Mechanism of the Permanganate Oxidation of Unsaturated Compounds. Part I. Short-lived Intermediates of the Oxidation of Acetylenedicarboxylic Acid

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Fast reaction techniques have been applied to the study of intermediates in the permanganate oxidation of acetylenedicarboxylic acid in acid. The accumulation and decay of Mn^{III} has been observed by stopped-flow spectrophotometry. The quenching of reacting solutions proves that oxalic acid is formed as an intermediate. The amount of oxalate found in the presence of pyrophosphate as scavenger for Mn^{III} provides evidence for a short-lived Mn^{IV} species. Oxygen-18 tracer experiments indicate complete oxygen transfer from permanganate to acetylenedicarboxylic acid. A number of mechanistic alternatives are systematically examined. It is suggested that the first step of oxidation is the formation of a cyclic intermediate containing manganese(V).

ALTHOUGH the literature on permanganate oxidations is extensive,[1,2] no mechanistic information is available on the reactions of acetylenic compounds with this oxidant except for a brief report on the present system.[3] Any kinetic study would require special techniques owing to the rapidity of the reactions between permanganate and unsaturated compounds. Since such processes involve the transfer of many oxidation equivalents, a mechanistic study must be extended to the detection of possible intermediates, both organic and inorganic. This is particularly important in acid where MnO_4^- is a five-equivalent oxidant and the intermediate oxidation states may all, in principle, have finite life times.

In the present paper we report on the permanganate oxidation of acetylenedicarboxylic acid in acid, with special reference to extrakinetic sources of mechanistic information, *viz.* the detection of short-lived intermediates and oxygen-18 tracer experiments.

RESULTS

Stoicheiometry.—At strong and medium acidities, the permanganate oxidation of acetylenedicarboxylic acid (H_2A) takes place according to equation (1) as can be easily verified by direct titration in dilute aqueous sulphuric or perchloric acid. The colour of MnO_4^- disappears immediately and a sharp end-point is observed.

$$HO_2C{\cdot}C{\equiv}C{\cdot}CO_2H + 2MnO_4^- + 6H^+ \longrightarrow 4CO_2 + 2Mn^{2+} + 4H_2O \quad (1)$$

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[1] R. Stewart, ' Oxidation by Permanganate ' in ' Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York and London, 1965.

[2] W. A. Waters, *Quart. Rev.*, 1958, **12**, 277.

[3] L. I. Simándi and M. Jáky, *Tetrahedron Letters*, 1970, 3489.

Intermediates from Permanganate.—The disappearance of permanganate can be conveniently followed by stopped-flow spectrophotometry at or around 540 nm. Using the u.v.–visible spectra of manganese in the oxidation states (III)—(VI), one can in principle detect these species if they occur as short-lived intermediates, and the corresponding life times are in the range accessible for the stopped-flow technique (minimum half-life of 15 ms for the instrument used [4]). If any of the intermediate valence states accumulates during the reaction, a mimimum on the transmission *vs.* time curve should be observed at a suitably selected wavelength.

We have examined the transmission *vs.* time curves between 200 and 800 nm, at 20 nm intervals, in the pH range between 0·5 and 4. A transient minimum was observed only in the 240—270 nm range, a typical curve being shown in Figure 1. The stopped-flow traces in other regions of the wavelength interval studied showed two kinds of behaviour: (i) steady decrease of the optical density reflecting the disappearance of MnO_4^- (between about 325 and 410 nm, and above 490 nm) and (ii) practically no change in the optical density during the reaction (horizontal traces at and in the close vicinity of 300 and 420 nm).

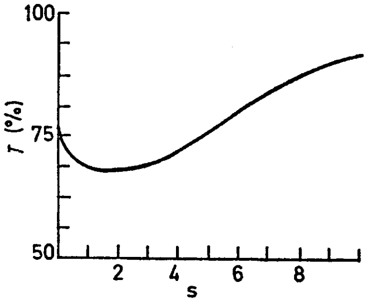

FIGURE 1 Stopped-flow trace illustrating the accumulation and decay of the manganese(III) intermediate; $[H_2A]_T = 10^{-3}$M, $[MnO_4^-]_0 = 1{\cdot}5 \times 10^{-3}$M, 0·2M-$HClO_4$, wavelength 250 nm, and 25 °C

As manganese(VI) and manganese(V) have strong absorption maxima around 600 and 700 nm, respectively,[1] observation (i) immediately eliminates both of these species as detectable intermediates. At the above wavelengths, the absorption of MnO_4^- is much weaker than those of MnO_4^{2-} and MnO_4^{3-}, thus the detection of the latter would have presented no difficulty.

The stopped-flow traces obtained in the presence of pyrophosphate, a strong complexing agent for Mn^{III} and possibly Mn^{IV}, have shown that (iii) the transient minimum between 240 and 270 nm is not present any more. Instead, the optical density increases steadily to reach a limiting value after the disappearance of MnO_4^-, (iv) horizontal traces are obtained at and in the vicinity of 300 and 430 nm, and (v) the optical density decreases steadily between 320 and 420 nm.

In order to identify the species that is responsible for the transmission minimum between 240 and 270 nm, it is necessary to know the spectra of the remaining two possible intermediates, Mn^{IV} and Mn^{III} in this wavelength range. We have recorded the spectra of Mn^{IV} and Mn^{III} in the presence and absence of pyrophosphate, under the conditions specified in the Experimental section (Figures 2 and 3). The spectra of Mn^{III} were found to be in good agreement with data reported earlier.[5] In the wavelength interval 240—450 nm, the spectrum of Mn^{IV} was in fair agreement with that described.[6] In view of this agreement and of the fact that the Mn^{IV} solutions did not show the Tyndall effect, the presence of a colloidal suspension was unlikely. Homogeneous solutions of Mn^{IV} species can exist under certain circumstances,[1,7] and they have been invoked as intermediates in various oxidations by Mn^{III} and in the process of precipitation of MnO_2 from Mn^{III} solutions.[6]

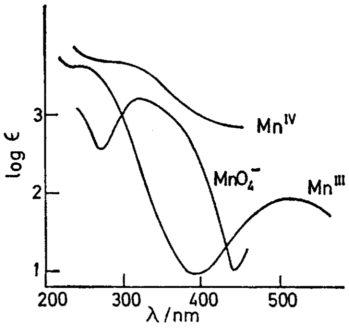

FIGURE 2 U.v.–visible spectra (25 °C); Mn^{III}, in the presence of 0·02M-$Na_4P_2O_7$ and 0·8M-$HClO_4$; Mn^{IV}, in the presence of 0·1M-$Na_4P_2O_7$ and 0·5M-$HClO_4$; and MnO_4^-, in aqueous solution without additives

The transmission minimum on the stopped-flow traces obtained between 240 and 270 nm is consistent with the accumulation of both Mn^{IV} and Mn^{III} since the molar extinction coefficient of both species exceeds that of MnO_4^- in this range. However, observation (ii) provides evidence against Mn^{IV}, because the horizontal traces indicate transformation of MnO_4^- into Mn^{III} without a detectable build-up of Mn^{IV} (*cf.* Figure 3, intersection of the spectra). Similar conclusions can be reached from observation (i).

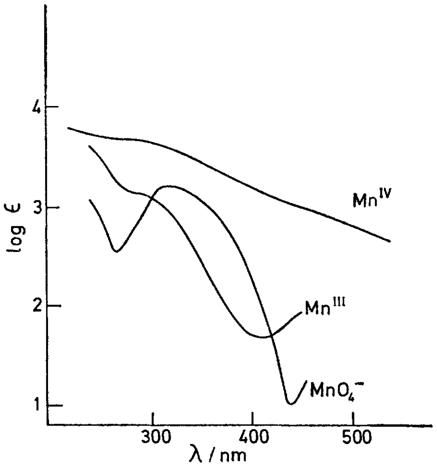

FIGURE 3 U.v.–visible spectra (25 °C); Mn^{III}, in the presence of 0·6M-$Mn(ClO_4)_2$ and 2M-$HClO_4$; Mn^{IV}, in 50% H_2SO_4; and MnO_4^-, in aqueous solution without additives

The addition of an excess of pyrophosphate has the advan-

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[4] L. I. Simándi, *Magyar Kém. Folyóirat*, 1969, **75**, 269.

[5] C. F. Wells, D. Mays, and C. Barnes, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1341.

[6] R. G. Selim and J. J. Lingane, *Analyt. Chim. Acta*, 1959, **21**, 536.

[7] W. A. Waters and J. S. Littler, 'Oxidation by Vanadium(V), Cobalt(III), and Manganese(III)' in 'Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York and London, 1965.

tage that under such conditions the complexation of Mn^{III} and Mn^{IV} by H_2A and the oxalic acid intermediate (*cf.* later) is suppressed and the pyrophosphate complexes predominate. Thus the stopped-flow traces with added pyrophosphate can be reliably evaluated on the basis of the spectra shown in Figure 2, the possible effect of the organic acids on the spectra being eliminated.

Observation (iii) is consistent with the fact that the Mn^{III}–pyrophosphate complex is a less vigorous oxidant than the aquo-ion.[1,6,8] Its disappearance is very slow, Mn^{III} being obtained as a stable product. Observation (iv) strongly indicates that Mn^{IV} is not built up during the reaction. The horizontal traces at 300 and 430 nm correspond to the intersection of the MnO_4^- and Mn^{III}–pyrophosphate spectra.

Thus it has been established that the intermediate, whose build-up and decay can be observed by stopped-flow spectrophotometry, is manganese(III). It will be shown subsequently that Mn^{IV} must also be an intermediate but its lifetime is too short for detection by the stopped-flow technique.

The manganese(III)–aquo-ion exists only in strongly acidic media,[8] otherwise it undergoes hydrolysis according to equation (2). In perchlorate media, $K_H = 0{\cdot}93$ mol l^{-1} at 25 °C.[9]

$$\mathrm{Mn_{aq}^{3+} + H_2O \overset{K_H}{\rightleftharpoons} MnOH^{2+} + H_3O^+} \qquad (2)$$

Upon decreasing the acidity, Mn^{III} disproportionates into Mn^{IV} and Mn^{II}, the former being precipitated as MnO_2. In the presence of complexing agents, *e.g.* sulphate, pyrophosphate, or fluoride, Mn^{III} remains in solution up to pH 5. Acetylenedicarboxylic acid is only slowly attacked by Mn^{III} and the redox interaction is preceded by rapid complex formation. This has been detected spectrophotometrically but, owing to the ensuing reaction, no attempts were made at determining the stability constants. Clearly, the nature of the intermediate Mn^{III} changes with pH, inasmuch as it undergoes hydrolysis and complex formation with the anions of acetylenedicarboxylic acid.

Intermediates from Acetylenedicarboxylic Acid.—In contrast to stoicheiometric equation (1), the reaction in neutral solutions is represented by (3), *i.e.* one mol of oxalate is formed for each mol of permanganate. We have found

$$\mathrm{2MnO_4^- + {}^-O_2C{\cdot}C{\equiv}C{\cdot}CO_2^- \longrightarrow 2(CO_2)_2^{2-} + 2MnO_2} \qquad (3)$$

that for excess of H_2A, oxalic acid is also produced in acid, its amount depending on the $H_2A : MnO_4^-$ mol ratio. The amount of oxalic acid formed in mixtures with various mol ratios is shown in Table 1.

TABLE 1

Dependence of the amount of oxalic acid on the initial $[H_2A] : [MnO_4^-]$ mol ratio; 1·98 mmol $KMnO_4$; 0·33M-$HClO_4$; 25 °C

$[H_2A] : [MnO_4^-]$	N_∞ [a]
0·5	0·0
0·8	0·26
1·0	0·40
1·2	0·39
2·0	0·50
5·0	0·59
10·0	0·53
30·0	0·52
0·54 (pH = 10)	0·96

Amount of oxalic acid per mol of MnO_4^-, mol/mol.

The results in Table 1 show that with increasing excess of the substrate, N_∞ approaches a limiting value of 0·5. At the stoicheiometric composition corresponding to equation (1), no oxalic acid is formed. Under these conditions all the permanganate originally present was reduced to Mn^{II} since no attempt had been made to stop the reaction before completion. Since the spectral changes in the u.v.–visible region during the reaction are dominated by those due to interconversion of the manganese species, the stopped-flow technique is not suitable for detecting the possible organic intermediate. We have applied the related quenching method, which permits the stopping of the reaction after a pre-set contact time (25—1000 ms for the instrument used), by rapid injection of a suitable reagent. The quenched solutions can be analysed by conventional methods. The reaction can also be stopped at the Mn^{III} stage by adding a scavenger, *e.g.* pyrophosphate, which rapidly binds Mn^{III} into a complex which is much less reactive as an oxidant.

In the quenching experiments, the reaction was stopped by the injection of aqueous iron(II) sulphate, which rapidly reduced the Mn^{III} present after the given contact time. The efficiency of quenching depends on the rate of this reduction. The amount of oxalic acid found after quenching the reaction with Fe^{II} is shown in Table 2.

TABLE 2

Results of quenching experiments with Fe^{II}; 4·00 mmol H_2A; 2·05 mmol $KMnO_4$; 0·1M-$HClO_4$

Contact time (ms)	$Ca(CO_2)_2,H_2O$ (g)	N_Q [a]
49·2	0·2030	0·68
98·5	0·1825	0·61
147·7	0·1990	0·67
245·0	0·2040	0·68

[a] Amount of oxalic acid per mol of MnO_4^-, mol/mol.

As indicated by the data in Table 2, the amount of oxalic acid in the quenched solutions is larger than that found after complete reaction. Consequently, oxalic acid is an intermediate and its concentration goes through a maximum during the reaction.

TABLE 3

Amount of oxalic acid in the presence of pyrophosphate as scavenger. 4·00 mmol $KMnO_4$; 4·00 mmol H_2A; 25 °C

Runs 1—4, Mn^{III}-pyrophosphate complex reduced with Na_2SO_3

Runs 5—9, complex decomposed with added NaOH

No.	pH [a]	N_{pyr} [b]
1	0·25	0·87
2	2·63	0·86
3	3·86	0·86
4	5·30	1·13
5	0·25	1·05
6	2·63	0·92
7	2·63	0·94
8	3·86	1·02
9	5·30	1·06

[a] Buffers: monochloroacetic acid (pH 2·63) and succinic acid (pH 3·86 and 5·30). [b] Amount of oxalic acid per mol of MnO_4^-, mol/mol.

Table 3 shows the amount of oxalic acid in the presence of added pyrophosphate as scavenger at various pH values.

According to Table 3, in the presence of pyrophosphate the amount of oxalic acid increases further and reaches the

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[8] G. Davies, *Co-ordination Chem. Rev.*, 1969, **4**, 199.

[9] C. F. Wells and G. Davies, *J. Chem. Soc.* (*A*), 1967, 1858.

limiting value of 1·0. The important consequence of this is that $N_{\text{pyr}} = 1$ is only conceivable if manganese(IV) is also an intermediate. 1 Mol of oxalic acid formed per mol of MnO_4^- can only be due to a reaction similar to that of equation (3), with the difference that Mn^{IV} is not precipitated as MnO_2. If the first manganese intermediate were Mn^{III}, the value of N_{pyr} could under no circumstances exceed 0·5. Apparently, the life time of Mn^{IV} is too short for detection by the stopped-flow technique.

TABLE 4

Oxygen-18 enrichment (D) of calcium oxalate samples from the quenching experiments

Sample	D_{ox}	x
$Ca(CO_2)_2,H_2O$	1·37	0·209
$Ca(CO_2)_2,H_2O$	1·35	0·144
$Ca(CO_2)_2,H_2O$	1·37	0·209

Enrichment of the medium $D_{\text{m}} = 2{\cdot}53$.

TABLE 5

Comparison of the experimental data with the results predicted by some combinations of reactions (6)

Reaction sequence [a]	Predicted result				Is Mn^{III} an intermediate?	Conclusion
	N_∞	N_{Q}	N_{pyr}	$n(x)$		
(a)–(b)–(α)	0	0—0·5	0—0·5	2 or 4 (0)	Yes	3 [d]
(2a)–(c)–(A)	0·83	0·83—1	0·83—1	1·66—2·0 (0·33—0·66)	Yes	3 [d]
(3a)–2(c)–(B)–(2·5α)	0·5	0·5—1	0·5—1	1·8—2·0 (0·2—0·4)	Yes	e
(a)–(c)–(C)–(α) [b]	0	0—1	0·5—1	2(0)	Yes	1 [d]
(a)–(c)–(C)–(α) [c]	0	0—1	0—0·5	2(0)	Yes	2 [d]
(a)–(c)–(2D) [b]	0	0—1	0—1	2(0)	No	2 [d]
(a)–(c)–(2D) [c]	0	0—1	0	2(0)	No	3 [d]
(2d)–(β)	1	0—1	0—1	1(1)	Yes	2 [d]
(12)	0·83	0·83—1·33	1·33	1·5(0·5)	Yes	4 [d]
(13)	0·83	0·83—1·33	1·33	1·25(0·75)	Yes	4 [d]
Experimental value	0—0·5	0·68	1·0	$x \leqslant 0{\cdot}2$	Yes	

[a] The numbers before the letters are the corresponding factors used in balancing the overall equation for the given sequence. [b] Pyrophosphate deactivates Mn^{IV}. [c] Pyrophosphate does not deactivate Mn^{IV}. In cases where notes *b* and *c* are not given, deactivation of Mn^{IV} does not affect the results. [d] The given sequence contradicts the experimental results. The numeral gives the number of wrong predictions out of a total of five. [e] The given sequence is consistent with all of the experimental data.

^{18}O *Tracer Experiments*.—A question of considerable importance is whether the oxidation by permanganate is accompanied with oxygen atom transfer from MnO_4^- to the substrate and if so, to what extent. To obtain an answer, we carried out the oxidation in ^{18}O-enriched water using the quenching device, and have determined the ^{18}O-content of the obtained $Ca(CO_2)_2,H_2O$ by means of mass-spectrometric analysis (Table 4). The ^{18}O-content (D) of the samples is given as enrichment relative to the natural abundance (0·204%) [equation (4)]. If the experimental

$$D = {}^{18}O(\%)/0{\cdot}204 \qquad (4)$$

^{18}O content of $Ca(CO_2)_2,H_2O$ is D_{ox}, and the enrichment of the medium D_{m}, then equation (5) applies where x is the

$$D_{\text{ox}} = [4 - x + D_{\text{m}}(1 + x)]/5 \qquad (5)$$

number of oxygen atoms derived from the medium. According to Table 4, of the four oxygen atoms of oxalic acid, a maximum of 0·2 originates from the medium. Measurements on the ^{18}O exchange between normal oxalic acid and ^{18}O-enriched water have shown that under conditions identical with those of the quenching experiments, induced exchange amounts to 0·2—0·4 atoms of oxygen. The results unambiguously prove that the permanganate oxidation of acetylenedicarboxylic acid takes place exclusively by oxygen atom transfer from MnO_4^-.

DISCUSSION

The interpretation of the results requires consideration of a number of alternative mechanisms, including the possible interactions between MnO_4^- and H_2A and the conceivable reactions between the intermediates and reactants. To enable systematic handling, we shall list the reactions of MnO_4^-, Mn^{IV}, and Mn^{III} that seem to be supported by experimental evidence and then, by examining a variety of possible sequences, comparison will be made between the predicted and actual experimental results. We shall concern ourselves primarily with the type of the redox interaction. Therefore, the components that have no importance from this aspect will not be included. Thus the symbols Mn^{IV} and Mn^{III} do not specify the actual co-ordination spheres of these ions, because this is immaterial in the present considerations.

To find the reaction series consistent with the experimental results, Table 5 lists some multi-step sequences that can be constructed from reactions (6). Along with these are shown the predicted results for the individual types of experiments performed. At the bottom of each column is shown the experimentally observed result. Where intervals are given for N_{Q} and N_{pyr}, the upper limit refers to the case when the reaction of Mn^{III} with the quenching and scavenging agent is much faster than its subsequent redox reactions, *i.e.* the deactivation of Mn^{III} is perfect. The lower limits refer to complete inefficiency of the quenching and scavenging reactant. All permanganate reactions occur with the transfer of two oxygen atoms, one to each bridgehead carbon of the double or triple bond. Although Mn^{IV} may, in principle, retain a maximum of two permanganate oxygen atoms in its co-ordination sphere (soluble species of the type MnO^{2+}, MnO_3^{2-}, and $H_2MnO_4^{2-}$ have been assumed [1,7,10]), we have regarded reactions (A) and (B) as ones not in-

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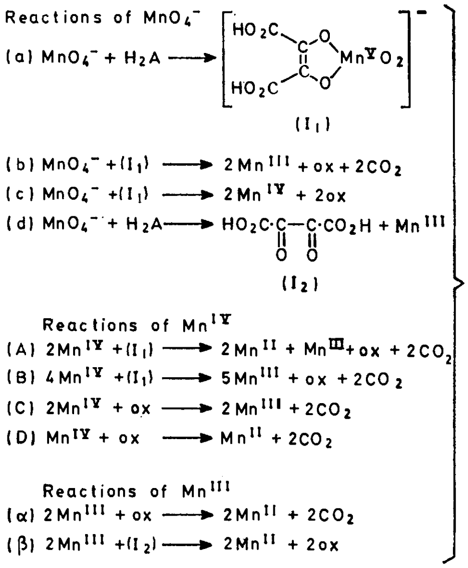
[10] J. W. Ladbury and C. F. Cullis, *Chem. Rev.*, 1958, **58**, 403.

volving the transfer of oxygen atoms that originally belonged to MnO_4^-. The occurrence of such an improbable event would somewhat increase the *n* values listed in Table 5, which can thus be considered as minimal. In the case of sequences involving any one of the reactions (b), (A), and (B), intervals are given for the predicted *n* and *x* values, because the mol of oxalic acid may be derived from positions 1 and 2 (lower limit) or 2 and 3 (upper limit) of the original four-atom chain.



(6)

Inspection of the data in Table 5 shows that the observed behaviour is consistent only with reaction sequence (a)–(c)–(B)–(α) [reactions (7)]. We suggest

$$\begin{array}{ll} \text{i.} & MnO_4^- + H_2A \longrightarrow (I_1) \\ \text{ii.} & MnO_4^- + (I_1) \longrightarrow 2Mn^{IV} + 2ox \\ \text{iii.} & 4Mn^{IV} + (I_1) \longrightarrow 5Mn^{III} + ox + 2CO_2 \\ \text{iv.} & 2Mn^{III} + ox \longrightarrow 2Mn^{II} + 2CO_2 \end{array} \qquad (7)$$

that the first, rapid reaction observed (*cf.* Figure 1) corresponds to the conversion of MnO_4^- into Mn^{III}, *i.e.* to the sum of (7i) — (7iii) [reaction (8)]. In the subsequent slower process, the Mn^{III} formed oxidises one half of the oxalic acid. Thus the overall reaction is represented by equation (9). If the $MnO_4^- : H_2A$ mol ratio is 2, then equation (1) is valid and there is no oxalic acid formed. It should be emphasised that the above sequence may, to a certain extent, be mixed with other combinations as parallel reactions, modifying the observed picture but slightly. From this aspect, it is of importance to consider how many of the five kinds of available information are at variance with the predictions of a given sequence. For example, the series (a)–(c)–(C)–(α) may contribute to (7), its only wrong prediction being that $N_\infty = 0$. Indeed, if the concentration of H_2A is decreased, reaction (C) may gradually replace (B) [*i.e.* (7iii)]. The data in Table 1 show that this actually occurs. As the $H_2A : MnO_4^-$ mol ratio approaches 0·5, the value of N_∞ tends to zero. Therefore, reaction (10) must also be included in the scheme, with the proviso that at higher H_2A concentrations it does not take place.

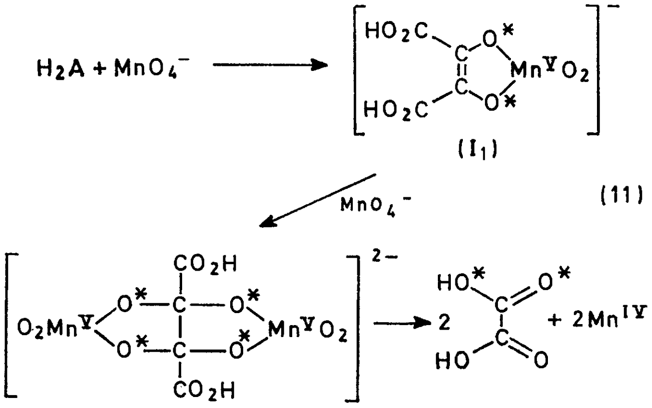
$$5MnO_4^- + 3H_2A \longrightarrow 5ox + 5Mn^{III} + 2CO_2 \qquad (8)$$

$$5MnO_4^- + 3H_2A \longrightarrow 2{\cdot}5ox + 5Mn^{II} + 7CO_2 \qquad (9)$$

$$2Mn^{IV} + ox \longrightarrow 2Mn^{III} + 2CO_2 \qquad (10)$$

The details of reaction (7iii) cannot be elucidated on the basis of the available data. The results require that Mn^{IV} disappear in a process producing one mol of oxalic acid for each mol of MnO_4^- consumed. There is ample evidence for the Mn^{III} intermediate, consequently, Mn^{IV} should bring about one electron oxidations, thus providing a source for Mn^{III}. Presumably, reaction (7iii) occurs *via* reactive intermediate radicals, which selectively capture Mn^{IV}.

The ^{18}O-tracer results permit further conclusions on the mechanism of reaction (7i)–(7ii). The fact that practically no ^{18}O from the medium is present in the oxalic acid implies that two oxygen atoms are transferred in both (7i) and (7ii), which thus should involve the steps (11). This route contributes 80% of the oxalic acid formed. In the remaining 20%, one to two oxygen atoms may be derived from the medium, depending on whether the oxalic acid contains C(1) and C(2) or C(2) and C(3). Since the experimental value of *x* is *ca.* 0·2, it seems likely that in reaction (7iii), oxalic acid is derived from C(1) and C(2). In mechanism (11), the transient formation of a cyclic intermediate, containing manganese-(v), is assumed although attempts at its detection have failed. Moreover, the tracer results and the amount of oxalic acid formed require that a dicyclic species be also involved since a unimolecular redox transformation of the first intermediate would result in a dioxo-(or tetrahydroxy-)derivative which has not been found. Oxidation of the dioxo-compound by Mn^{III} would yield oxalic acid with one oxygen atom derived from the medium, in obvious contradiction to the experimental data.



(11)

The first cyclic intermediate is analogous to that involved in the oxidation of alkene derivatives by alkaline or neutral permanganate.[11]

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[11] K. B. Wiberg and K. A. Saegebarth, *J. Amer. Chem. Soc.*, 1957, **79**, 2822, and references therein.

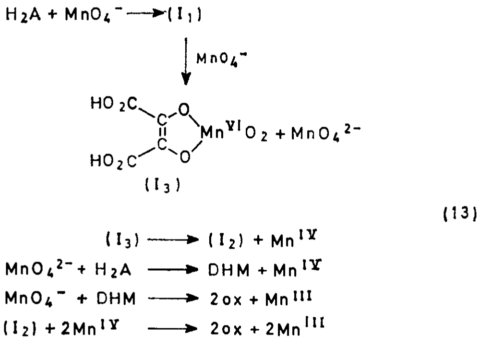
In the present case the cyclic species has a structure similar to that of dihydroxymaleic acid, which has been found very reactive towards acidic permanganate.[12] This also seems to support the possible formation of a second ring before the first cyclic ester could react further.

We have included two other mechanisms into Table 5 which, however, cannot be constructed from reactions (6). In principle, (I_1) may undergo hydrolysis to

$$\begin{aligned}
\mathrm{MnO_4^-} + \mathrm{H_2A} &\longrightarrow \mathrm{DHM} + \mathrm{MnO_4^{3-}} \\
\mathrm{MnO_4^-} + \mathrm{DHM} &\longrightarrow 2\mathrm{ox} + \mathrm{Mn^{III}} \\
\mathrm{MnO_4^{3-}} + \mathrm{H_2A} &\longrightarrow \mathrm{DHM} + \mathrm{Mn^{III}} \\
2\mathrm{Mn^{III}} + \mathrm{ox} &\longrightarrow 2\mathrm{Mn^{II}} + 2\mathrm{CO_2}
\end{aligned} \qquad (12)$$

yield dihydroxymaleic acid (DHM) and manganese(V), which would then react as shown in (12).* In calculating the predicted values for *n* and *x*, MnO_4^{3-} was assumed to retain two oxygen atoms from MnO_4^-. Table 5 shows that the above mechanism is not consistent with the experimental results.

It has been suggested that the oxidation of olefins by alkaline permanganate occurs *via* a manganese(VI) intermediate.[1,11] By analogy to this concept, the sequence (13) is conceivable.



The inconsistency of sequence (13) with the results (Table 5) indicates that the combination reaction $Mn^{V} + Mn^{VII} = 2Mn^{VI}$ is not operative in acidic media.

In considering the mechanistic alternatives, we have neglected the Guyard reaction[10] occurring between MnO_4^- and Mn^{II}. The reason for this is that, as witnessed by traces similar to Figure 1 and rate measurements,[12] these two species do not coexist at any time during the overall process. Manganese(II) is formed in the second, slower stage only and by this time MnO_4^- has already disappeared.

A detailed kinetic study of the reaction will be reported in a forthcoming paper.

EXPERIMENTAL

Materials.—Acetylenedicarboxylic acid (m.p. 180·5 °C) (Fluka) was purified by multiple precipitation from ether with petroleum ether. All other chemicals were of reagent grade.

Determination of Oxalic Acid.—Calcium oxalate was precipitated in an acetic acid medium. After weighing the dry product, it was dissolved in perchloric acid and titrated against standard permanganate. The solutions quenched with iron(II) sulphate were first made alkaline and the precipitated hydroxides were filtered off. At the pH of oxalate precipitation, ethylenediaminetetra-acetic acid was added for masking, then an excess of calcium chloride for precipitating calcium oxalate. In the presence of pyrophosphate, the Mn^{III} complex was decomposed by sodium hydroxide. After filtering off MnO_2 and $Mn(OH)_2$, the pyrophosphate was precipitated with zinc acetate at pH 5, followed by the precipitation of oxalate. The Mn^{III}–pyrophosphate complex was reduced by sulphite in some experiments, with subsequent application of the above procedure.

Quenching Experiments.—The reagent solutions were contained in two syringes whose pistons were driven by a constant speed motor. After passing through a mixing chamber, the reacting solution flowed down a capillary of known length, at the end of which the reaction was quenched by injection of a suitable solution. The contact time was determined by the flow velocity and the length of the reaction zone, both of which could be varied to give reaction times between 25 and 1000 ms. The quenched effluent was analysed by conventional methods.

Tracer Experiments.—These were carried out by mixing $KMnO_4$ in normal water and H_2A in ^{18}O-enriched water on the quenching device (contact time 50 ms). The reaction was stopped by injecting a solution of sodium hydroxide. Oxalic acid was determined as described above. The isotope composition of oxalic acid was determined with a mass spectrometer.

Spectrum of Mn^{IV}.—Potassium permanganate was reduced to MnO_2 with formic acid in a weakly alkaline medium (Na_2CO_3). The fresh precipitate was washed and allowed to stand for 1 day in contact with sulphuric acid, or perchloric acid containing sodium pyrophosphate. After filtering, the Mn^{IV} content was determined iodometrically. The spectra were recorded on a Hitachi–Perkin-Elmer 124 instrument in Infrasil cells.

Spectrum of Mn^{III}.—The solutions were prepared by reducing permanganate with Mn^{II} in 4M-$HClO_4$, in the presence or absence of pyrophosphate. To suppress disproportionation of Mn^{III}, 0·6M-$Mn(ClO_4)_2$ was added.

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* This possibility has been pointed out by a Referee.

[12] L. I. Simándi and M. Jáky, unpublished results.