

Studies of Manganate(V), -(VI), and -(VII) Tetraoxyanions by Pulse Radiolysis. Optical Spectra of Protonated Forms

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The tetrahedral oxyanions of manganate(VII), -(VI), and -(V) were reduced by pulse radiolytically generated free radicals derived from alcohols or formate and the hydrated electron. The UV–vis spectra of the unstable forms $\text{O}_3\text{Mn}^{\text{V}}(\text{OH})^{2-}$ and $\text{O}_3\text{Mn}^{\text{VI}}(\text{OH})^-$ show bleaching of the low-energy charge transfer bands at 325 and 610 nm that are associated with the fully deprotonated forms MnO_4^{3-} and MnO_4^{2-} , respectively. The corresponding acid dissociation constants were found to be $\text{p}K_{\text{a}}(\text{O}_3\text{Mn}(\text{OH})^{2-}/\text{MnO}_4^{3-}) = 13.7 \pm 0.2$ and $\text{p}K_{\text{a}}(\text{O}_3\text{Mn}(\text{OH})^-/\text{MnO}_4^{2-}) = 7.4 \pm 0.1$. Mononuclear Mn(IV) in 10 M NaOH exhibits a strong UV absorbance and a moderate absorption band at 650 nm. The β -carbon radical derived from *tert*-butyl alcohol adds to an oxo ligand of MnO_4^{2-} to produce a transient hypomanganate(V)–diol pseudo ester. This species hydrolyzes by solvent- and base-dependent pathways in alkaline solutions. A similar reaction occurs between the *tert*-butyl radical and MnO_4^- to form a manganate(VI) ester which is believed to convert to a chelated form. It was found that while the $^{\bullet}\text{CO}_2^-$ radical reduces manganate(VI) to hypomanganate(V) without formation of an observable transient, in reaction with permanganate(VII) it forms an adduct which upon hydrolysis yields manganate(VI). Rate constants for the reduction of manganate species in higher oxidation states by alcohol radicals, $^{\bullet}\text{CO}_2^-$, O_2^- , and e_{aq}^- are reported.

Introduction

Recently we studied the hypervalent oxidation states of iron^{1–3} and chromium⁴ by pulse radiolysis and premix pulse radiolysis. These techniques permit us to generate and study the subsequent reactions of these species as well as their spectral and hydrolytic properties. In this study, we have examined the reactions of reducing radicals ($^{\bullet}\text{CO}_2^-$, O_2^- , e_{aq}^- , alcohol radicals) with the tetraoxyanions of manganese in order to determine some characteristics of manganese(IV), -(V), and -(VI) in aqueous alkali.

The instability of hypomanganate(V) and manganate(VI) in other than strongly alkaline solutions is presumably related to the existence of protonated forms which undergo rapid disproportionation reactions.^{5,6} Lister and Yoshino⁷ estimated from kinetic studies that the protonation of manganate(VI), MnO_4^{2-} , occurs near pH 10 which is substantially higher than the values for the structural analogues $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$ ($\text{p}K(\text{HCrO}_4^-/\text{CrO}_4^{2-}) = 6.5$ at $\mu = 0$)⁸ or $\text{Fe}^{\text{VI}}\text{O}_4^{2-}$ ($\text{p}K(\text{HFeO}_4^-/\text{FeO}_4^{2-}) \approx 7.4$ – 7.8 at $\mu \approx 0.1$ – 0.3 M).^{9–11} A study of the dependence of the formal potential of the $\text{MnO}_4^{2-}/\text{MnO}_4^{3-}$ couple¹² on $[\text{NaOH}]$ is consistent with protonation of hypomanganate(V) in the pH range ≈ 12 – 14 . However, these protonations have not been confirmed by direct spectrophotometric or titrimetric methods.

Spectrophotometrically determined $\text{p}K_{\text{a}}$'s and electronic spectra of the species $\text{O}_3\text{Mn}^{\text{VI}}(\text{OH})^-$ and $\text{O}_3\text{Mn}^{\text{V}}(\text{OH})^{2-}$ are reported in this study.

We have previously used alcohol radicals as reductants for substitutionally inert species such as ferrate(VI) and permanganate(VII).¹³ The site of the electron transfer is presumably the oxy ligands although we have not been able to identify intermediates in these very fast (k 's $> 10^9$ $\text{M}^{-1} \text{s}^{-1}$) redox reactions. In this report we identify adducts of the *tert*-butyl alcohol radical ($^{\bullet}\text{CH}_2\text{C}(\text{OH})(\text{CH}_3)_2$) with manganate(VI) and permanganate(VII) and of the $^{\bullet}\text{CO}_2^-$ radical with permanganate(VII) that appear to be transient manganate(VI)–diol esters. Pseudoesters of this type are believed to be intermediates in the widely used and studied oxidation of olefins by permanganate(VII).^{14–16} Manganate ester intermediates have also been proposed in the oxidations by Mn(VI) as well as oxidations induced by Mn(V).^{17–19}

Earlier pulse radiolysis studies of manganate(VI) and permanganate(VII) reduction in aqueous solutions showed that these strong oxidizing agents react at diffusion-controlled rates with the hydrated electron ($k(\text{Mn}(\text{VI}) + \text{e}_{\text{aq}}^-) = 2.0 \times 10^{10}$ $\text{M}^{-1} \text{s}^{-1}$; $k(\text{Mn}(\text{VII}) + \text{e}_{\text{aq}}^-) = 2.6 \times 10^{10}$ $\text{M}^{-1} \text{s}^{-1}$) and somewhat slower with alcohol radicals ($k(\text{ethanol radical} + \text{Mn}(\text{VII})) = 3.3 \times 10^9$ $\text{M}^{-1} \text{s}^{-1}$; $k(2\text{-propanol radical} + \text{Mn}(\text{VII})) = 7.2 \times 10^9$ $\text{M}^{-1} \text{s}^{-1}$).^{20–23} The oxidation of manganate(VI) by the O^- radical was reported to proceed at a rate of 8×10^8 $\text{M}^{-1} \text{s}^{-1}$.²³

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The identities of oxidation states and products in our studies are defined by the nature of a particular reaction; e.g., it is presumed throughout that Mn(VII) can only go to Mn(VI) upon reaction with e_{aq}^- or such radiation-generated one-electron-reducing radicals as CO_2^- , alcohol radicals, etc. This is one of the main advantages of pulse radiolysis in that the relative simplicity and rapidity of the reactions permit a reasonable identification of short-lived intermediates. However the small amounts (micromoles) of transient product(s) and the limited time scale on which they are observed often prevent the use of more conventional techniques for characterizing the intermediates especially since some high-valent manganese species undergo disproportionation and conproportionation reactions. We have attempted, where possible, to define the nature of transients by considering features of their absorption spectra and kinetic characteristics.

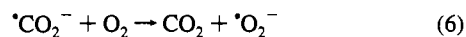
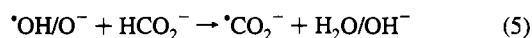
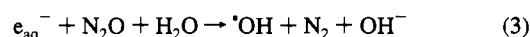
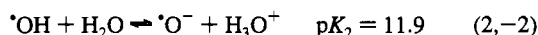
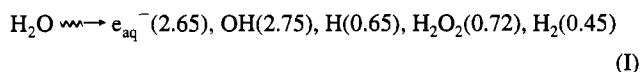
Experimental Section

All chemicals were used as received: methanol (absolute; AR Mallinckrodt); ethanol (200 proof, USP; U.S. Industrial Chemical Co.); 2-propanol (AR Mallinckrodt); *tert*-butyl alcohol (AR Mallinckrodt); NaOH (99.999%, G. F. Smith Chemical Co.); K_2MnO_4 (GFS Chemicals); $KMnO_4$ (Baker Reagent). All solutions were prepared from distilled water that was passed through a Millipore ultrapurification system. Sodium hydroxide solutions were prepared from analytical concentrate (carbonate-free) 10 M NaOH (J. T. Baker Chemical Co.).

Pulse-radiolytic experiments were carried out using a 2 MeV Van de Graaff accelerator which is computer-interfaced with a premixing apparatus consisting of three Hamilton Precision Liquid Dispenser (PDL II) Units. The premix apparatus, which has a dead time of ≈ 100 –200 ms and is computer operated by remote control, serves for the study of unstable reaction mixtures by pulse radiolysis. Pulse lengths of 100–900 ns with doses ranging from 3 to 30 Gy were used. The thiocyanate dosimeter (0.01 M KSCN, 0.026 M N_2O , pH 5.5) was used as a calibrant by taking $G((SCN)_2^-) = 6.13$ (radicals/100 eV absorbed energy) and $\epsilon_{472nm} = 7950 \pm 15 M^{-1} cm^{-1}$. Pulse studies were carried out in a thermostated (25.0 ± 0.3 °C) quartz cell with a 2.0 cm light path. Routine kinetic analysis of transients was performed by on-line least-squares fitting of 2000 absorbance/time data points acquired per run. Complex kinetics were treated using the program INTKIN, developed by Dr. H. A. Schwarz of BNL, which allows direct fitting of these data to complicated reaction schemes.

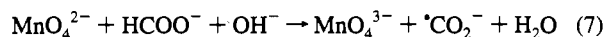
Water exposed to ionizing radiation yields free radicals and molecular products as given by eq 1. The numbers in parentheses in eq 1 are G values, that is, the number of molecules formed or transformed per 100 eV of energy dissipated in water. By use of suitable scavengers, specific oxidizing or reducing conditions can be obtained which allow a particular reaction to be studied in isolation.

In the present study, reducing radicals (alcohol radicals, CO_2^- , O_2^- , and e_{aq}^-) were used to reduce high-valent manganate species to oxidation states that are less stable. The following reactions and equilibria describe the generation of these reducing radicals in alkaline solutions:^{24,25}



The alcohol radicals were generated by pulse radiolysis in N_2O -saturated solutions containing 0.02–0.03 M alcohol. In solutions saturated with argon, the OH radicals are scavenged by alcohol (eq 4) while e_{aq}^- reduces permanganate(VII) or manganate(VI) directly at near-diffusion-controlled rates (vide infra).^{22,25} The CO_2^- and O_2^- radicals were generated in argon- or O_2 -saturated 1.0–20.0 mM formate solutions, respectively.

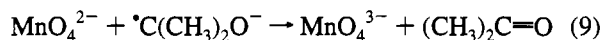
Manganate(VI) solutions were prepared by dissolving K_2MnO_4 in alkali. The solutions were filtered to remove MnO_2 and analyzed spectrophotometrically by assuming $\epsilon_{610nm} = 1500 M^{-1} cm^{-1}$.²² Solutions of hypomanganate(V) were prepared by addition of an excess of sodium formate to manganate(VI) in 10 M NaOH. While formate reduces manganate(VI) quantitatively to hypomanganate at a rate of $k_7 = 0.44 \pm 0.08 M^{-1} s^{-1}$, the latter does not react significantly with formate. This was confirmed by maintenance of an isosbestic point in the Mn(VI)/Mn(V) spectra at 657 nm¹⁶ and the observation of the well-known spectrum of the blue MnO_4^{3-} ,^{16,26} which is stable under these conditions for at least 25–30 min. The stoichiometry of this reaction, as observed at 420 nm, is a 2:1 $MnO_4^{2-}:HCO_2^-$ ratio. Since, $k_8 \gg k_7$ (vide infra), there is an uncertainty as to whether the reduction occurs in a 2-e step or in two 1-e steps, e.g., (7) or (8).



The extinction coefficients of hypomanganate(V) were calculated on the basis of a quantitative conversion of manganate(VI) to hypomanganate(V) by the formate reaction (Cary 210 scans) and under pulse radiolytic conditions from the known concentration of alcohol radicals generated per pulse. In the latter technique, spectra are obtained by evaluating at a given wavelength $\Delta Abs/[free radicals]_{tot}$ and correcting the resulting value by the extinction of the parent compound. The final extinction coefficients are then plotted as a function of wavelength (point-by-point spectra).

Results

Reduction of Manganate(VI) by Alcohol Radicals. It was previously shown¹³ that radicals derived from 2-propanol and ethanol efficiently reduce permanganate(VII) and ferrate(VI) with rate constants greater than $10^9 M^{-1} s^{-1}$. These alcohol radicals are strong reductants since electron transfer yields stable carbonyl compounds. In alkali the α -carbon radicals are deprotonated ($pK_a(^*CH(CH_3)OH/^*CH(CH_3)O^-) = 11.51$,²⁷ 11.6,²⁸ $pK_a(^*C(CH_3)_2OH/^*C(CH_3)_2O^-) = 12.03$,²⁷ 12.2²⁸). The rate constants for the reduction of manganate(VI) to hypomanganate(V) by alcohol radicals (methanol, ethanol, 2-propanol, and *tert*-butyl alcohol), e.g. (9), were determined at 610 nm under first-



order conditions ($[manganate(VI)]_0 = 50$ –250 μM) in 0.1 M NaOH and are listed in Table 1.

Determination of $pK_a(O_3MnOH^-/MnO_4^{2-})$ and $pK_a(O_3MnOH^{2-}/MnO_4^{3-})$. MnO_4^{2-} and MnO_4^{3-} become unstable upon protonation. Therefore, one-electron reductions by free radicals

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Table 1. Rate Constants of Reactions of Free Radicals with MnO_4^{2-} and MnO_4^-

substrate	radical	$k(\text{MnO}_4^{2-}), \text{M}^{-1} \text{s}^{-1}$	$k(\text{MnO}_4^-), \text{M}^{-1} \text{s}^{-1}$
CH_3OH	$\cdot\text{CH}_2\text{O}^-$	$(1.9 \pm 0.2) \times 10^9^a$	
$\text{CH}_3\text{CH}_2\text{OH}$	CH_3CHO^-	$(1.8 \pm 0.2) \times 10^9^a$	$(3.30 \pm 0.5) \times 10^9^b$
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	$\text{CH}_3\text{C}^*(\text{O}^-)\text{CH}_3$	$(2.0 \pm 0.2) \times 10^9^a$	$(7.20 \pm 1.0) \times 10^9^a$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)_2$	$\cdot\text{CH}_2\text{C}(\text{OH})(\text{CH}_3)_2$	$(3.3 \pm 0.3) \times 10^8^a$	$(1.85 \pm 0.2) \times 10^9^c$
HCO_2^-	$\cdot\text{CO}_2^-$	$(8.1 \pm 1.0) \times 10^8^d$	$(6.90 \pm 0.5) \times 10^9^d$
O_2	$\cdot\text{O}_2^-$	$(1.8 \pm 0.2) \times 10^3^d$	$(9.50 \pm 1.0) \times 10^5^d$

^a The observed rate constants are averages of ≥ 8 runs at 25 °C in 0.1 M NaOH. ^b From ref 13 at pH 10.4 (alcohol radicals are in the protonated forms). ^c Premix pulse radiolysis at pH 9.4, 0.05 M Na_2HPO_4 /borate buffer at 23 ± 1 °C. ^d 1.0 M NaOH, at 25 °C.

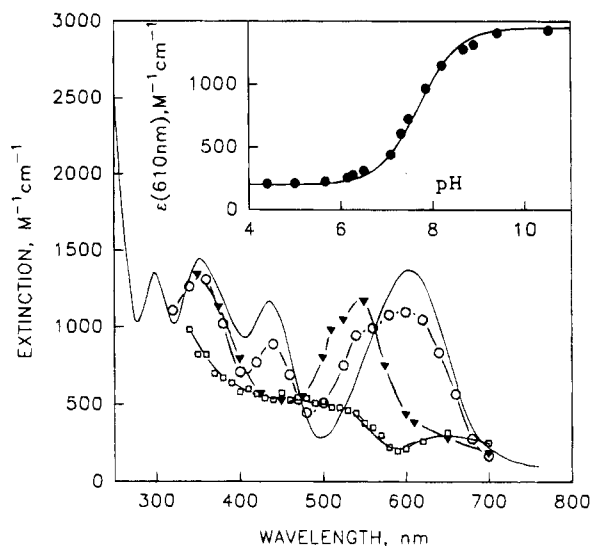
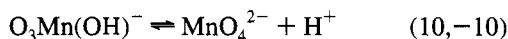


Figure 1. Spectrum of $\text{O}_3\text{Mn}(\text{OH})^-$ (\square) in argon-purged 0.025 M phosphate, 0.1 M ethanol, pH 4, spectrum of MnO_4^{2-} (solid curve) in 0.1 M NaOH, and manganate(VI) adduct spectra of the $\cdot\text{CO}_2^-$ radical (\circ) in N_2O -saturated 2 mM formate and of the *tert*-butyl alcohol radical (\blacktriangledown) in N_2O -saturated 0.1 M *tert*-butyl alcohol solution at pH 9.4 (≈ 1 mM borate buffer). These spectra were recorded 2–10 μs after the pulse. The inset shows the pH dependence of the manganate(VI) extinction coefficient at 610 nm in 0.025 M phosphate buffer, 0.1 M ethanol. The solid line was calculated using $\text{p}K_{10} = 7.4$.

of either MnO_4^- (which is stable from pH 1 to 13) or MnO_4^{2-} (pH > 12) is a convenient method for accurately determining spectral changes which arise from protonation of the corresponding reduced manganese species.

The spectra of manganate(VI) in the pH range 4–9 were determined by reducing permanganate(VII) with ethanol radicals and e_{aq}^- in 0.25 M phosphate buffers containing 0.1 M ethanol (Figure 1). The pH dependence of the molar extinction coefficient of manganate(VI) at 610 nm (inset of Figure 1) indicates that MnO_4^{2-} has a $\text{p}K_{10}$ of 7.4 ± 0.1 :



We did not observe significant disproportionation of $\text{O}_3\text{Mn}(\text{OH})^-$ to produce Mn(VII) at pH 4 over a 1 s observation period. The small amount of Mn(VI) (micromolar range) produced by the pulse would require a bimolecular rate in excess of $\approx 10^5 \text{M}^{-1} \text{s}^{-1}$ to detect this process. The assignment of the spectrum in Figure 1 (measured $\approx 2 \mu\text{s}$ after the pulse and stable for ≈ 1 s afterward) to a form of Mn(VI) is shown by the fact that it deprotonates (10, -10) to form MnO_4^{2-} .

Figure 2 shows the spectra of hypomanganate(V) obtained by scanning a 10 M NaOH solution in which manganate(VI) was reduced by formate and the point-by-point spectrum obtained by the ethanol radical reduction of manganate(VI) in 0.01 M NaOH ($\mu = 2.0$, adjusted with NaCl). As is apparent from Figure 3, the absorbance of hypomanganate(V) at 325 nm is sensitive to pH change in the range $0.01 \text{M} \leq [\text{NaOH}]_0 \leq$

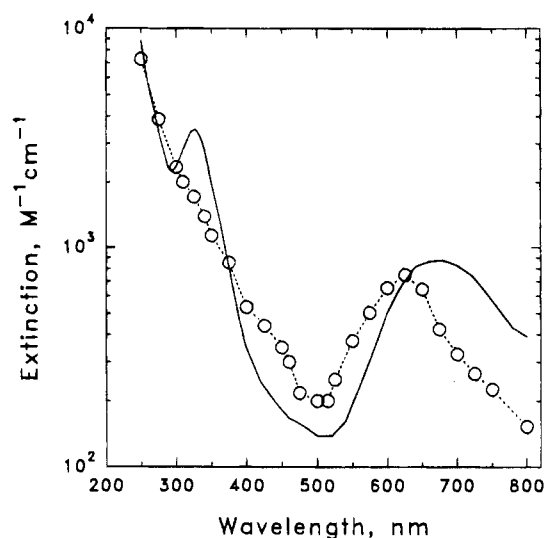


Figure 2. Scanned (solid line) spectrum of MnO_4^{3-} in 10 M NaOH compared with the point-by-point (\circ) spectrum of $\text{O}_3\text{Mn}(\text{OH})^{2-}$ obtained by the pulse-radiolytic reduction of MnO_4^{2-} in 0.01 M NaOH.

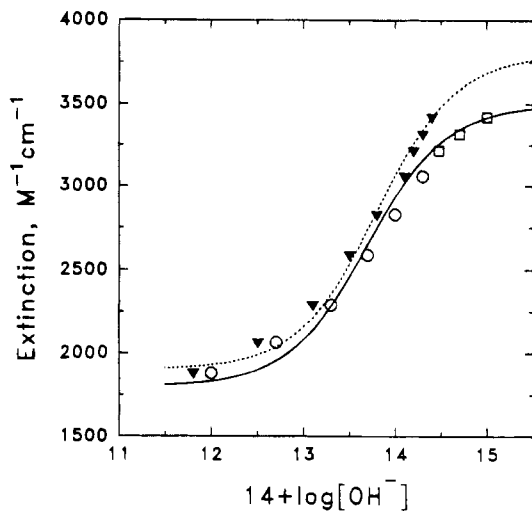
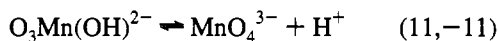


Figure 3. Plots of molar extinction coefficients at 325 nm of hypomanganate(V) as a function of pH ($[\text{NaOH}]$ range from 0.01 to 10 M). (\circ , \square) The curve is calculated assuming $[\text{OH}^-]$ is equivalent to $[\text{NaOH}]$; (\blacktriangledown) $[\text{OH}^-]$ is corrected for sodium ion hydrolysis (vide infra). Pulse radiolysis measurements (\circ) were obtained at constant ionic strength ($\mu = 2.0 \text{M}$, NaCl). Points (\square) at 3, 5, and 10 M NaOH were measured using solutions of hypomanganate(V) prepared by formate reduction of manganate(VI). The solid curve reflects $\text{p}K_{11}(\text{O}_3\text{Mn}(\text{OH})^{2-}/\text{MnO}_4^{3-}) = 13.7$, and the dashed curve through the corrected points (\blacktriangledown) is calculated for $\text{p}K_{11} = 13.6$.

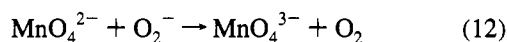
10.0 M. In the range between 0.01 and 2.0 M, the ionic strength was maintained at a constant $\mu = 2.0 \text{M}$ by addition of appropriate amounts of NaCl. Above 3.0 M NaOH, hypomanganate(V) solutions were sufficiently stable to be scanned in a Cary 210 spectrophotometer. In Figure 3, the extinction coefficients are plotted with the simplification that $[\text{OH}^-] =$

[NaOH]. In spite of some deviation from a sigmoidal shape, the dependence of the 325 nm absorption on [NaOH] suggests a $pK_{11} \approx \text{pH } 13.7$:



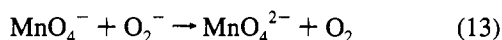
An alternative evaluation of the data was carried out by assuming that the concentration of free hydroxide ion is reduced by ion-pairing between sodium and hydroxide ions. The association constant is about 0.3 M^{-1} at high ionic strength,²⁹ and recalculation of $[\text{OH}^-]$ according to the approximation $[\text{OH}^-] \approx [\text{NaOH}]/(1 + 0.3[\text{Na}^+])$ leads to the alternate curve (solid triangles) in Figure 3. The best fit in this case is also consistent with $pK_{11} \approx 13.7$, but it suggests that some $\text{O}_3\text{Mn}(\text{OH})^{2-}$ may be present in 10 M NaOH solution.

Reduction of Manganate(VI) by $\cdot\text{CO}_2^-$ and O_2^- . The reaction of formate with MnO_4^{2-} is sufficiently slow that pulse irradiation of these solutions was possible without the use of the premixing technique. In N_2O -saturated formate solutions, the strongly reducing $\cdot\text{CO}_2^-$ radical generated by reactions 3 and 5 reduces manganate(VI) to hypomanganate(V) with a $k_8(\text{MnO}_4^{2-} + \text{CO}_2^-) = (8.0 \pm 1.0) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in 1.0 M NaOH. No transients were observed in these experiments. In presence of dioxygen, $\cdot\text{CO}_2^-$ reduces O_2 to the much weaker reductant O_2^- (reaction 6) which reacts with MnO_4^{2-} (reaction 12) at a relatively slower rate, $k_{12} = (1.8 \pm 0.2) \times 10^3 \text{ M}^{-1}$

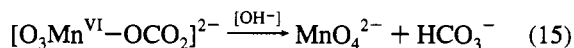


s^{-1} . Under conditions where O_2 and manganate(VI) compete for $\cdot\text{CO}_2^-$, the intermediacy of O_2^- radicals does not affect the overall stoichiometry of manganate reduction. In the latter case, the corresponding kinetic traces show a fast and slow component that are resolvable.

Reactions of $\cdot\text{CO}_2^-$ and O_2^- with Permanganate(VII). The rate constants for reactions of $\cdot\text{CO}_2^-$ and O_2^- radicals with permanganate(VII) were studied by the premix pulse radiolysis technique because of the relatively rapid reaction between MnO_4^- and formate. A N_2O -saturated KMnO_4 solution was mixed with a buffer (0.1 M $\text{Na}_2\text{HPO}_4/\text{borate}$; pH 9.4) containing formate that was saturated with either argon or oxygen, depending on which of the two radicals ($\cdot\text{CO}_2^-$ or O_2^-) was being studied. The reaction of O_2^- with MnO_4^- occurs without observable intermediates as expected, and the measured second-order rate constant is $k_{13} = (9.5 \pm 0.8) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.



In the absence of dioxygen, the initial interaction between the $\cdot\text{CO}_2^-$ radical and MnO_4^- produces an intermediate which hydrolyzes to give the final spectrum of MnO_4^{2-} . This is presumed to be an adduct to an oxygen ligand of permanganate-(VII) since its spectrum differs only slightly from that of manganate(VI). The overall process is suggested to occur by reactions 14 and 15. The spectrum of the manganate(VI)-car-



bonate complex is shown in Figure 1. Reaction 15 occurs at a rate $k_{15} = 80 \pm 10 \text{ s}^{-1}$ under the conditions of the experiment.

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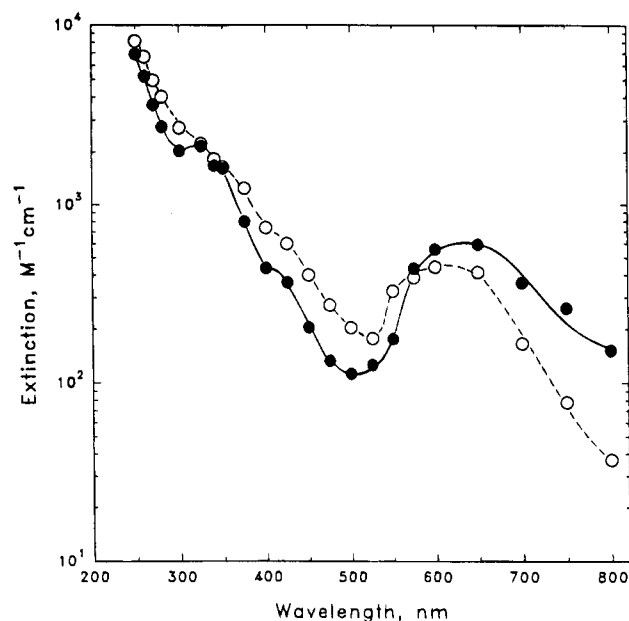
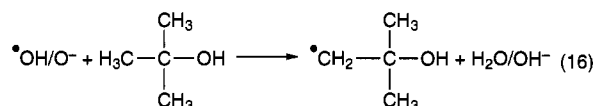


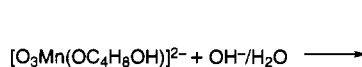
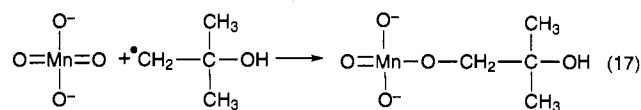
Figure 4. Point-by-point spectrum (○), measured 50 μs after the pulse, of the Mn(V) ester formed by the reaction of *tert*-butyl alcohol radicals with MnO_4^{2-} in 1 M NaOH. The spectrum (○) of A, in reaction 18, decays to the final spectrum (●) of B ($\text{MnO}_4^{3-}/\text{O}_3\text{Mn}(\text{OH})^{2-}$); 1.0 M NaOH and 25 °C.

Reaction of Manganate(VI) with the *tert*-Butyl Alcohol. Hydrogen abstraction by OH radicals from *tert*-butyl alcohol (reaction 16) produces primarily β -carbon radicals which

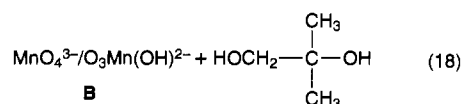


dimerize rapidly.³⁰ Not only are these radicals capable of oxidizing low-valent metals through metal-carbon-bonded intermediates,^{31,32} but as is being shown in this study, they are also good one-electron-reducing agents for high-valent manganates.

tert-Butyl alcohol radicals generated (reaction 16) in 0.025–2.0 M NaOH solutions reduce manganate(VI) to hypomanganate(V). For measurements at low base concentrations ($[\text{NaOH}] < 0.05 \text{ M}$), where manganate(VI) solutions become unstable, powdered K_2MnO_4 was added to the N_2O -saturated 0.05 M *tert*-butyl alcohol solutions and pulse-irradiated within 1 min. The concentration of $\text{K}_2\text{MnO}_4 \approx 100 \mu\text{M}$ in these solutions was measured independently. The overall reduction proceeds by the formation of a transient (A) that has an absorption spectrum similar to that of $\text{O}_3\text{Mn}(\text{OH})^{2-}$ and which subsequently decays by a true first-order process to give the spectrum of $\text{MnO}_4^{3-}/\text{O}_3\text{Mn}(\text{OH})^{2-}$. The spectra of the intermediate (A) and of the final product (B) are shown in Figure 4. Reactions 17 and 18



A



B

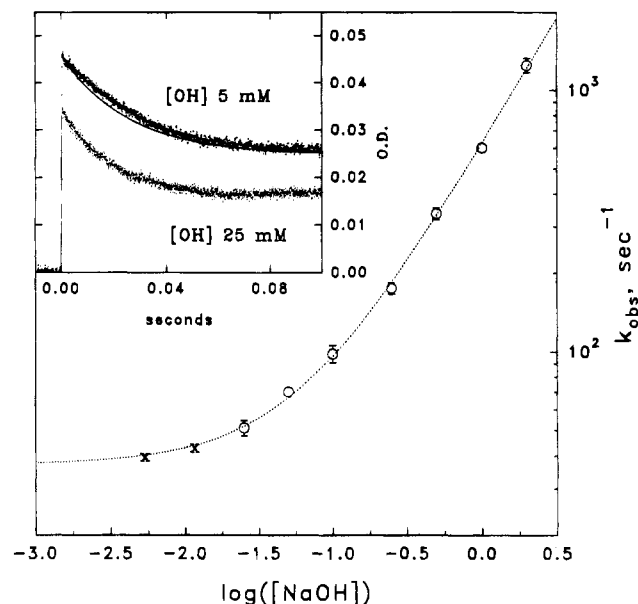


Figure 5. Dependence of the first-order rate of hydrolysis of the Mn(V) ester (reaction 14) on $[\text{NaOH}]$ at 25 °C. All experiments were carried out at $\mu = 1.0 \text{ M}$ ($\text{NaOH} + \text{NaClO}_4$) except for the run in 2.0 M NaOH. The data were fitted by the rate law described in the text. Inset: Decay of the *tert*-butyl alcohol radical adduct observed at 280 nm in 5 mM NaOH (upper trace) and 25 mM NaOH (lower trace). The upper trace was fitted using reactions 18 and 19,-19. The deviation from a single-exponential decay is indicated by the line calculated using reaction 18 alone. Calculated decay rates at 5 and 10 mM NaOH are indicated by x in the main figure.

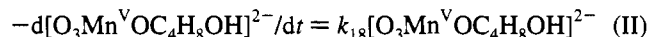
Table 2. Rates of Hydrolysis of the $\text{O}_3\text{Mn}^{\text{V}}(\text{OC}_4\text{H}_8\text{OH})_2^{2-}$ Ester^a

$[\text{NaOH}]$	$k_{\text{obs}}, \text{s}^{-1}$	$[\text{NaOH}]$	$k_{\text{obs}}, \text{s}^{-1}$
0.025	50 ± 3	0.50	337 ± 18
0.050	70 ± 3	1.00	602 ± 17
0.10	98 ± 7	2.00	1250 ± 50
0.25	175 ± 9		

^a The observed rate constants are averages of ≥ 6 runs measured at 25 °C and 1 M ionic strength ($\text{NaClO}_4 + \text{NaOH}$) except the last run at 2 M NaOH.

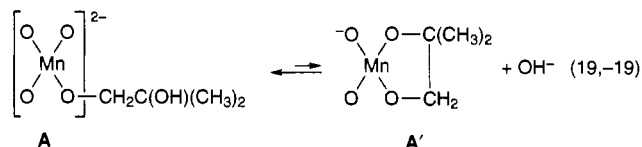
are consistent with these assignments and $k_{17} = (3.3 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{18}(\text{obs}) = 600 \pm 17 \text{ s}^{-1}$ in 0.1 M NaOH containing 0.9 M NaClO_4 ($\mu = 1.0 \text{ M}$).

The rate of reaction 18 was measured over the range $0.025 \text{ M} \leq [\text{NaOH}] \leq 2.0 \text{ M}$. This dependence is shown in Figure 5. The rate decreases with $[\text{NaOH}]$ becoming base independent at $[\text{NaOH}] < 10 \text{ mM}$. A good fit to the data is achieved using eq II, in which the hypomanganate(V) pseudoester decays by



solvent- and base-catalyzed pathways and where $k_{18} = k_{\text{aq}} + k_{\text{base}}[\text{OH}^-]$. The rate constants were evaluated as $k_{\text{aq}} = 37 \pm 3 \text{ s}^{-1}$ and $k_{\text{base}} = 590 \pm 10 \text{ M}^{-1} \text{ s}^{-1}$ by a nonlinear least squares fit.

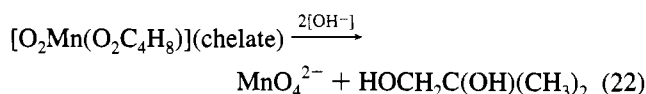
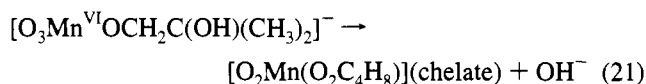
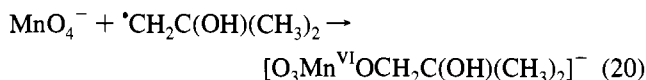
When the measurements were extended to 5 and 10 mM NaOH, the decay of the hypomanganate(V) ester exhibited small but significant deviations from first-order behavior amounting to an inhibition of the hydrolysis reaction. A comparison of kinetic traces obtained at $[\text{NaOH}] = 5$ and 25 mM is illustrated in Figure 5. In the 5 mM NaOH experiment, the trace requires a fit to two exponentials. The weakly inhibiting effect can be explained if one assumes that a small amount of the chelated diester, A', is in equilibrium with A in (19,-19). As can be seen from the inset of Figure 5, the equilibrium (19,-19) is



most likely shifted well to the left ($\approx 90\%$) in 5 mM NaOH and is negligible in 25 mM NaOH. If $k_{19} \approx k_{\text{aq}}$ and $k_{-19}/k_{\text{base}} = 100$, the observed behavior is accounted for.³³

It should be noted that we did not observe pulse-generated micromolar amounts of Mn(V) to undergo significant decomposition within 300 ms (the longest period of observation) even at base concentrations of 0.01 M although stock solutions of MnO_4^{3-} decompose rapidly in 2 M NaOH. Under our conditions, the Mn(V) ester always decomposes by dissociation to MnO_4^{3-} (reaction 18) and the organic product on a much shorter time scale. Also, because the small amounts generated by the pulse favor the first-order dissociation of the ester, it could not be determined whether the Mn(V) ester also decomposes by a second-order pathway.

The interaction of *tert*-butyl alcohol radicals with permanganate(VII) produces what is likely a fully chelated manganate(VI) ester. This reaction was studied only at pH 9.4. The *tert*-butyl radicals initially react with MnO_4^- at a rate $k_{20} = (1.85 \pm 0.20) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ to produce a spectrum that appears similar to that of MnO_4^{2-} or $[\text{O}_3\text{Mn}^{\text{VI}}\text{OCO}_2]^{2-}$. Then a first-order process ($k_{21} = 55.0 \pm 10.0 \text{ s}^{-1}$) is observed that produces a relatively small spectral shift which suggests formation of a second transient. The decay of this second intermediate to MnO_4^{2-} and the *tert*-butyl alcohol oxidation product occurs at a rate of $k_{22} = 0.8 \pm 0.2 \text{ s}^{-1}$. The overall mechanism proposed for this system is described by reactions 20-22.



Unlike the case of the hypomanganate complex, the rationale for proposing that chelation goes virtually to completion in this system is based on the very slow rate at which the Mn(VI) adduct decays to give the free tetraoxoanion in comparison to the fast hydrolysis of the carbonate complex described earlier. An approximately 100-fold increase in complex stability is consistent with a chelated form. The rate of the proposed ring-closure step is about the same as the rate of the dissociation of carbonate from the $[\text{O}_3\text{Mn}^{\text{VI}}]$ moiety proposed in reaction 15. This seems reasonable if MnO_4^{2-} forms relatively weak complexes with oxygen ligands of this type.

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(33) Kinetic traces at 5, 10, and 25 mM NaOH were fitted by numerical integration of (18) and (19,-19). The presumed chelated Mn(V) diester of hypomanganate(V) was assumed to absorb $\approx 30\%$ more strongly than the monoester. It was assumed that aquation and chelation occur at the same rate ($k_{\text{aq}} = k_{18}$) and that dechelation is mainly base-catalyzed but that its rate is about 2 orders of magnitude greater than k_{base} . This reduces to the simpler rate expression (II) at $[\text{NaOH}] \geq 25 \text{ mM}$.

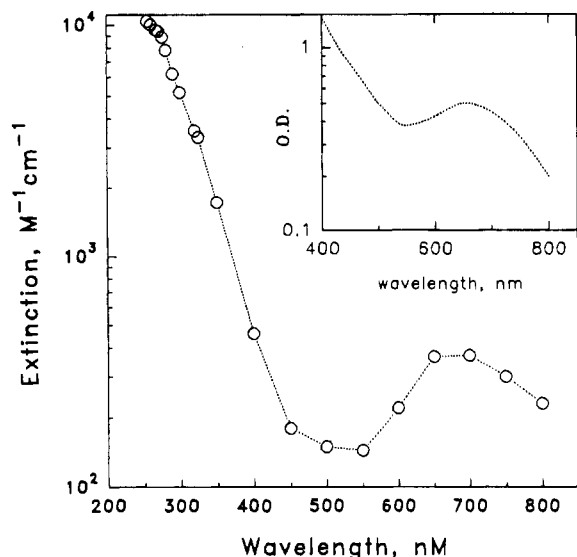
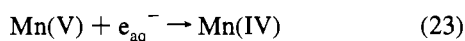


Figure 6. Point-by-point absorption spectrum (○) of Mn(IV) in 10 M NaOH obtained by pulse-radiolytic reduction of MnO_4^{3-} with $\cdot\text{CO}_2^-$ radicals and e_{aq}^- . Measurements of the absorption differences were made $\approx 5 \mu\text{s}$ after the pulse. Inset: Spectrum of MnO_2 dissolved in concentrated KOH (adapted from ref 34).

One-Electron Reduction of Hypomanganate(V) to Manganate(IV) in 10 N NaOH. Manganate(IV) is conveniently generated from hypomanganate(V) by reduction with e_{aq}^- and $\cdot\text{CO}_2^-$ radicals in argon-saturated 10 M NaOH solutions containing formate. The spectrum of manganate(IV) is shown in Figure 6. Reaction 23 was studied by monitoring the decay



of e_{aq}^- at 600 nm where its absorption coefficient is $\epsilon = 12\,500 \text{ M}^{-1} \text{ cm}^{-1}$.²⁵ The value of $k_{23} = (5.0 \pm 1.0) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is less than the essentially diffusion-controlled values ($2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) reported earlier²⁵ for the corresponding reactions with MnO_4^- and MnO_4^{2-} . This difference may be due to the high viscosity of the 10 M NaOH medium.

Mononuclear Mn(IV) would likely be blue or blue-green on the basis of the spectral characteristics shown in Figure 6. The dissolution of pyrolusite (MnO_2) in concentrated base³⁴ gives a spectrum (inset in Figure 6) which is similar to that obtained under our conditions but is likely to be that of a polynuclear Mn(IV) species (see Discussion).

Discussion

The protonation of MnO_4^{2-} occurs at a pH which is typical of oxydianions and well below the estimate from kinetic data of Yoshino and Lister.⁷ As in the case of $\text{O}_3\text{Fe}^{\text{VI}}(\text{OH})^-$, the characteristic strong bands of the dianions {at 510 nm for FeO_4^{2-} ($3d^2$) and at 610 nm for MnO_4^{2-} ($3d^1$)} are virtually eliminated in the monoprotonated forms. The intense spectra of transition metal oxyanions are usually attributed to transitions within molecular orbitals which are formed by mixing of the metal and ligand orbitals³⁵ although the exact assignment of these bands is difficult.³⁶⁻³⁸ An investigation of the spectra of chromate(VI) esters (type $\text{O}_3\text{Cr}(\text{OR})^-$; R = H, alkyl, acyl) showed that the lowest energy band of CrO_4^{2-} is greatly diminished in intensity by the substitution of an O^{2-} ligand but

that the nature of R has relatively little effect.³⁹ This is considered consistent with the characterization of these bands as charge transfer in origin since protonation or alkylation of an oxide ligand reduces the overlap between ligand p_π orbitals and the metal d_π system—hence the weaker intensity of the transition. The strong bands of MnO_4^- (525 nm) and of MnO_4^{3-} (325 nm) have been similarly characterized as charge transfer bands.^{38,40}

The effect of protonation on these bands appears to be analogous in all the described systems. Muller et al.⁴¹ suggested that protonation affects orbital energies by reducing π -antibonding interactions between oxide ligands and the metal d orbitals. The sensitivity of the manganate(VI) absorptions indicates that the prominent spectral features of $\text{MnO}_4^{2-}/\text{O}_3\text{Mn}(\text{OR})^-$ are of the charge transfer type. These are also consistent with our assumption in the case of the *tert*-butyl alcohol and $\cdot\text{CO}_2^-$ radical adducts that these are derivatives with essentially the same coordination sphere as MnO_4^{2-} , since the bands, while shifted, remain very similar to that of the green ion.

The tetrahedral structure of MnO_4^{3-} ($3d^2$) has been demonstrated by substitution of hypomanganate(V) into crystalline phosphates where its absorption spectrum is virtually the same as that in concentrated NaOH solutions.⁴² MnO_4^{3-} protonates at a relatively high pH ($\text{p}K_{10} = 13.7$) in contrast to PO_4^{3-} ($\text{p}K(\text{HPO}_4^{2-}) = 12.2, \mu = 1.0 \text{ M}$)⁴³ or VO_4^{3-} ($\text{p}K(\text{O}_3\text{V}(\text{OH})^{2-}) = 13.2, \mu = 3.0 \text{ M}$)⁴⁴ with a resulting intensity loss of the 325 nm peak. The absorption maximum of $\text{O}_3\text{Mn}(\text{OH})^{2-}$ ($\approx 650 \text{ nm}$) is, however, only slightly shifted (670 nm) upon deprotonation to MnO_4^{3-} . This suggests that the previous assignment of the absorption(s) at longer wavelengths to a d-d transition⁴⁰ is likely correct since protonation of a ligand should have a relatively small effect upon the t_2-e energy gap in metal-centered orbitals.

It remains uncertain to what extent the hypomanganate(V) ion is fully deprotonated in strong base. The relatively constant absorption spectrum in $> 5 \text{ M}$ NaOH solutions could be due to the progressively lower concentrations of free hydroxide ion in more concentrated base although this effect is difficult to quantitate. The plateauing in the absorbance vs $[\text{OH}^-]$ curve (open symbols) above $\approx 5 \text{ M}$ NaOH in Figure 3 reflects nearly complete formation of the trianion when one assumes that $[\text{NaOH}] = [\text{OH}^-]$. In support of this, Carrington et al.³⁶ have shown that the $\text{MnO}_4^{2-}/\text{MnO}_4^{3-}$ formal potential becomes constant at $[\text{NaOH}] \geq 6 \text{ M}$. Protonation may compete with extensive ion-pairing between MnO_4^{3-} and sodium ions under these extreme conditions, and this may account for the deviations from a sigmoidal shape in the Figure 3 data. An alternative treatment, which accounts for a presumed reduction of free hydroxide anion due to pairing with Na^+ , suggests that about 15% of hypomanganate(V) may be present as HMnO_4^{2-} in 10 M NaOH. This does not significantly change the best-fit value of $\text{p}K_{11}$ owing to an uncertainty in the actual extinction coefficient of MnO_4^{3-} at 325 nm ($\epsilon = 3600 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$, Figure 3). The markedly increased stability with respect to second-order disproportionation to MnO_2 and MnO_4^{2-} (≈ 200 -fold) of MnO_4^{3-} in 10 M NaOH relative to 3 M NaOH⁶ is likely

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due to specific properties of the concentrated alkali (e.g. viscosity and low free water content) as well as changes in the amount of protonated hypomanganate(V).

Approximately the same spectral changes which arise from protonation of MnO_4^{3-} are observed when the *tert*-butyl alcohol radical reacts with MnO_4^{2-} (Figure 4), which accords with our supposition that an ester link through an oxygen ligand has been formed. It is possible that the radical might attach directly to the metal atom, since 5-coordinate Mn(V) complexes have been characterized,⁴⁵ rather than to an oxygen ligand. The relatively slow exchange of oxygen ligands with solvent water⁴⁶ renders an inner-sphere attack upon the metal center rather less likely than attack upon the oxygen ligands. The close similarity in the spectra of $\text{O}_3\text{Mn}(\text{OH})^{2-}$ and $\text{O}_3\text{Mn}(\text{OC}_4\text{H}_8\text{OH})^{2-}$ is consistent with hypomanganate(V) having the same inner coordination sphere. After hydrolysis, 2-methylpropane-1,2-diol is the only plausible organic oxidation product of the *tert*-butyl alcohol radical.

The Mn(V) pseudoester formed in reaction 17 is most likely not a chelated form although the vicinal hydroxyl functions would permit such rearrangement. This reaction complicates the hydrolysis kinetics at lower pH. The rate law for hydrolysis of the $[\text{O}_3\text{Mn}^{\text{V}}(\text{OC}_4\text{H}_8\text{OH})]^{2-}$ ester indicates that the $\text{O}_3\text{Mn}^{\text{V}}(\text{OR})^{2-}$ system is fairly labile ($k_{\text{aquation}} = 37 \text{ s}^{-1}$) and susceptible to inner-sphere attack by strong nucleophiles like OH^- . It is of interest to note that Mn(V)-diol esters have long been proposed as intermediates in the oxidation of olefins to diols by permanganate(VII), a process in which oxygen atoms from Mn(VII) are incorporated into the diol. However, in spite of numerous studies, their direct observation as intermediates has been elusive. Our data indicate that manganese(V) esters are unstable in alkali but that their decomposition may be sufficiently slow to be detected by stopped-flow techniques if they are formed rapidly. A complication for detection of hypomanganate(V) intermediates in these systems is the fast ($>10^4 \text{ M}^{-1} \text{ s}^{-1}$) reaction between permanganate(VII) and hypomanganate(V).⁴⁷ The latter has been detected in the reaction of sulfite with permanganate(VII) by rapid-scanning techniques.⁴⁸

The reactions of $\cdot\text{CO}_2^-$ and *tert*-butyl alcohol radicals with

MnO_4^- produce ligand adducts that ultimately hydrolyze at very different rates. The very slow rate of formation of free MnO_4^{2-} from the *tert*-butyl alcohol adduct in comparison to the carbonate adduct strongly suggests that the ligand is chelated in this case. Since, at present, knowledge of the aqueous chemistry of complexed manganate(V) and manganese(VI) is limited, further investigations of these derivatives will be necessary to fully characterize them.

The absorption spectrum of aqueous mononuclear manganate(IV) has not been reported previously. The spectrum of pyrolusite dissolved in concentrated KOH shows a maximum at 650 nm, but its closeness to hypomanganate(V) signal (670 nm) and the absence of an ESR signal led Lott et al.³⁴ to conclude that disproportionation of manganate(IV) in strong alkali to Mn(III) and hypomanganate(V) is spontaneous. They noted that octahedrally coordinated Mn(IV) oxalate in $\text{K}_2\text{Mn}(\text{C}_2\text{O}_4)_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ ⁴⁹ gives similar green solutions as do some mixed-valence complexes such as $\text{Mn}^{\text{III,IV}}$ EDDA.⁵⁰ It is likely that the ESR silence of Mn(IV) (d^3) in pyrolusite solutions was due to the dimeric or polymeric nature of Mn(IV). Solutions of the Mn(IV) oxalate complex are also ESR silent presumably because they contain μ -oxo-bridged Mn(IV) dimers.⁵¹ The increased absorbance at 400–500 nm relative to the 650 nm absorption in the pyrolusite spectrum may be characteristic of hydrolytic linkages. If so, the yellow/brown colors of various soluble Mn(IV) products⁵² obtained after permanganate oxidations suggest that these are highly polymeric.

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