

Formation of manganate(V) in oxidations by permanganate ion in strongly alkaline solutions

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Abstract

The oxidation of tartronate and mesoxalate ion by permanganate has been studied in 0.1–2.0 M aqueous NaOH. Manganate(VI) ion is formed in the first rapid phase, which is kinetically first order with respect to both MnO_4^- and the substrate. The second-order rate constant depends on the OH^- ion concentration, which implies higher reactivity of the species with deprotonated 2-hydroxy groups. The proposed mechanism consists of outer sphere electron transfer to the MnO_4^- ion, generating an anion-radical and manganate(VI). The latter reacts with both substrates in the second, slower phase, affording manganate(V) as a relatively stable product in strong alkali. The anion-radical is oxidized by MnO_4^- in a rapid step.

Introduction

Oxidations by permanganate ion find extensive application in organic synthesis [1–7] especially since the advent of phase transfer catalysis [3, 4, 6], which permits the use of solvents like methylene chloride and benzene. Kinetic studies are important sources of mechanistic information on these reactions, as demonstrated by results referring to unsaturated acids in both aqueous [1–20] and non-aqueous media [21].

The manganese chemistry involved in these multistep redox reactions is an important source of information as (i) the manganese intermediates are relatively easy to identify when they have sufficiently long lifetimes [5, 7, 10–12] and (ii) the oxidation states of the intermediates permit useful conclusions as to the possible reaction mechanisms, including the nature of intermediates from the organic substrate. Direct evidence is available for the transient formation of manganese(III) in the oxidation of acetylene and olefin type compounds in acidic aqueous solutions [5, 14, 22].

It is reasonable to assume that manganese(V) is an intermediate on the path from MnO_4^- to Mn(III). With unsaturated substrates, a cyclic hypomanganate diester seems to be the most favorable intermediate structure. However, despite occasional claims to the contrary, this species has not yet been unequivocally identified in any permanganate oxidation [7, 13, 14].

A detectable yellow intermediate in the permanganate oxidation of cinnamic acid, which was thought to be the long sought hypomanganate(V) ester [13], has later been identified as a soluble manganese(IV) species [10]. Subsequently, soluble or colloidal manganese(IV) turned out to be the most often encountered short-lived manganese intermediate in permanganate oxidations [10–12, 15–19].

In our continuing search for manganese(V) intermediates, we focused attention on strongly alkaline media, where hypomanganate(V) is expected to be relatively stable. In a study of the permanganate oxidation of sulfite ion [23, 24], it has been for the first time possible to detect the MnO_4^{3-} ion as a short-lived intermediate, using the combination of rapid-scan spectrophotometry with the stopped-flow technique. It is formed in the disproportionation of manganate(VI) and is itself disproportionated subsequently, affording the stable soluble manganese(IV) product.

In strongly alkaline aqueous solutions, the stable reduction product of permanganate is the manganate ion [1], MnO_4^{2-} . No mechanistic information is available on such reactions which would permit one to distinguish between a direct one-electron reduction to manganese(VI) and a Mn(VII) → Mn(V) conversion, followed by reaction (1).



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Results and discussion

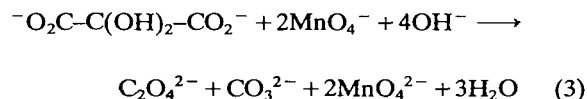
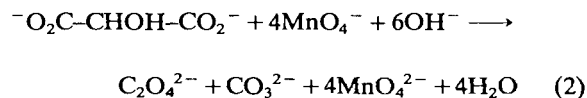
In order to explore the mechanism of oxidations by permanganate ion in strongly alkaline aqueous solutions, we have selected tartronic (TA) and mesoxalic acid (MA) as organic substrates. The site of oxidative attack is expected to be the CHOH moiety of TA and the (ionized) OH group(s) of hydrated MA, predicting simple oxidation products.

Stoichiometry

0.5 mmol of the substrate (tartronic acid or sodium mesoxalate, Fluka) was dissolved in 30 cm³ 1.0 M aqueous NaOH. 30 cm³ 0.1 M KMnO₄ was added and the solution was left to stand at 25 °C for 15 min (MA) and 180 min (TA), respectively. Upon adding excess solid KI, the solution was acidified and the I₂ titrated with standard thiosulfate. The average number of oxidation equivalents consumed by 1 mol of substrate was 4.04 ± 0.06 for TA and 1.96 ± 0.06 for MA, from 3 parallel runs.

Two mmol of each substrate dissolved in 50 cm³ 1.0 M aqueous NaOH was reacted with a slight excess of KMnO₄ (10 mmol for TA, 5 mmol for MA). After the reaction, the product manganate(VI) and the unreacted permanganate were reduced to manganese dioxide (hydrated) with 10 cm³ 0.5 M hydrazine hydrate. After filtering, neutralization with HCl, acetic acid and NH₄Cl were added, and oxalic acid was precipitated with CaCl₂. The amount of CaC₂O₄ · H₂O found was 2.0 ± 0.1 mmol (i.e. 1.0 ± 0.05 mol/mol) for both TA and MA, from the average of 3 runs.

Spectrophotometric monitoring of the reactions demonstrated the existence of a fast initial phase, lasting for a few seconds, in which MnO₄⁻ is converted to MnO₄²⁻ without any other detectable product absorbing in the UV-Vis region. The stoichiometry of the first phase is given by eqns. (2) and (3) for TA and MA, respectively.

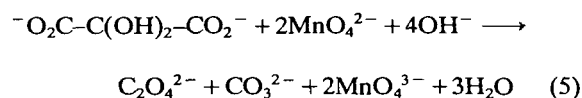
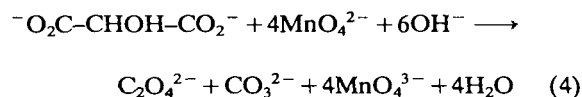


The kinetics of the rapid phase have been studied by the stopped-flow technique (see later) for both TA and MA. In principle manganate(V) may be an intermediate (cf. eqn. (1)), but we were unable to observe any transient in the first phase.

The second phase of the reaction is the oxidation of the substrate by MnO₄²⁻, which, depending on

the concentration of TA and MA, may last from several minutes to 1–2 h. Typical time evolution of the spectra is shown in Fig. 1 for the reaction of MA with MnO₄²⁻.

The most remarkable feature of these spectra is that up to about 90% reaction only one absorbing product is formed with λ_{max} of 670 and 325 nm. It can be positively identified as manganate(V), i.e. hypomanganate, on the basis of the 670 nm band [25]. Thus MnO₄²⁻ acts as a one-electron oxidant and the overall stoichiometry is analogous to eqns. (2) and (3), as demonstrated also by the amount of oxalic acid formed.



At the alkali concentrations used (8 M KOH), hypomanganate is quite stable and only slowly produces a weak opalescence due to colloidal and/or solid MnO₂. Neutralization immediately leads to disproportionation of hypomanganate and of its primary product manganate(VI), the stable product being MnO₂.

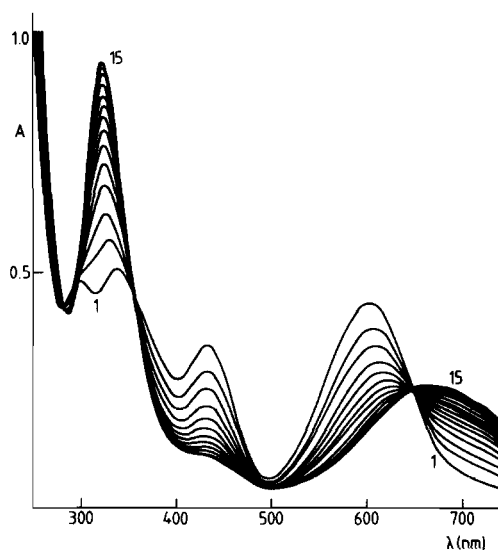
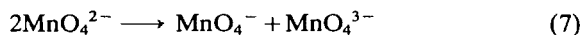
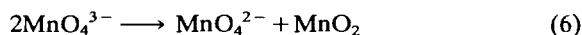
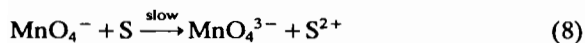


Fig. 1. Time evolution of the visible spectra upon reaction of 1.47×10^{-3} M MnO₄²⁻ with 3.0×10^{-3} M mesoxalic acid in 12 M KOH (r.t., 0.2 cm cells, Beckman ACTA MIV instrument). Spectra 1–10 were taken at 10 min intervals; spectra 11–15 at 5 min intervals.

The permanganate ion formed in the disproportionation is consumed by the excess substrate.

When a manganate(V) solution thus prepared is treated with alkaline MnO_4^- , a very fast synproportionation, the reverse of reaction (7), is observed. This confirms earlier assumptions on the rapidity of that process. Thus it cannot be excluded that in oxidations by alkaline MnO_4^- a two-electron step may be followed by rapid synproportionation.



(S is an oxidizable substrate)

Kinetic measurements

The oxidation of TA and MA was followed in a flow-through spectrophotometric cell, filled by a simple stopped-flow device. Aqueous alkaline solutions were used; the NaOH concentration was varied between 0.1 and 2.0 M at constant ionic strength (2.0 M). The disappearance of MnO_4^- was monitored at 540 nm. Pseudo-first-order conditions were ensured by an at least ten-fold excess of substrate. Excellent first-order plots were obtained up to 90% reaction. The slope was found to be proportional to the substrate concentration, thus first-order behavior is observed with respect to both reactants (Table 1). The apparent second-order rate constant k_0 is a function of NaOH concentration (Table 2).

The observed kinetic behavior is consistent with the mechanism shown in Scheme 1, involving at least two reacting species for both TA and MA, formed via deprotonation of the 2-hydroxy group(s) in TA and hydrated MA.

Assuming that protonation and deprotonation are much faster than oxidation, we have for the apparent second-order rate constant:

$$k_0 = \frac{k_1 + k_2 K[\text{OH}^-]}{1 + K[\text{OH}^-]} \quad (10)$$

TABLE 1. Pseudo-first-order rate constant as a function of substrate concentration^a

[Substrate] ₀ × 10 ² (M)	$k_{\text{obs}} \times 10^3$ (s ⁻¹)	
	MA	TA
1.0	14.8	2.07
2.0	28.0	4.02
3.0	47.8	6.12
4.0	58.0	8.13
5.0	72.1	10.3

^a[KMnO_4] = 1.0×10^{-3} M; [NaOH] = 0.5 M; $I = 2.0$ M; $T = 25$ °C. Each rate constant is the average result of 3 parallel runs reproducible to within $\pm 5\%$.

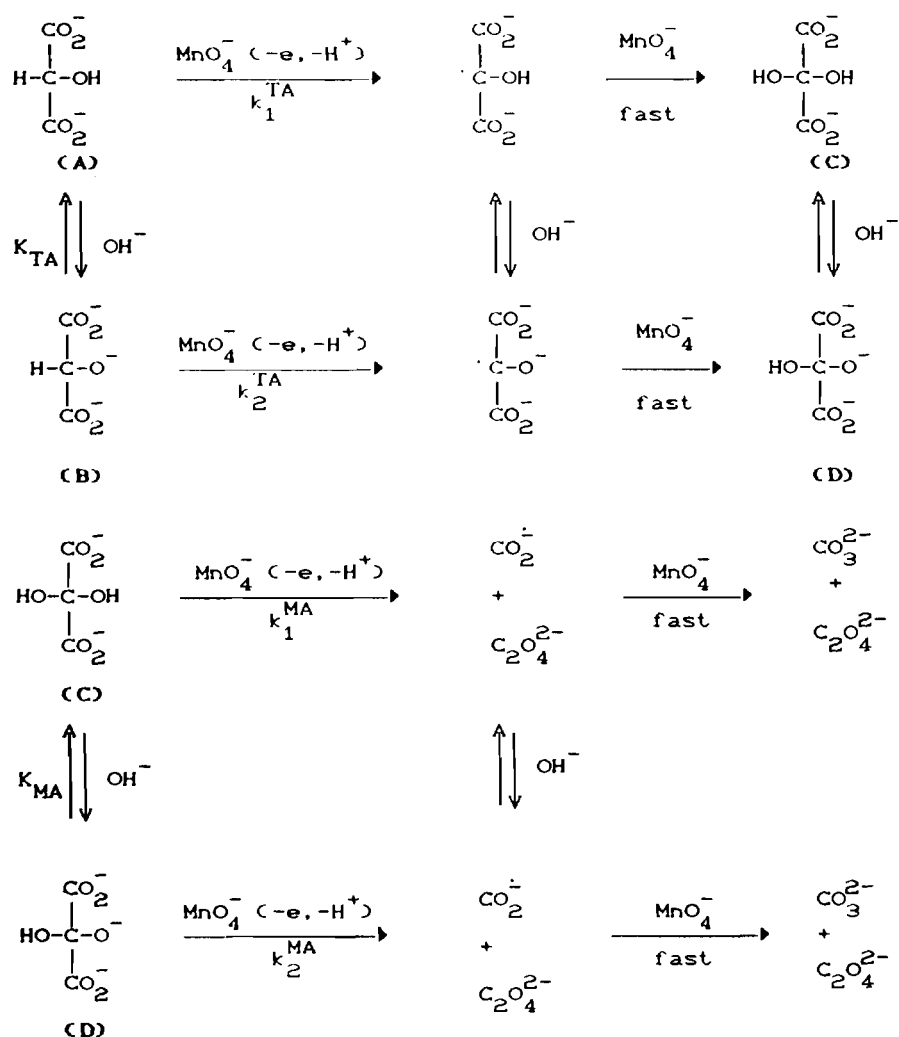
TABLE 2. Apparent second-order rate constant as a function of NaOH concentration^a

[NaOH] (M)	k_0 (M ⁻¹ s ⁻¹)	
	MA	TA
0.10	0.72	0.046
0.25	1.22	0.110
0.50	1.48	0.213
0.75	1.57	0.312
1.00	1.64	0.403
2.50	1.68	0.563
2.00	1.74	0.644
0.10 ^b	0.28	0.018
pH 5 ^c	3×10^{-2}	no reaction

^a[KMnO_4]₀ = 1.0×10^{-3} M; [MA]₀ = 1.0×10^{-2} M; [TA]₀ = 2.5×10^{-2} M; $I = 2.0$ M; $T = 25$ °C. Each rate constant is the average result of 3 runs reproducible to within $\pm 5\%$. ^bIonic strength 0.1 M. ^cAdjusted with succinic acid buffer.

The fitting of eqn. (10) to the experimental results afforded the rate and equilibrium constants listed in Table 3.

In the mechanism depicted by Scheme 1, the proposed rate-determining step is outer-sphere electron transfer to permanganate ion, followed by release of a proton to the strongly basic environment. With MA electron transfer leads to C–C bond cleavage in line with the observed products. Although this may also be pictured as H-atom transfer to the oxidant similarly to earlier work on alcohol oxidation [1, 26–28], the reactivity trends can be more readily reconciled with electron transfer. The values of k_2^{TA} and k_2^{MA} are quite close to each other, which is acceptable if we regard these steps as electron abstraction from an ion with 3– charge. This is a favourable process especially as the resulting anion-radical has considerable stability. If, however, this step were an H-atom abstraction, we would expect greater differences due to the different bond energies of C–H and CO–H hydrogen atoms. The radical anion produced rapidly reacts with a second molecule of MnO_4^- to give either the final products (from MA) or another intermediate (from TA), which incidentally is identical with C/D, i.e. mesoxalic acid. This pattern is consistent with the greater reactivity of MA, which ensures rapid oxidation of the intermediate. Both the TA and MA species with intact OH group(s) are much less reactive than their deprotonated counterparts (cf. k_1^{TA} versus k_2^{TA} and k_1^{MA} versus k_2^{MA}). This can be explained by that in the dianions the electrons in the vicinity of the reaction center (the C-2 atom) are in covalent bonds and thus held more tightly than in the trianions. This behaviour cannot simply be interpreted in terms



Scheme 1.

TABLE 3. Rate and equilibrium constants at 25 °C (ionic strength 2.0 M)

Substrate	k_1 ($\text{M}^{-1} \text{s}^{-1}$)	k_2 ($\text{M}^{-1} \text{s}^{-1}$)	K (M^{-1})
TA	$(9.1 \pm 0.8) \times 10^{-4}$	2.38 ± 0.41	0.195 ± 0.043
MA	0.1 ± 0.01	1.87 ± 0.03	6.42 ± 0.47

of electrostatic repulsion, which would predict an opposite trend. The difference between k_1^{TA} and k_1^{MA} is obviously also due to different energies of the electrons in the C-H and C-C bonds.

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