Mechanism of the Permanganate Oxidation of Unsaturated Compounds. Part VI.† Kinetic Investigation of the Oxidation of Methylmaleic Acid, Methylfumaric Acid, and Dimethylmaleic Acid

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The kinetics of the permanganate oxidation of methylmaleic (MMA), methylfumaric (MFA), and dimethylmaleic (DMA) acids have been studied by the stopped-flow technique in aqueous solution between pH 0.0 and 5.0. Manganese(III) has been detected as a short-lived intermediate in all cases. The reactions are first order with respect to both MnO_4^- and the substrate. The second-order rate constant depends strongly on the pH. The rate of interconversions of the acid, the mono-, and the di-anion is much higher than the rate of oxidation. The rate constants are, in the above order (at 25 °C, in $dm^3\ mol^{-1}\ s^{-1}$): 150, 660, and 310 (MMA); 1 240, 370, and 98 (MFA); 240, 90, and 54 (DMA). Low activation enthalpies and high negative activation entropies are observed in all cases. The rate-determining step is the *cis*-attack of permanganate on the double bond, resulting in the formation of a short-lived, undetectable cyclic hypomanganate (MnO_4^{3-}) ester. The relative reactivities reflect the influence of steric factors.

In Parts III [1] and IV,[2] the kinetics and mechanism, as well as the short-lived intermediates of the permanganate oxidation of maleic and fumaric acids have been studied in acidic solution. As steric conditions play an important part in the oxidation of maleic and fumaric species,[2] the effect of methyl substitution may provide further insight into the nature of the factors governing the relative reactivities of olefinic substances towards permanganate. Therefore, we have studied the kinetics and mechanism of the oxidation of methylmaleic acid (MMA), methylfumaric acid (MFA), and dimethylmaleic acid (DMA) in acidic solution by the stopped-flow technique.[3]

RESULTS AND DISCUSSION

Stoicheiometry.—The titration of MMA, MFA, and DMA with permanganate in acidic solutions gives a drawn out end-point, because, although the reaction with the double bond is rapid, the products of primary oxidation react but slowly with the oxidant. The results of direct and reverse titrations are summarised in Table 1. The data warrant the conclusion that DMA consumes 8, and MMA and MFA 10 oxidation equivalents, up to the point where the reaction practically stops, *i.e.* no further change occurs within *ca.* 30 min. The results in Table 1 are consistent with stoicheiometric equations (1) and (2), in agreement with previous findings.[4] Besides CO_2, acetic acid is the sole end-product in line with the fact that it is oxidised by permanganate very slowly both in acidic and neutral media.

$$5HO_2CC(CH_3){=}C(CH_3)CO_2H + 8MnO_4^- + 24H^+ \longrightarrow 10CH_3CO_2H + 10CO_2 + 8Mn^{2+} + 12H_2O \quad (1)$$

$$HO_2CC(CH_3){=}CHCO_2H + 2MnO_4^- + 6H^+ \longrightarrow CH_3CO_2H + 3CO_2 + 2Mn^{2+} + 4H_2O \quad (2)$$

TABLE 1

Titration of DMA, MMA, and MFA with permanganate

Substrate	Oxidation equivalents consumed * (1)	(2)	(3)
Dimethylmaleic acid	7.4	7.8	8.6
Methylmaleic acid	9.2	9.6	9.6
Methylfumaric acid	9.0	9.8	10.4

* (1) Direct titration in 10% H_2SO_4 (end-point: the colour of MnO_4^- persists for 1 min). (2) Reaction with excess of MnO_4^- in 6% H_2SO_4 for 30 min; excess of oxalic acid added and titrated with MnO_4^-. (3) Substrate neutralised with Na_2CO_3, reaction with excess of MnO_4^- for 15 min; excess of oxalic acid added and titrated with MnO_4^- after acidification.

Intermediates.—As described earlier in detail,[5] the known u.v.–visible spectra of manganese species between the oxidation states +7 and +2 permit the detection of short-lived intermediates by recording the stopped-flow traces of the reaction at various wavelengths between 200 and 800 nm. We have found that at 260 nm and in its immediate vicinity, the stopped-flow traces clearly show the accumulation and decay of an intermediate. In the presence of a five-fold excess of pyrophosphate over MnO_4^- with other things being equal, the transmission

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† Part V, L. I. Simándi and M. Jáky, *J.C.S. Perkin II*, 1973, 1861.

[1] Part III, M. Jáky, L. I. Simándi, L. Maros, and I. Molnár-Perl, *J.C.S. Perkin II*, 1973, 1565.

[2] Part IV, L. I. Simándi and M. Jáky, *J.C.S. Perkin II*, 1973, 1856.

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

[4] R. Kuhn, A. Winsterstein, and L. Karlowitz, *Helv. Chim. Acta*, 1929, **12**, 64.

[5] M. Jáky and L. I. Simándi, *J.C.S. Perkin II*, 1972, 1481.

minimum practically disappears as the decay of the intermediate becomes very slow. In view of the fact that the molar absorbance of manganese(III) exceeds that of MnO_4^- in the above region, the short-lived intermediate can be identified as manganese(III). Since complex formation with pyrophosphate is known to convert manganese(III) into a relatively unreactive oxidant, it behaves as a stable product on the time scale of the stopped-flow experiment. Evidence against the accumulation of manganese(V) as an intermediate is provided by the absence of traces passing through a transmission minimum around 700 nm, where hypomanganate, (MnO_4^{3-}),[6] and very probably its esters, are known to have a strong absorption maximum.

Recently, Lee and Brownridge[7] claimed to have detected a relatively stable hypomanganate ester in the oxidation of *trans*-cinnamic acid by acidic permanganate. Their conclusion is based on the appearance of a transient minimum on the transmission *versus* time curve recorded at 415 nm. We observed similar minima for the substrates studied in this work, which, however, did not appear in the presence of pyrophosphate. Consequently, this intermediate is formed from manganese(III), probably *via* the known disproportionation[6,8] into manganese-(II) and -(IV). Thus, the 415 nm intermediate is apparently some kind of soluble manganese(IV) which is reduced before being precipitated as MnO_2.

In order to identify the organic intermediates formed as a result of the $\text{Mn}^{\text{VII}} \longrightarrow \text{Mn}^{\text{III}}$ process, the reactions were performed in the presence of pyrophosphate and quenched with sulphite, which reacts very rapidly with both the manganese(III)–pyrophosphate complex and the residual MnO_4^-. Utilising the kinetic results (see later), the time of quenching was selected so that *ca.* 95% of the MnO_4^- added were converted to manganese(III). In the quenched solutions of all three substrates we have detected pyruvic acid (strongly positive test with sodium nitroprusside).[9] In the case of MMA, four different test reactions for glyoxylic acid (with 2,7-dihydroxynaphthalene, pyrogallolcarboxylic acid, phenylhydrazine, and β,β′-binaphthol)[9] gave strongly positive results, whereas for MFA the test was negative or very weakly positive. We have measured the amount of CO_2 accompanying the $\text{Mn}^{\text{VII}} \longrightarrow \text{Mn}^{\text{III}}$ process; the results are given in Table 2.

TABLE 2

Amount of CO_2 evolved from solutions quenched with sulphite

	CO_2 (mol per mol MnO_4^-)
DMA	1.00 ± 0.02
MMA	0.56 ± 0.06
MFA	1.48 ± 0.08

Acid Dissociation Constants.—The stepwise dissociation constants have been determined by pH-metric titration as described earlier.[2] The p*K* values obtained are listed in Table 3.

TABLE 3

p*K* Values at 25 °C (ionic strength 1.5M)

	pK_1	pK_2
DMA	3.97	5.25
MMA	2.07	5.07
MFA	2.72	4.17

Estimated accuracy ±0.05 p*K* units.

Kinetic Measurements.—Owing to the rapidity of the reactions studied, the kinetic measurements have been performed by the stopped-flow technique. The disappearance of permanganate was followed at 540 nm. The ionic strength was maintained at 1.5M with added $NaClO_4$. The pH was varied between 0.0 and *ca.* 5.7, depending on the substrate.

In the presence of at least a 10-fold excess of DMA, MMA, or MFA, the disappearance of MnO_4^- obeys a first-order rate law, *i.e.* the plot of log $(A - A_\infty)$ against time gives excellent straight lines. The slopes observed in the presence and absence of pyrophosphate are identical, indicating that the Guyard reaction[6] occurring between MnO_4^- and manganese(II) when the latter is present plays no role under these conditions. In other words, manganese(II) does not appear in the system before all the permanganate is consumed. At a given pH, the pseudo-first-order rate constant is proportional to the substrate concentration (Figure 1). The kinetic equation for the oxidation of all three substrates can thus be given by equation (3), where $[H_2A]_T$ is the overall substrate concentration. The observed second-order rate constant *k*

$$-d[MnO_4^-]/dt = k_{obs}[MnO_4^-] = k[H_2A]_T[MnO_4^-] \quad (3)$$

shows a pronounced pH-dependence with all three substrates, as illustrated in Figure 2. The kinetic be-

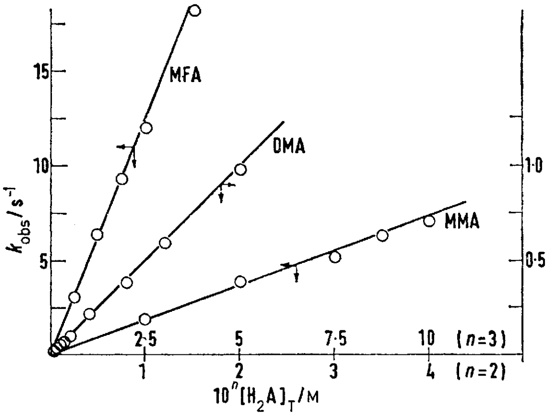

FIGURE 1 Pseudo-first-order rate constant *versus* the overall substrate concentration (*t* 25 °C; ionic strength 1.5M; pH 3.63 for DMA, and 0.88 for MMA and MFA)

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

[7] D. G. Lee and J. R. Brownridge, *J. Amer. Chem. Soc.*, 1973, **95**, 3033; 1974, **96**, 5517.

[8] 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.

[9] F. Feigl, ' Spot Tests in Organic Analysis,' Elsevier, London and New York, 1956.

haviour described is consistent with a common mechanism in which the rate-determining step is a bimolecular reaction between MnO_4^- and any of the three possible species involved in the dissociation equilibria of the diacid type substrates [equation (4)]. If one assumes that the dissociation equilibria are attained much faster than the rate of the reaction with permanganate, k can be written as in equation (5),[2] where a_H is the hydrogen ion activity.

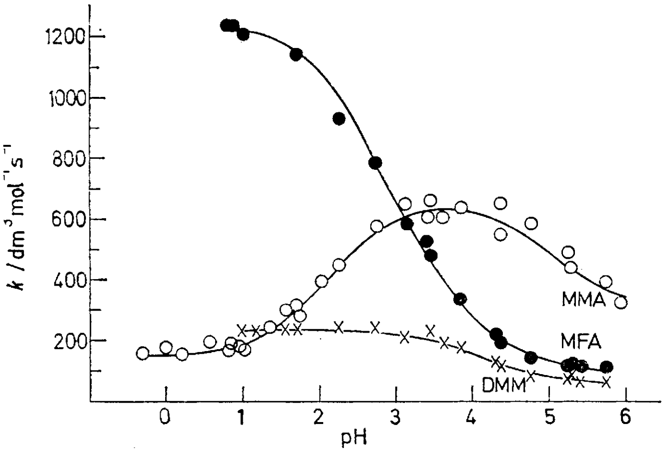


FIGURE 2 pH-Dependence of the second-order rate constant k (t 25 °C; ionic strength 1.5M)

$$\begin{tikzcd}
 & H_2A \arrow[r, "k_1"] \arrow[d, shift right, "K_1"'] & X_1 \\
MnO_4^- + & HA^- \arrow[u, shift right] \arrow[r, "k_2"] \arrow[d, shift right, "K_2"'] & X_2 \\
 & A^{2-} \arrow[u, shift right] \arrow[r, "k_2"] & X_3
\end{tikzcd} \qquad (4)$$

$$k = \frac{k_1 a_H{}^2 + k_2 K_1 a_H + k_3 K_1 K_2}{K_1 K_2 + K_1 a_H + a_H{}^2} \qquad (5)$$

In order to determine the individual rate constants k_1—k_3, referring to species H_2A, HA^-, and A^{2-}, respectively, equation (5) was fitted to the experimental k *versus* pH curve, using a computer program based on a ' steepest descent ' type gradient method. In the procedure, the values of the acid dissociation constants K_1 and K_2 were those obtained by pH-metric titration. Rapid convergence was obtained in all cases. The solid lines in Figure 2 represent the curves calculated with the resolved constants.

TABLE 4

Resolved second-order rate constants [a] ($dm^3 mol^{-1} s^{-1}$) at 25 °C; ionic strength 1.5M

Substrate	k_1	k_2	k_3	Ref.
Methylfumaric acid	1 240	370	98	This work
Methylmaleic acid	150	660	310	This work
Dimethylmaleic acid	240	90	54	This work
Fumaric acid	15 000	3 000	1 180	2
Maleic acid	1 080	1 880	1 000	2

[a] Estimated accuracy ±8%.

The activation parameters have been determined in the temperature range 11—40 °C at pH values that ensure unequivocal assignment to a given rate constant without determination of the temperature dependence of the acid dissociation constants. The results obtained are listed in Table 5.

TABLE 5

Arrhenius parameters [a] for the permanganate oxidation of MFA, MMA, and DMA

	$\Delta H^‡$/ kJ mol⁻¹	$\Delta S^‡$/ J mol⁻¹ K⁻¹
Methylfumaric acid (pH 0.81)	17.6	−128
Methylfumarate(2−) (pH 5.42)	19.7	−141
Methylmaleic acid (pH 0.0)	15.0	−153
Methylmaleate(1−) (pH 3.6)	18.4	−130
Dimethylmaleic acid (pH 1.56)	15.5	−148

[a] Estimated accuracy ±10%.

The effect of the ionic strength has been examined at pH values ensuring the predominance of the H_2A or A^{2-} species. Upon decreasing the ionic strength from 1.5 to 0.1M, k_1 remains practically constant, whereas k_3 drops to about one half of its original value for all three substrates. This behaviour is consistent with the participation of two negatively charged species in the rate-determining step in the case of A^{2-} [*cf.* equation (4)]. As expected, the reaction of the neutral H_2A is not susceptible to changes in the ionic strength of the medium.

In principle, the rate-determining step (4) may be followed by the fast reaction of a second MnO_4^- ion with the intermediate X. This would lead to the same kinetic equation (3), with the only difference that the observed second-order rate constant k would include a factor of 2 *i.e.* $k = 2k'$, where k' should be assigned to steps (4). In order to elucidate this point, kinetic measurements have been performed at a $[MnO_4^-] : [H_2A]_T$ ratio of 1 : 1, under otherwise identical conditions. In these circumstances the involvement of the factor of 2 strongly influences the form of the integrated rate equation, depending on whether the reactants are consumed in a 1 : 1 or a 2 : 1 ratio. Linear transformation of the rate data was only possible if this ratio was assumed to be 1 : 1, *i.e.* if integrated rate equation (6) was used. The value of k derived from this plot was identical with that obtained from the kinetic data at the same pH and ionic strength

$$[MnO_4^-]^{-1} - [MnO_4^-]_0^{-1} = kt \qquad (6)$$

but in the presence of a 10-fold excess of H_2A. Thus the rate-determining step (4) is *not* followed by the fast reaction of a second MnO_4^- ion.

In order to obtain information on the fate of the manganese(III) intermediate, we have performed the following experiments.

(1) The pyrophosphate complex of manganese(III) does not oxidise the substrates used, as shown by spectrophotometric measurements. The same has been demonstrated for the aquomanganese(III) species in strong acid.

Consequently, the decay of manganese(III) must be due to its reaction with the organic intermediate(s). It should be noted that this decay does not reach any significant extent before the complete disappearance of MnO_4^-. This fact is important because it eliminates the Guyard reaction occurring between MnO_4^- and manganese(II), which could influence the kinetics of the main reaction (5).

(2) The disappearance of manganese(III) has been followed spectrophotometrically at 510 nm in separate experiments in the presence of pyrophosphate. The decay curve can be described by rate equation (7) where S is the organic intermediate attacked by Mn^{3+}. As the

$$-d[Mn^{3+}]/2dt = k_{Mn}[S][Mn^{3+}] \qquad (7)$$

reactions of MnO_4^- and Mn^{3+} are much different in rate, it can be assumed that $[S]_0 = [Mn^{3+}]_0 = [MnO_4^-]_0$, and therefore, equation (7) integrates to (8) if we assume that S and Mn^{3+} are consumed in a 1 : 2 ratio, as often observed for manganese(III) oxidations.[9] In equation (8) A and A_0 are the absorbance of the solution at times t and

$$k_{Mn}t = \frac{2.303}{[MnO_4^-]_0} \log \frac{A + A_0}{2A} \qquad (8)$$

zero, respectively. As the intermediates X may be cleaved in more than one way to yield manganese(III) and organic fragments (see later), equation (7) is approximate because it implies a single oxidisable organic fragment. In spite of this, equation (7) provides useful information when the values of k_{Mn} are compared with the rate constants obtained from kinetic runs with manganese(III) and pyruvic or glyoxylic acid, which have been identified as intermediates of the reactions with permanganate. The values for k_{Mn} are listed in Table 6 together with the results for the oxidation of glyoxylic and pyruvic acid by pyrophosphatomanganese(III). The data clearly show that the disappearance of manganese(III), when formed as intermediate, is considerably faster than in the case of reactions with either pyruvic or glyoxylic acid under otherwise identical conditions. Consequently, the latter two cannot be the only organic intermediates with MMA and MFA. The intermediate formation of glyoxylic acid from DMA is excluded for structural reasons (see mechanism) but pyruvic acid is conceivable. However, the latter reacts by a factor of *ca.* 0.65 slower than the actual intermediates.

TABLE 6

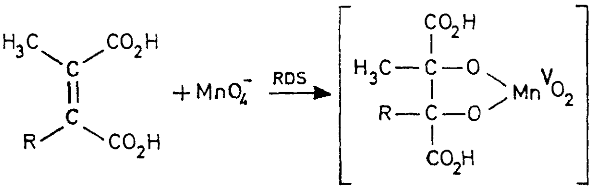
Values of k_{Mn} ($dm^3\ mol^{-1}\ s^{-1}$) determined from equation (8) $[S]_0 = [Mn^{3+}]_0 = 1.5 \times 10^{-3}$M; $[HClO_4] = 0.1$M; [pyrophosphate] = 7.5×10^{-3}M; ionic strength 1.5M; t = 25 °C

Substrate	k_{Mn}
DMA	1.7
MMA	7.2
MFA	6.2
Glyoxylic acid [a]	3.7
Pyruvic acid [a]	1.1

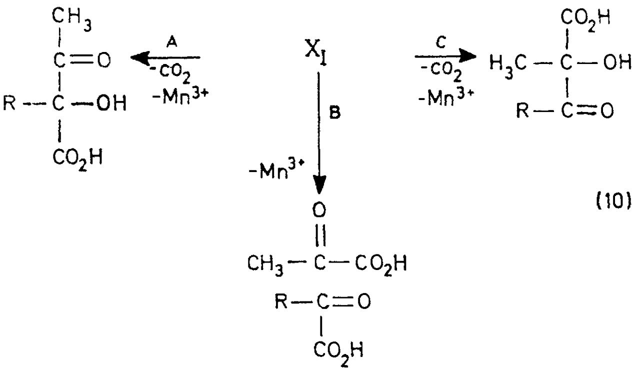
[a] Pyrophosphatomanganese(III) prepared by reacting MnO_4^- with manganese(II).

The present kinetic results are consistent with reaction mechanism (4), *i.e.* the rate-determining step is a bimolecular reaction between MnO_4^- and any of the substrate species which are in rapid acid–base type equilibrium with each other. No evidence has been found for either acid catalysis or autocatalysis.

As it is unreasonable to assume that more than two electrons would be transferred in one elementary step, it seems justified to assign the oxidation state of manganese in intermediates X_1—X_3 as +5, in line with earlier suggestions.[1,2,7,10] This intermediate, however, escapes detection by the stopped-flow technique, apparently, owing to its short life-time. The first detectable intermediate has been positively identified as a manganese(III) species, and this seems to be a characteristic feature of the permanganate oxidation of olefin and acetylene derivatives in acidic solutions.[1,2,5,11] According to the kinetic results, the rate-determining step (RDS) involves one molecule of each permanganate and the substrate. In view of this, the first step of the oxidation sequence can be written as equation (9). Similar steps are assumed for the other possible species involved in the acid–base equilibria. As manganese(V) cannot be detected by the stopped-flow technique, step (9) must be followed by (10) in which manganese(III), the first detectable intermediate, is formed in a rapid two-electron process. By analogy to the behaviour of maleic and fumaric acid,[1] intermediate X_1 may split in three ways, *viz.* at the C(1)–C(2), C(2)–C(3), and C(3)–C(4) bonds (paths A, B, and C, respectively). In two of these cases, oxidative decarboxylation occurs. The CO_2 evolution data in



X_1 (9)



(10)

(R = H or CH_3)

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

[11] L. I. Simándi and M. Jáky, *J.C.S. Perkin II*, 1972, 2326; 1973, 1861.

Table 2 show the involvement of paths A and C, although to different extents. The products of both A and C are susceptible to decarboxylation [12] under the conditions of CO_2 determination (100 °C), which would tend to increase the amount of CO_2 formed towards a maximum of 2 mol per mol MnO_4^-. The contribution of the individual paths cannot be assessed from the data but MMA seems to split predominantly at the C(2)–C(3) bond.

The relative values of rate constants k_1—k_3 resemble those observed in the case of maleic and fumaric acid. MFA (*trans*) is *ca.* 8 times more reactive than its *cis*-counterpart (MMA), apparently for the same steric reasons as for the oxidation of fumaric and maleic acid,[2] *viz.* rehybridisation at C(2) and C(3) upon *cis*-attack of MnO_4^- and the forced mutual approach of the *cis*-substituents. Similarly to maleic acid, k_2 for MMA is greater than either k_1 or k_3, which may be due to the lower steric hindrance to *cis*-attack of the planar hydrogen-bonded structure of the monoanion, in which the conditions for hydrogen bonding are more favourable than in the undissociated acid. In the dianion, the carboxylate groups would tend to avoid one another by turning about the C(1)–C(2) and C(3)–C(4) bonds and thus emerging from the plane of the molecule.

The relative values of the rate constants for MFA are apparently free of steric effects and reflect the trend expected from electrostatic considerations.

The introduction of a methyl substituent in all cases decreases the reactivity relative to the corresponding unsubstituted species; however, the extent of the effect depends on the charge and the configuration. A large decrease is observed for the *trans*-configuration (factors of 12, 8, and 12, respectively for k_1, k_2, and k_3), the effect being weaker for the *cis*-species (factors of 7, 2, and 3, in the above order). Although polar effects cannot be fully excluded, the drop of the reactivity upon methyl substitution seems to be due mainly to steric reasons. This is supported by the fact that various chloro- and bromo-derivatives of maleic acid show slightly or much lower reactivities [13] than does MMA.

In general the rates of the reactions discussed seem to be entropy controlled, the apparent activation enthalpies never exceeding 20 kJ mol^{-1}. This is a characteristic feature of the permanganate oxidation of unsaturated compounds. The formation of a five-membered cyclic intermediate (X_1) implies that upon going to the transition state, the degree of ordering of the reactants greatly increases. Solvation effects probably also contribute to the entropy of activation; these become more important for the mono- and di-anions.

Work is in progress to study the effect of halogen substituents on the rate of permanganate oxidation.

EXPERIMENTAL

Analytical grade chemicals were used throughout. Methylfumaric acid (Fluka), methylmaleic anhydride (Fluka), and dimethylmaleic anhydride (Fluka) were used without further purification. The anhydrides are completely hydrolysed in the acidic media used, as shown by their near-u.v. spectra.

The details of the pH-metric titrations and the stopped-flow kinetic measurements have been described elsewhere.[2]

The CO_2 evolved during the $MnO_4^- \longrightarrow Mn^{III}$ process was collected in a standard $Ba(OH)_2$ solution covered with a pentane layer to avoid contact with the atmosphere. The vessel was first evacuated, then the reactants mixed and after 5 s enough $FeCl_2$ solution added to quench the manganese(III) formed. The aqueous solution was then boiled to transfer the CO_2 formed to the $Ba(OH)_2$ solution. All operations were performed in a closed system so that no gases could escape through the pentane layer.

We thank Professor F. Nagy for advice on programming and Mrs. Gy. Boda for assistance in the experiments.

[5/1209 *Received*, 20*th June*, 1975]

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[12] J. Denis, *Amer. Chem. J.*, 1907, **38**, 589.

[13] Nguyen Thanh Son, M. Jáky, and L. I. Simándi, in preparation.