$ M⁻² s⁻¹ at 25 °C.

$$-d[Mn(III)]/dt = k_{Mn3}[Mn(III)][Br^{-}]^{2} = k_{obs}[Br^{-}]^{2}$$
(10)

This value is somewhat larger, but still within about an order of magnitude of what one might have predicted on the basis of the earlier data, $k_{Mn3} = 1.86 \times 10^4 M^{-2} s^{-1}$ at 4.5° C in 90% AcOH. The same form of the rate law, and similar value of the rate constant under the two sets of conditions suggest that Mn(III) generated in the Mn(IV)/Mn(II) reaction is not dramatically different from that obtained in the Ce(IV) reaction. Given the presence of water in earlier experiments, there were probably some aqua ligands present in that complex, but the nuclearity of the two Mn(III) species is probably the same as judged by the kinetic dependencies. The kinetic data are summarized in Table 2.

We next examined the kinetics of bromide oxidation with Mn(III) prepared by dissolving the commercial $Mn(OAc)_3$ in acetic acid. In this case, the kinetic traces obtained with large excess of bromide could not be fitted to a single exponential, but required a double exponential treatment, as shown in Fig. S2a and S2b (ESI).[†] Both rate constants increased linearly with an increase in $[NaBr]^2$, as shown in Fig. S2c and S2d (ESI),[†] and yielded third-order rate constants $k = (2.83 \pm 0.21) \times 10^6 M^{-2} s^{-1}$ and $(4.60 \pm 0.16) \times 10^5 M^{-2} s^{-1}$. The absorbance changes in the two stages were comparable. We interpret these data to mean that at least two forms of Mn(III) exist in solution in comparable amounts, and that the two forms react with bromide in parallel reactions. The rate constant for the oxidation of bromide with the more reactive form is within less than 20% of that obtained with Mn(III) derived

from the Mn(IV)/Mn(II) reaction, suggesting that the same Mn(III) species is probably involved.

The slower of the two Mn(III)/NaBr reactions is still quite fast and exhibits second-order in [NaBr], indicating that only minor differences exist between the two Mn(III) forms. One possibility is a different number and/or coordination mode of acetate ligands that are not equilibrated instantaneously on the time scale of the reaction with NaBr. Thus, even though the solid $Mn(OAc)_3$ yielded solutions that were less uniform than those prepared by reduction of Mn(IV), the kinetics of the reaction with NaBr were comparable for all three sources.

Discussion

Both the oxidation of Mn(II) and Mn(III), and the reduction of KMnO₄ generate a species that is soluble and reasonably stable in acetic acid, even in the presence of 5% water. In an earlier study²² it was assumed that the reaction between Mn(II)/Mn(III) and MCPBA in acetic acid generated Mn(IV), but no characterization was carried out to confirm that assumption. In the present work, the assignment of the 4+ oxidation state is based on (a) formation of the same product by four different reactions, (b) magnetic susceptibility, and (c) stoichiometry and products of two independent reactions, *i.e.* those of the oxidation of Mn(OAc)₂ and of NaBr.

Nearly identical UV-vis spectral features of Mn(IV) derived from the four sources, and comparable kinetics in all of the cases tested confirm that all four methods generated the same species, although method 3 (oxidation of Mn(III) with mcpba) yielded smaller than expected amounts of Mn(IV). Other, unreactive forms of Mn(III) appear to be present in solid samples of "Mn(OAc)₃." This notion is also supported by the observed biphasic kinetics in the reaction with NaBr.

The yield of Mn(IV) in freshly prepared solutions was quantitative with respect to the amount of Mn(II) or Mn(VII) used in the preparation by any of the methods employed. This was confirmed in titrations with Mn(II) and with NaBr. Also, there was no noticeable intercept in the plot of k_{obs} against [Mn(II)] for the comproportionation reaction, Fig. 5, indicating that the equilibrium in eqn (9) is favorable in the forward direction. Although the reverse of reaction 9 played no noticeable role in any of the kinetic or spectroscopic work, Mn(II) was observed by ESR in much more concentrated samples (1–10 mM) of slightly decomposed Mn(IV) suggesting some contribution from disproportionation of Mn(III) generated by oxidation of the solvent by Mn(IV).

Even though HOAc reportedly reduces KMnO_4 ,³⁰ it is not certain whether HOAc was the actual reductant in method 1. The HOAc used was from several sources, including the highest purity available (99.99+ %) but rates of Mn(IV) formation decreased greatly upon successive additions of KMnO₄. Acceptably fast reactions (complete in ≤ 10 min) were observed only at ≤ 0.1 mM KMnO₄. Most likely, the solvent contained trace amounts of an impurity that either reduced KMnO₄ or catalyzed the KMnO₄/HOAc reaction before being converted to an inactive form. Despite this uncertainty, we continued to use method 1 because it was convenient, required no additional reagents, and gave a product that appeared in every respect identical to that

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obtained by other methods. Also, identical results were obtained with several different sources of HOAc.

The effect of solvent on the lifetime and thermodynamic stability of soluble Mn(IV) is remarkable. In aqueous solutions, $Mn_{aq}O^{2+}$ is believed to be too short-lived to be observed or chemically trapped.³¹ In AcOH, on the other hand, soluble form(s) of Mn(IV) persist for several hours even in the presence of 5% water. In aqueous solutions, the very fast $Mn_{aq}O^{2+}/Mn_{aq}^{2+}$ reaction, $k > 10^5$ M^{-1} s⁻¹, is believed to be the main pathway for the loss of the (transient) $Mn_{aq}O^{2+}$.³¹ In AcOH, reaction 9 is much slower ($k_9 =$ 110 M⁻¹ s⁻¹), and not significantly affected by small amounts of water ($k_9 = 149 \text{ M}^{-1} \text{ s}^{-1}$ in 95% AcOH). The different behaviour of Mn(IV) in the two solvents must be related to the differences in polarity, hydrogen bonding, and ion-pairing, as already noticed and discussed for Mn(II) and Mn(III).^{26,32}

The oxidation of NaBr with Mn(III) is fast regardless of the source of Mn(III). Minor differences do exist between different sources, but the second-order dependence on bromide persists, and the rate constant determined for freshly generated solution species is almost the same as that for samples prepared by dissolution of commercial Mn(OAc)₃. Under most conditions, the reaction is much faster than the Mn(IV)/NaBr reaction. This makes the mechanism for the latter difficult to assign because the involvement of Mn(III) as an intermediate is hard to establish. None the less, the different kinetic dependencies, i.e. first order in [NaBr] in Mn(IV) reaction, and second-order in [NaBr] in Mn(III) reaction do suggest a change in mechanism. From the data on Mn(III)/bromide reaction in 10% H₂O, it was concluded that the reaction involved one-electron intramolecular oxidation of coordinated bromide followed by elimination of Br2⁻⁻, eqn (11).⁵ This mechanism is also applicable to the reaction in this work which retained the second-order dependence on [NaBr] in both glacial and 95% AcOH with two other sources of Mn(III).

$$Mn^{III} + 2NaBr \iff Mn^{III}Br_2 \xrightarrow{HOAc} Mn^{II} + HBr_2$$
 (11)

If a similar, 1 e⁻ mechanism were utilized by the Mn(IV)/NaBr reaction, the observed first order dependence on [NaBr] in glacial acetic acid would require that the much more energetic bromine atom, Br', be released instead of HBr₂'. Even though this possibility cannot be completely excluded, it is considered unlikely, especially in 95% AcOH, where the binding of bromide to Mn(IV) is so strong that the kinetics exhibit saturation. Small amounts of dibromo complex(es) should be easily available, but are clearly not kinetically relevant, suggesting that another mechanism must be at work. We favour a two-electron process of eqn (6) which bypasses halogen radicals and produces HOBr and Mn(II) instead. The observed Br_2/Br_3^- is formed rapidly from HOBr and NaBr in reaction 7. The source of oxygen in HOBr may be a molecule of water from the first or second coordination sphere of manganese. It is less likely that the molecule contains a Mn-oxo group, see later, which rules out a mechanism proposed for the oxidation of nitrite³³ by MnO₂. Also, as mentioned above, the reaction of Br(I) with NaBr in glacial acetic acid must proceed without prior hydrolysis.

The observation of saturation kinetics in 95% AcOH, but not in glacial acetic acid is believed to be caused by weak dissociation of NaBr into free ions in glacial acetic acid. In the presence of 5% water, greater percentage of NaBr is ionized, which facilitates ion pairing and complex formation despite an increase in solvent polarity.

The potential role of Mn(IV) in Mn-catalyzed autoxidation of aromatics will depend on reaction conditions and concentrations of various species involved. At low concentrations of Mn(II) and NaBr, the rate laws for the reactions with Mn(IV) have the same general form (mixed second-order kinetics), and the observed rate constants and activation parameters are similar. Thus, the two reactions will be competitive in a wide range of temperatures if the concentrations of bromide and Mn(II) are low and not too different from each other.

At high and comparable concentrations of Mn(II) and bromide, the reaction of Mn(IV) with Mn(II) will benefit from the fact that the dependence on Mn(II) remains first order, whereas bromide exhibits saturation kinetics. The Mn(IV)/Mn(II) reaction generates Mn(III) which in turn oxidizes bromide to HBr_2 , eqn (11), a key oxidant and hydrogen atom abstracting species in the chain oxidation of aromatic substrates. The Mn(IV)/bromide reaction, on the other hand, produces bromine, which may be involved in the undesirable formation of bromoaromatics and methyl bromide, as well as in the oxidation of solvent. The conditions favouring the Mn(II)/Mn(IV) route should be therefore more productive in the process of catalytic autoxidation of alkylaromatics.

Conclusions

Four independent reactions, including oxidation of Mn(II) with oxygen atom donors and reduction of KMnO₄ by acetic acid are shown to generate a Mn(IV) species. In addition to the most reasonable interpretation of the chemistry generating the manganese product, the assignment of the 4+ oxidation state is based on the magnetic susceptibility data ($\mu = 3.57$ BM) and stoichiometry and products of oxidation of Mn(OAc)₂ and NaBr. The former reaction produces two equivalents of Mn(III) for each equivalent of Mn(IV). The reaction with NaBr generates one equivalent of Br₂/Br₃⁻ with a rate law that exhibits first-order dependence on NaBr.

The data are insufficient to infer the structure of Mn(IV) generated in this work, but, as pointed out by a reviewer, the ready oxidation of $Mn(OAc)_3$ suggests similar structures for the two and points to $Mn^{IV}(OAc)_3^+$ as the most reasonable possibility.

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