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Oxidation of Ethylenediaminetetraacetic Acid by Permanganate Ion: A Kinetic Study

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Potassium permanganate oxidizes ethylenediaminetetraacetic acid (EDTA) to ethylenediamine-*N*,*N'*,*N'*-triacetic acid (EDTRI) and CO_2 in acidic (pH 3–5) perchlorate media. The reaction proceeds through an intermediate, the formation of which is first-order in each reactant. The bimolecular rate constant at 25 °C is calculated to be 0.23 $M^{-1}\ s^{-1}$ at pH 4.4. The rate constants for the formation of the intermediate initially decrease with decreasing $[H^+]$ and pass through a minimum near pH 4.0. The biomolecular rate constants, 0.52 $M^{-1}\ s^{-1}$ and 0.40 $M^{-1}\ s^{-1}$, are calculated at pH 3.0 and 5.0. The magnetic moment of the intermediate, 4.9 μ_B, supports a Mn(III) species as a long-lived intermediate. Electrochemical and electronic spectroscopic data are also consistent with the formation of a Mn(III) intermediate in which EDTA or partially oxidized EDTA is coordinated to the manganese center. The reduction potential for the intermediate was measured to be 0.59 V vs SCE, which can be compared with 0.57 V vs SCE for the $Mn^{III}(EDTA) + e \rightleftharpoons Mn^{II}(EDTA)$ electrode reaction. The intermediate decays to products by a first-order process ($k = 2.2 \times 10^{-3}\ s^{-1}$ at pH 4.4), and the rate constants increase with decreasing $[H^+]$ in the pH range 3–4 and then level off at pH > 4. Intramolecular electron-transfer processes within the intermediate led to products Mn(II), EDTRI, and CO_2. The decomposition of the intermediate is significantly retarded in the presence of pyrophosphate ion. The rate data are consistent with a mechanism in which pyrophosphate ion complexes with the intermediate with an estimated formation constant of $1.1 \times 10^2\ M^{-1}$. The phosphato complex also decomposes by a first-order process ($k = 1.5 \times 10^{-5}\ s^{-1}$) presumably through an intramolecular electron-transfer mechanism.

Introduction

In an earlier study[1] we showed that (carboxylato)oxochromium(V) complexes oxidize ethylenediaminetetraacetic acid (EDTA) to ethylenediaminetriacetic acid (EDTRI) and CO_2. This six-electron oxidation proceeds through a Cr(V)–EDTA intermediate, which undergoes rapid internal electron transfer to yield Cr(III) and the EDTA oxidized products. Although this system yielded information regarding substitution at the hypervalent chromium(V) center, mechanistic details for the multielectron EDTA oxidation remained largely unknown. Here we describe the EDTA oxidation by permanganate in the pH range 4–5, a process that proceeds through a Mn(III) intermediate. Although the oxidant potassium permanganate and the sequestrant ethylenediaminetetraacetic acid have long been key items in the chemist's armamentarium, surprisingly little systematic attention[2] appears to have been devoted to the direct reaction between these laboratory staples. The present study provides a detailed kinetic picture for oxidation of this amino polycarboxylic acid including the characterization of major oxidation products and the growth and decay of the less usual oxidation state of manganese.

Experimental Section

Materials. Stock solutions of Na_2EDTA (Baker) in water were prepared from the primary standard grade reagent. Potassium permanganate solutions were prepared, preserved, and standardized against oxalic acid as described.[4] Sodium perchlorate (Aldrich, 99%+ purity) and sodium pyrophosphate (Sigma) were used without further purification. Cation-exchange (Dowex 50W-X8, 100–200 mesh, H^+ form) and anion-exchange (Dowex 1-X8, 100–200 mesh, Cl^- form) resins were pretreated before use.[5] The Mn(III)–EDTA complex was prepared by following the method of Yoshino et al.[3] Chromium analyses were performed by peroxide oxidation in NaOH solution.[6]

Physical Measurements. UV–visible spectroscopic measurements were performed on computer-interfaced double-beam spectrophotometers (Perkin-Elmer Lambda 600, Varian DMS 100). Nuclear magnetic resonance experiments were carried out on a 300-MHz instrument (General Electric, GN 300), and cyclic voltammeteric measurements were done on a potentiostat/galvanostat (Princeton Applied Research, Model 173) equipped with a universal sweep generator programmer (PAR, Model 175). The voltammograms were recorded on an X-Y recorder by connecting it with a logarithmic current converter (PAR, Model 375). The magnitude of *iR* drop across the working and reference electrodes was minimized by the use of a positive-feedback *iR* accessory of the current converter. The pH values were measured by a pH meter (Orion, Model 500) using a combination electrode.

Methods. A. Rate Measurements. Permanganate ion oxidations of EDTA were carried out by using at least a 10-fold excess of EDTA. The reaction was monitored at several wavelengths, 418, 460, 490, 505, and 525 nm. Absorbance–time traces at 418 and 460 nm showed an initial increase, followed by a decrease in absorbance, whereas at other wavelengths a monotonic decrease in absorbance was noted. The latter traces, however, were not single-exponential decays. Rate constants were evaluated from the absorbance–time traces by using appropriate rate expressions. The reproducibility of these constants is better than 8%.

B. Cyclic Voltammetry. A three-electrode cell, utilizing glassy-carbon (working), calomel (reference), and Pt-wire (auxilliary) electrodes, was employed. The electrolyte concentration was maintained at 0.5 M by $NaClO_4$. The pH values were adjusted with dilute $HClO_4$ or NaOH. The reference electrode was kept in the perchlorate electrolyte during the acquisition of the voltammograms only. No precipitation of $KClO_4$ at the junction of the Pt wire and KCl solution inside the electrode was apparent as evidenced by the nature of *i–E* curves; an appreciable precipitation usually distorts and sometimes destroys voltammograms completely due to the marked increase in the cell resistance. Voltammograms obtained by using a calomel electrode filled with saturated sodium chloride were similar to those recorded against SCE except that $E_{1/2}$ values are shifted positive by 20 mV. The $E_{1/2}$ values were calculated from the arithmetic mean of the cathodic and anodic peak potentials and reported with respect to the saturated calomel electrode.

C. Magnetic Susceptibility Measurements. Magnetic susceptibility measurements were formed in aqueous solution by following the method of Evans.[7] EDTA and MnO_4^- of desired concentrations were mixed and placed in an NMR tube (outer tube internal diameter 5 mm) *tert*-Butyl alcohol was added to this solution such that the alcohol concentration is about one-fifth of $[MnO_4^-]$. A coaxial tube (internal diameter 2 mm) containing the same alcohol concentration in the electrolyte only was placed inside the outer tube. Two methyl resonances for the alcohol in the inner and outer tubes were observed. Only one accumulation was sufficient to record the resonances with signal-to-noise ratio greater than 50, and no pulse repetition delay was therefore required. By use of 1K data points and 1000-Hz sweep width, total time elapsed during the experiment was estimated to be 256 ms, which also includes data acquisition time. When MnO_4^- and the alcohol were taken in the outer tube, separate resonances for methyl groups in the outer and inner tubes

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(1) Easom, K. A.; Bose, R. N. *Inorg. Chem.* **1988**, *27*, 2331.
(2) The Mn(III)–EDTA complex was prepared[3] by the direct reaction of EDTA with Mn(IV). The tetravalent manganese species was generated in situ by oxidation of ethanol by MnO_4^-.
(3) Yoshino, Y.; Ouchi, A.; Tusunoda, Y.; Kojima, M. *Can. J. Chem.* **1962**, *40*, 775.
(4) Skoog, D. A.; West, D. M. In *Fundamentals of Analytical Chemistry*, 4th ed.; Saunders: New York, 1982; p 756.
(5) Gould, E. S. *J. Am. Chem. Soc.* **1967**, *89*, 5792. The anion-exchange resin was pretreated similarly except that HCl was used instead of $HClO_4$.
(6) Haupt, G. W. *J. Res. Natl. Bur. Stand. Sect. A* **1952**, *48*, 414.
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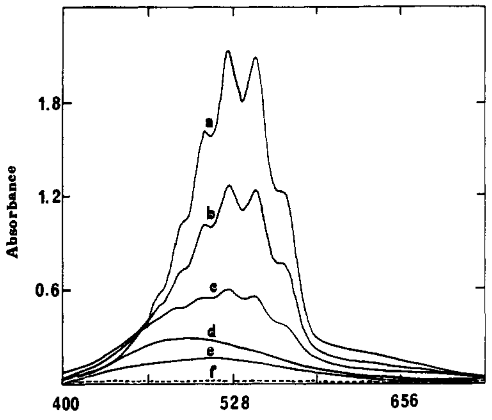

Figure 1. Visible spectral changes associated with the EDTA (10.0 mM) oxidation by MnO_4^- (1.0 mM) at pH 4.40 in $NaClO_4$ (μ = 0.5 M). Spectra a–f are recorded at t = 0 (immediately after mixing), 3, 6, 12, 21, and 63 min.

were not observed. Magnetic susceptibility, χ_g, was calculated by utilizing the relationship

$$\chi_g = \frac{3}{4\pi}\frac{\Delta f}{f m_0} + X_0 + X_0\left(\frac{d_0 - d_s}{m_0}\right)$$

where d_s and d_0 are the densities of the solution and solvent, respectively, f is the spectrophotometer frequency (Hz), X_0 is the mass susceptibility of the solvent, and m_0 is the mass of solute per cubic centimeter. Due to the negligible difference in density of the solvent and solution, the third term was neglected. Gram susceptibility was then converted to molar susceptibility, and then diamagnetic corrections were applied by assuming that an EDTA molecule is attached to the metal center. Magnetic moment was then calculated from the relationship

$$\mu_{eff} = 2.828(\chi_M T)^{1/2}\ \mu_B$$

where χ_M is the corrected molar susceptibility.

In a typical experiment, utilizing 1.25 mM MnO_4^- and 25.0 mM EDTA (pH = 3.0), we observe a 15.6-Hz separation between the methyl resonances in the inner and outer tubes for the intermediate, as described in the Results and Discussion. The corrected molar susceptibility can be calculated as 9.8×10^{-3} cm^3/mol, which corresponds to a magnetic moment of 4.84 μ_B at 25 °C.

Examination of Products from the Oxidation of EDTA. Carbon dioxide produced upon mixing permanganate with EDTA was swept by argon through a closed reaction vessel and was collected in NaOH traps. Upon completion of the reaction, the carbonate and hydroxide mixture was titrated with HCl to phenophthalein and then to bromocresol green end points. A blank titration containing NaOH alone was also carried out. The difference in the amount of HCl used to reach the second end point for the blank and that for the trap was indicative of the amount of CO_2 produced. In a typical experiment, 10 mL of $KMnO_4$ (0.2 mmol) mixed with EDTA (2.0 mmol) was placed in a vessel connected with three NaOH traps. The amount of CO_2 produced was found to be 0.32 mmol. Two other trials yielded 0.29 and 0.30 mmol of CO_2.

Other EDTA oxidized products form complexes with Cr(III). A solution of $Cr^{III}Cl_3$ (1.5 mmol) was added to the product of the reaction containing 0.10 mmol of MnO_4^- and 1.0 mmol of EDTA. The mixture was allowed to stand for 24 h. Various Cr(III) complexes thus formed were charged first onto cation- and then anion-exchange columns. Unreacted $Cr(III)_{aq}$ and other cationic species stayed on the first column, and $Cr[EDTA)]^-$ was then adsorbed on the anion-exchange resin. A third fraction was adsorbed on neither column. This fraction exhibited absorption bands at 540 (ϵ = 130) and 385 nm (ϵ = 110 M^{-1} cm^{-1}) and corresponds to 7.5×10^{-5} mol of $Cr^{III}(EDTRI)(H_2O)$, a neutral complex.[8]

Results and Discussion

Spectral changes associated with the permanganate–EDTA reaction are shown in Figure 1. The molar absorptivities of the products in the visible region are negligible (<2 M^{-1} cm^{-1}) consistent with the formation of Mn(II) (but not the other oxidation states of Mn). The reaction yielded 1.50 mol of CO_2 and 0.75 mol of ethylendiaminetriacetic acid (EDTRI)/mol of permanganate. The overall EDTA–MnO_4^- redox reaction can then be represented by

$$6Mn(VII) + 5EDTA = 6Mn(II) + 5EDTRI + 10CO_2 \qquad (1)$$

for which we expect theoretical yields of 1.67 mol of CO_2 and 0.83 mol of EDTRI/mol of MnO_4^-. Lower yields for both products in triplicate measurements indicate the occurrence of minor side reactions.[9]

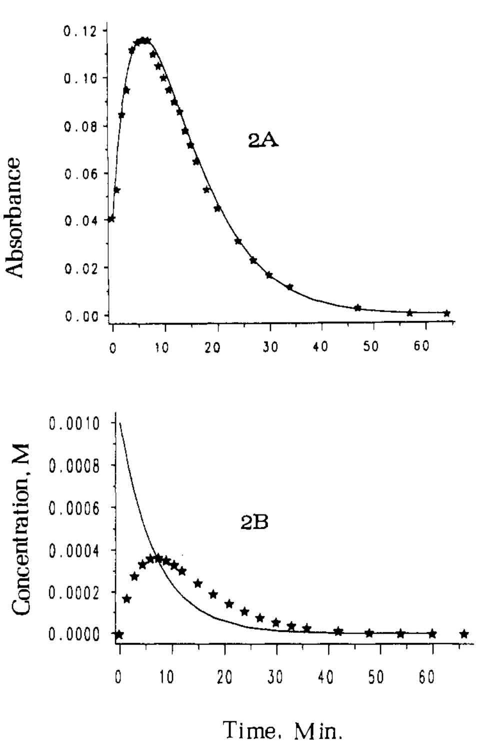

Figure 2. (A) Observed (asterisk) and computer-simulated (solid curve) absorbance–time traces[13b] for the MnO_4^- (1.0 mM)–EDTA (10.0 mM) reaction at 418 nm (pH 4.40, μ = 0.5 M). The simulated trace is generated by utilizing eq 5 with $k_1 = k_2 = 2.33 \times 10^{-3}$ s^{-1}, ϵ_I = 270 M^{-1} cm^{-1}, D_0 = 0.041, and D_∞ = 0.0. (B) Concentration vs time plots for MnO_4^- (solid line) and the intermediate (asterisk) for the permanganate–EDTA reaction, indicating that the traces in (A) are composites of the absorbances due to MnO_4^- and the intermediate throughout the reaction. Experimental conditions are those in (A).

The reaction passes through an absorbing intermediate. All kinetic profiles are in accord with consecutive first-order reactions.

$$MnO_4^- + EDTA \xrightarrow{k_1} \text{intermediate} \qquad (2)$$

$$\text{intermediate} \xrightarrow{k_2} \text{products} \qquad (3)$$

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(8) Ogino, H.; Watanabe, T.; Nobuyuki, T. *Inorg. Chem.* **1975**, *9*, 2093.

(9) Among the minor side reactions, formation of EDTRI, CO_2, and formic acid should yield lower CO_2 (1.25 mol/mol MnO_4^-), as shown in Scheme I of the text. A slightly lower yield of EDTRI may reflect the efficiency of recovery of $Cr^{III}(EDTRI)$ through the ion-exchange separations or formation of further oxidized products such as ethylenediamine-N',N'-diacetic acid (EDDA).[10] If this reaction were to occur, it is estimated that 1.5×10^{-3} mol of EDDA/mol MnO_4^- would account for the observed 8% difference in EDTRI yield. This reaction, however, should not change the ratio of CO_2 to MnO_4^-. Attempts were made to separate the $Cr(EDDA)(H_2O)_2^+$ product[11] from the cation-exchange column. A minor band was eluted with 1.0 M $HClO_4$ corresponding to an unipositively charged species. This species exhibited bands at 547 and 391 nm of almost equal intensity, differing markedly from the Cr(III)–EDDA complex.[11] Upon treatment with H_2O_2 in basic solution, this eluate forms a brownish black precipitate in addition to the oxidation to chromate. This band most likely contained a binuclear (Mn and Cr) EDTA complex.

(10) EDDA was detected in the decomposition products of the $Mn(EDTA)^-$ complex: Shirakashi, T.; Ogino, H.; Tanaka, N. *Nippon Kagakee Kaishi* **1972**, 1658. Shirakashi, T.; Tanaka, N. *Ibid.* **1974**, 1061; *Chem. Abstr.* **1975**, *82*, 3650r.

(11) $Cr(EDDA)(H_2O)_2^+$ exists in α- and β-forms: Weyh, J. A.; Pierce, R. L. *Inorg. Chem.* **1971**, *10*, 858. The absorption spectra of these two forms exhibit bands at 529 (ϵ = 77 M^{-1} cm^{-1}) and 401 nm (ϵ = 47 M^{-1} cm^{-1}) for the α-cis isomer and 527 (ϵ = 119 M^{-1} cm^{-1}) and 392 nm (ϵ = 72 M^{-1} cm^{-1}) for the β-form.

Table I. Rate Data[a] for the Permanganate Ion[b] Oxidation of EDTA at 25 °C, μ = 0.5 M ($NaClO_4$)

[EDTA],[c] mM	$[P_2O_7^{n-}]$,[d] mM	pH	10^3k_1, s^{-1}	10^3k_2, s^{-1}
10.0		3.01	4.9	0.11
25.0		3.0	14	0.13
10.0		3.41	3.7	0.21
10.0		3.79	2.2	0.70
10.0		4.40	2.3	2.3 (2.3)[e]
20.0		4.40	4.1	1.9
30.0		4.40	5.7	2.4
40.0		4.40	9.0	1.8
50.0		4.40	11	2.3
10.0		5.0	4.0	2.1
10.0	5.0	4.40	2.3	1.5 (1.5)
10.0	10.0	4.40	2.2	1.1 (1.1)
10.0	20.0	4.40	1.8	0.70 (0.71)
10.0	30.0	4.40	1.9	0.54 (0.55)
10.0	40.0	4.40	1.8	0.39 (0.44)

[a] Most rate constants are the mean of the values evaluated at 418 and 460 nm. [b] Permanganate ion concentrations were in the range 0.5–1.0 mM. [c] EDTA is predominately in the 2– form in this pH range, and its contribution to the ionic strength was taken into account. [d] More than 97% of the pyrophosphate is in the 2– form, and contributions from various forms to the ionic strength were considered. [e] Values in parentheses are calculated according to eq 6 by using a = 2.3×10^{-3} s^{-1}, b = 1.6×10^{-3} M^{-1} s^{-1}, and c = 108 M^{-1}.

Rate constants (k_1 and k_2) and molar absorptivity of the intermediate were calculated by using a nonlinear least-squares iterative computer program[1] according to eq 4,[12] where D_0, D, and D_∞ are

$$D = D_0e^{-k_1t} + \frac{\epsilon_1[A_0]k_1}{k_2 - k_1}(e^{-k_1t} - e^{-k_2t}) + \frac{D_\infty}{k_2 - k_1}(k_1e^{-k_2t} - k_2e^{-k_1t}) + D_\infty \quad (4)$$

the absorbance at zero time, at time t, and at infinite time. The initial concentration of MnO_4^- is $[A_0]$, and ϵ_1 is the extinction coefficient of the intermediate. Under conditions where k_1 and k_2 approach the same numerical value ($k_1 = k_2 = k$), eq 5 was

$$D = D_0e^{-kt} + \epsilon_1k[A_0]te^{-kt} - D_\infty e^{-kt}(1 + kt) + D_\infty \quad (5)$$

utilized.[13a,14] In these computations, the experimentally determined parameters were kept invariant and initial estimates of unknown parameters were provided. In each iteration new parameters were generated by minimizing the square of the deviations of observed and calculated absorbances until the convergence criterion was satisfied. The convergence condition was set such that the difference in absolute numerical values in two consecutive cycles divided by the magnitude of the parameter is equal to or less than 5×10^{-5}.

Table II. Cyclic Voltammetric Parameters for Mn^{III}(EDTA) and the Intermediate Formed during the Reaction of MnO_4 plus EDTA in 0.5 M NaClO at pH = 3.0

compd	scan rate, mV/s	$E_{p(ox)}$,[a] V	$E_{p(red)}$,[b] V	ΔE_p,[c] V	$E_{1/2}$,[d] V
Mn^{III}(EDTA)	50	0.667	0.464	0.203	0.567
intermediate	2	0.625	0.545	0.080	0.585
	5	0.638	0.537	0.101	0.588
	10	0.659	0.516	0.143	0.588
	20	0.674	0.504	0.170	0.589
	50	0.682	0.480	0.202	0.581
	50	0.720	0.480	0.240	0.680[e]

[a] Oxidation peak potential. [b] Reduction peak potential. [c] $\Delta E_p = E_{p(ox)} - E_{p(red)}$. [d] Vs SCE. [e] Vs calomel electrode filled with saturated sodium chloride solution.

Table I lists the rate constants at various EDTA concentrations and pH's. Pseudo-first-order rate constants for formation of the intermediate increase linearly with [EDTA] whereas increasing concentrations of amino polycarboxylic acid have no effect on the decomposition of the intermediate. The same constants at a specific [EDTA] appear to pass through a minimum near pH 4. An initial decrease in k_1 with decreasing $[H^+]$ followed by insignificant changes in the pH of 3.8–4.4 were observed. Finally, about a 2-fold increase in k_1 was apparent with the change in pH from 4.4 to 5.0. Because of the limited solubility of EDTA below pH 3, we were unable to extend the rate studies in acidic media with $[H^+] > 10^{-3}$ M. The first-order rate constants for the decomposition of the intermediate (k_2) increase with pH initially and then level off at pH > 4.4. Due to the opposite trend in variations of k_1 and k_2 with $[H^+]$ in the pH range <3.8, we were able to characterize the oxidation state of the intermediate as discussed below. For example, at pH 3.0, the ratio of k_1/k_2 is 45 with 10 mM EDTA. Under these conditions, absorbance–time traces can be treated separately.

Additions of pyrophosphate ion retard the decomposition of the intermediate significantly but exhibit no systematic effect on its formation of the same. The first-order rate constant for this decomposition is not a linear function of the phosphate ligand, however. A substantial curvature exists in the k_2 vs [pyrophosphate] plot at concentrations greater than 10 mM. Rate data can be described adequately by

$$k_2 = \frac{a + b[\text{pyrophosphate}]}{1 + c[\text{pyrophosphate}]} \quad (6)$$

A nonlinear least-squares fit of the rate data according to eq 6 yielded the values of b and c as $(1.6 \pm 2) \times 10^{-3}$ M^{-1} s^{-1} and 108 ± 6 M^{-1}. The value of "a", 2.3×10^{-3} M^{-1} s^{-1}, was kept invariant, since this value is known at zero pyrophosphate concentration. This rate law is consistent with a mechanism in which a rapid equilibrium exists between the parent intermediate and an intermediate–phosphate complex and with the phosphato complex decomposing at a much smaller specific rate than does the parent intermediate. Reactions 7–9 illustrate the situation, where I, P_2,

$$I + P_2 \overset{K_F}{\rightleftharpoons} I\text{-}P_2 \quad (7)$$

$$I \xrightarrow{k_i} \text{products} \quad (8)$$

$$I\text{-}P_2 \xrightarrow{k_p} \text{products} \quad (9)$$

and $I\text{-}P_2$ represent the parent intermediate, pyrophosphate ion, and intermediate–pyrophosphate complex. The values of the rate constant and formation constant can be evaluated as k_i (=a) = 2.3×10^{-3} s^{-1}, k_p (=b/c) = 1.5×10^{-5} s^{-1}, and K_F (=c) = 1.1×10^2 M^{-1}.

The magnetic susceptibility experiments of the reaction mixture were performed under conditions where 95% of the total manganese is in the form of the intermediate. For example, at pH 3.0 the susceptibility experiments were performed after 5 min of mixing utilizing 1.25 mM MnO_4^- and 25 mM EDTA. On the basis of our rate data, we calculate that the reaction mixture contains 2.5% MnO_4^-, 95% intermediate, and 2.5% products

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(12) Bose, R. N.; Viola, R. E.; Cornelius, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3336.

(13) (a) Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1985**, *24*, 2833. The equation was derived by following the reaction sequence

$$A + B \xrightarrow{k} \text{intermediate} \xrightarrow{k} \text{products}$$

in which the concentration of the intermediate[13] [I] relates to [I] = $k[A_0]te^{-kt}$. (b) One reviewer has noted that the half-life of the descending part of the curve in Figure 2A is 10 min and therefore the first-order rate constant for the decay of the intermediate should be 1.16×10^{-3} s^{-1}. Rate profiles for consecutive first-order processes are composite throughout the entire reaction time especially for the reactions where the magnitude of the two rate constants are very close to each other. The estimates of rate constants based on the apparent half-life determination utilizing any part of a kinetic curve would therefore be erroneous. The true half-life for one of the rate processes (hence the rate constant) can be estimated safely from the last 25% of the reaction if the rate constants differ by a factor of 4 or more.

(14) See, for example: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; Chapters 4 and 9.

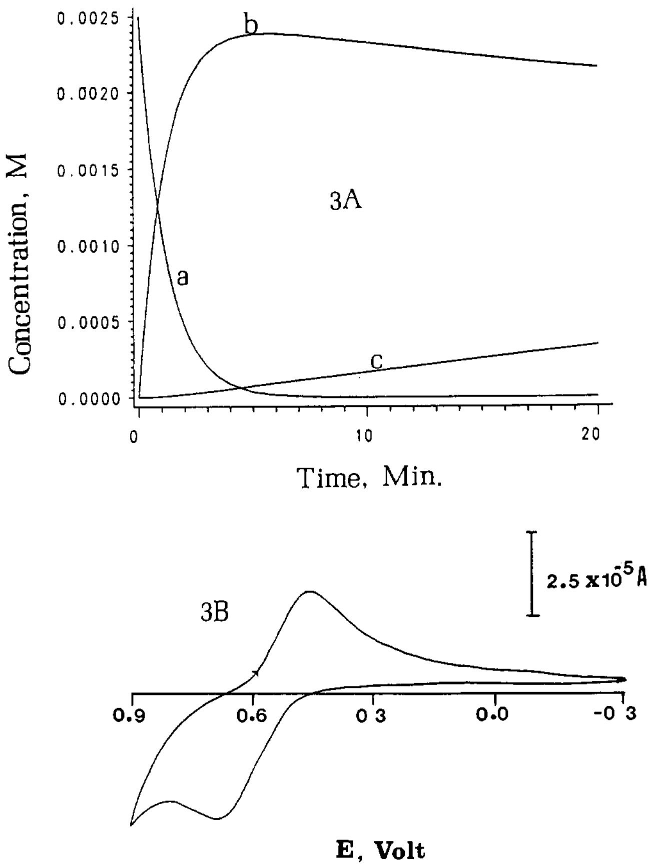


Figure 3. (A) Concentration–time profiles for MnO_4^- (curve a), the intermediate (curve b), and Mn(II) (curve c) for the oxidation of EDTA (25.0 mM) by permanganate ion (2.5 mM) at pH 3.0 (μ = 0.5 ($NaClO_4$)). Magnetic susceptibility and cyclic voltammetry measurements are performed after 4–6 min of mixing the reagents, where the concentration of the intermediate is 95% of the total permanganate employed. (B) Cyclic voltammogram of the intermediate with a 50 mV/s sweep rate. Other conditions are the same as in (A).

(Figure 3). The data acquisition time (256 ms) for the NMR experiment is negligible compared to the reaction time. The uncorrected apparent molar susceptibility was calculated to be 9.7×10^{-3} cm^3/mol, which can be corrected to a value of 9.8×10^{-3} cm^3/mol for a Mn(EDTA) complex. The corresponding magnetic moment can be calculated as 4.84 μ_B. Since the reaction mixture contains 95% intermediate, this magnetic moment indicates that the intermediate contains four unpaired electrons.

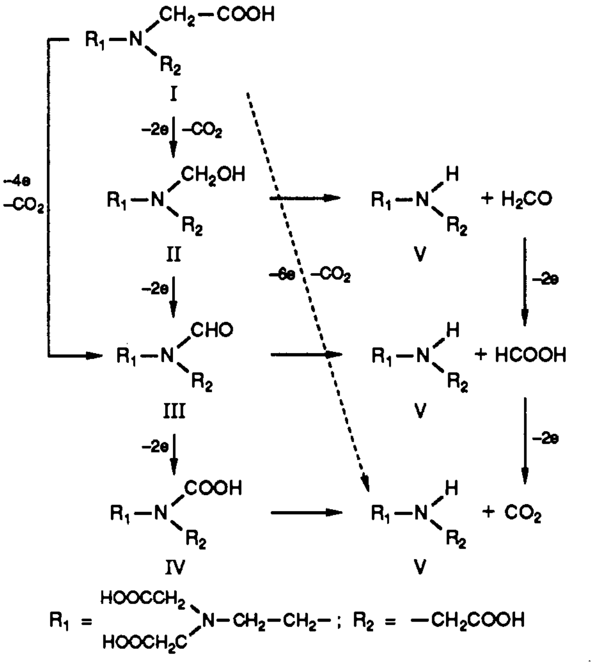
Cyclic voltammetry experiments were also performed on the intermediate at pH 3.0 under conditions described for the magnetic susceptibility measurements. Since the intermediate decomposes slowly at this pH ($t_{1/2} \approx$ 2–4 h), the initial voltammograms should exhibit the redox behavior of the intermediate only. The voltammograms exhibit a reduction peak and an oxidation peak in the voltage range 0.7–0.5 V. Although the peak separations are dependent on sweep rate, the $E_{1/2}$ value was found to be constant, 0.59 V vs SCE within the experimental error (Table II). At a slow scan rate of 2 mV/s the peak separation was calculated as 80 mV, indicating a quasi reversible one-electron electrode process. Cyclic voltammograms of Mn^{III}(EDTA) complex also show redox peaks in the same voltage range for which the $E_{1/2}$ value was calculated as 0.57 V vs SCE. The peak separations of these voltammograms were also comparable to those for the intermediates.

Table III. Molar Absorptivities[a] of the Intermediate at Various Wavelengths in the Presence (ϵ_2) and Absence (ϵ_1) of Pyrophosphate Anion

wavelength, nm	ϵ_1, M^{-1} cm^{-1}	ϵ_2, M^{-1} cm^{-1}
525	270 ± 25	240 ± 20
505	325 ± 30	270 ± 20
490	475 ± 30	470 ± 40
460	460 ± 30	472 ± 35
418	250 ± 20	140 ± 20

[a] Calculated by using an iterative nonlinear least-squares program (see Experimental Section); uncertainties are calculated from triplicate measurements.

Scheme I



Manganese(III), -(IV), -(V), and -(VI) are described as intermediates[15-20] in MnO_4^- oxidations of unsaturated dicarboxylic acids, aldehydes, and other organics. Although all these oxidation states may participate in the present reaction, neither Mn(V) nor Mn(VI) is likely to be the long-lived intermediate, since a monotonic decrease in absorbance in the region 600–700 nm was observed during the reaction. These two states absorb more intensely than the parent Mn(VII) in this range.[19] A manganese(IV) or manganese(III) species is perhaps the long-lived intermediate in this reaction. The former oxidation state is usually encountered in neutral or basic solution with the organic reductants[20,21] whereas our investigation encompasses the pH range 3–5.

A manganese(III) intermediate is supported by the following observations: (i) The magnetic susceptibility of the intermediate was found to be 4.85 ± 0.05 μ_B at 25 °C. These values are closely related to four unpaired electrons on the basis of the "spin-only" formula. (ii) The reduction potential of the intermediate is close to the same potential for the Mn^{III}(EDTA) complex. (iii) Pyrophosphate anion retarded the decomposition of the intermediate significantly. This phosphate ligand is used as a scavenger for Mn(III).[17,20,23] The phosphate ligand complexes with the tri-

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(15) Freeman, F.; Kappos, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6628; *J. Org. Chem.* **1986**, *51*, 1654. Freeman, F.; Chang, L. Y. *J. Am. Chem. Soc.* **1986**, *108*, 4504. Freeman, F.; Chang, L. Y.; Kappos, J. C.; Sumarta, L. *J. Org. Chem.* **1987**, *52*, 1460.

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positive oxidation state of manganese and makes it a poor oxidizing agent.[24] The participation of the phosphate ligand is also reflected in the molar absorptivity of the intermediate at 505 nm (Table III). (iv) The molar absorptivities calculated (in the absence of pyrophosphate) at various wavelengths (Table III) point to an absorption band near 500 nm, in common with other (amino polycarboxylato)manganese(III) complexes.[25] (v) The molar absorptivity of this species, 300 M^{-1} cm^{-1} at 505 nm lies between the values observed for Mn^{III}(HEDTA) (HEDTA) = hydroxyethylethylenediaminetriacetic acid) and Mn^{III}(EDTA), as expected if the partially oxidized EDTA is coordinated to this metal center. (vi) The rate constant for the decomposition of the intermediate is close to the values observed for the decomposition of other Mn(III)–amino polycarboxylato complexes[25,26] as discussed below.

The formation of EDTA oxidized products may proceed through several steps such as decarboxylation and subsequent formation of alcohol and aldehyde and finally a second decarboxylation reaction. Suggested routes that would lead to EDTRI and CO_2 are depicted in Scheme I.[27] A $4e^-$ oxidation product, an aldehyde (III), may coexist with the Mn(III) intermediate if the subsequent reaction of this organic product with MnO_4^- proceeds more slowly than the corresponding reaction with the Mn(III) intermediate. Second-order rate constants for oxidations of aliphatic aldehydes[28] with MnO_4^- have been reported to lie in the range 2–5 M^{-1} s^{-1} corresponding to a first-order rate constant, (4–10) × 10^{-4} s^{-1}, considering that 20% of the Mn exists as intermediate at its peak concentration.

Since the molar absorptivity of the intermediate is less than that of Mn^{III}(EDTA) at its absorption maximum, a partially oxidized EDTA molecule, perhaps an aldehyde (III) (a $4e^-$ oxidation product) may be coordinated to the Mn(III) center. In the presence of pyrophosphate ion, the intermediate is more probably a mixed-ligand complex in which pyrophosphate and partially oxidized EDTA are attached to the manganese center. Hamm and co-workers[24,25] reported that Mn^{III}(HEDTA) decomposes about seven times faster (4.2×10^{-5} s^{-1}) than Mn^{III}-(EDTA) (for which Mn^{III}(EDTRI), CO_2, and H_2CO were identified as products). The intermediate in this study decomposes seven times faster than these amino polycarboxylato complexes of Mn(III). The first-order decomposition of the intermediate is proposed to be an internal electron transfer[29] to form Mn(II) and organic oxidation products, as shown in Scheme I.

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(23) A retardation in decomposition of the intermediate by pyrophosphate ion may not alone be sufficient to justify a Mn(III) intermediate. The same ligand may also be a scavenger for Mn(IV). Freeman and coworkers[21] argued that some of the reported Mn(III) intermediates[16] in organic oxidations by permanganate ions should be Mn(IV) species, instead. Our other data (see text) are more consistent for a Mn(III) than a Mn(IV) intermediate.

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$$\text{(P-EDTA)Mn}^{III} + \text{EDTA} \overset{K}{\rightleftharpoons} \text{(P-EDTA)Mn}^{III}\text{–EDTA}$$

$$\text{(“P-EDTA”)Mn}^{III}\text{(EDTA)} \xrightarrow{k_{et}} \text{Mn(II)} + \text{EDTRI} + CO_2 + \text{EDTA}$$

“P-EDTA” is the partially oxidized EDTA molecule attached to Mn(III), as discussed in the text.

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Cryoelectrochemical Study of the Cleavage of Radical Anions of Diiron and Diruthenium Carbonyl Dimers

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Electrochemical reduction of the diiron complexes $[Fe(CO)_2(\eta^5\text{-}Cp)]_2$ and $[Fe(CO)_2(\eta^5\text{-}Cp^*)]_2$ proceeds at room temperature by two electrons, but at low temperature is a one-electron reaction producing dimer radical anions that are stable on the voltammetric time scale. Analysis of the reaction kinetics at intervening temperatures shows that the two-electron reaction occurs through the radical anion, which dissociates to a mononuclear anion and a radical. The second electron is delivered homogeneously to the radical by a second dimer radical anion. The cleavage rate constant for $[Fe(CO)_2(\eta^5\text{-}Cp)]_2^{\bullet-}$ is 10^2 times that for $[Fe(CO)_2(\eta^5\text{-}Cp^*)]_2^{\bullet-}$ (at 0 °C), and the rate for the related dimer $[Ru(CO)_2(\eta^5\text{-}Cp)]_2^{\bullet-}$ was too fast to measure and at least 10^4 times larger than that for $[Fe(CO)_2(\eta^5\text{-}Cp^*)]_2^{\bullet-}$. The rates of the dimer radical anion cleavage fall in the same order as the rates of isomer interconversion in the parent dimers and raise the possibility that the rate of cleavage may be controlled by an intramolecular cleavage-precursor step.

The photochemical[1-6] and electrochemical[7-16] reactivity of fluxional, carbonyl-bridged metal dimers like those in Figure 1 has been an active area of research. Their reactions yield a variety of products, including mononuclear anions of the form $[M(CO)_2(\eta^5\text{-}Cp)]^-$, which can be prepared by both electrochemical[12-16] and chemical reductive cleavage.[17,18] While the electrochemically induced dimer cleavage was first[13,14] described to occur via a two-electron-reduced dimer, Parker and co-workers[12] later reported that electrochemical cleavage of $[Fe(CO)_2(\eta^5\text{-}Cp)]_2$ (**1**) occurs following one-electron reduction to the dimer radical anion.

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