

58. *A Kinetic Study of the Oxidations of Formaldehyde and Formic Acid by Manganic Sulphate.*

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A kinetic study has been made of the oxidation of formaldehyde, formic acid, and deuterioformic acid by manganic sulphate in sulphuric acid. These oxidations, unlike that of cyclohexanone, are retarded by manganous ions. With formaldehyde, as with cyclohexanol, the retardation reaches a limiting value at a quite low (0.04M) concentration of manganous ion, but with formic acid the retardation is much more pronounced if the initial manganese(III) concentration is more than 0.005M; the reaction kinetics then include a term involving $[\text{Mn}^{\text{III}}]^3/[\text{Mn}^{\text{II}}]$, and the primary kinetic isotope effect is almost doubled. A comparative discussion of reaction mechanisms is given in which it is suggested that manganese(IV) may play some part in oxidations effected by manganic sulphate in the presence of strong sulphuric acid.

THE oxidation of several types of organic compounds of tervalent manganese, stabilised in aqueous solution by means of pyrophosphate, has been studied during 1953—1958 by Waters and his colleagues¹ and revealed many reactions whereby free radicals could be generated in aqueous solution. Manganic pyrophosphate proved to be a selective oxidant that attacked aldehydes, ketones, 1,2-glycols, and α -hydroxy- and α -keto-acids, but not saturated monohydric alcohols or olefins. Recently we have shown that formaldehyde and formic acid, which are not oxidised by manganic pyrophosphate,^{1a} resemble saturated alcohols in their oxidation by several reagents.² Littler³ has shown that solutions of manganic sulphate, which has the high redox potential of 1.51 v, attacks cyclohexanol at a reasonable rate at 50° and consequently we have extended his work to a study of the oxidation of formaldehyde and formic acid by the same reagent, making also further kinetic studies of the oxidation of cyclohexanol and cyclohexanone when needed for the comparison of reaction kinetics. Our measurements have been carried out spectrophotometrically, by using the changes in absorption of our solutions at 510 m μ , which corresponds to the absorption maximum of compounds of manganese(III). Details of our operational technique have already been reported;^{2,3} reference in the Tables to pseudo-first-order rate constants relates to the slopes of the plots of log [Oxidant] against time for the corresponding reactions. Third-order rate constants refer to the slopes of the plots of $1/[\text{Oxidant}]^2$ against time, exemplified by Fig. 3. Otherwise the initial slope of the plots of [Oxidant] against time was taken.

RESULTS

Oxidation of Formaldehyde, Cyclohexanol, and Cyclohexanone (cf. Tables 1—3).—The rate of oxidation of formaldehyde by manganese(III) sulphate was of the first order in oxidant for 95% of the reaction; as, however, the concentration of manganese(III) was increased, the magnitude of the first-order rate constant increased (Table 1a), but not to an extent such that one could clearly define a higher-order term in manganese(III). Such an effect was sought, but not found, in the oxidation of cyclohexanol by manganese(III) (Table 2a).

The effect of inserting manganous ions into the reaction medium under conditions of constant ionic strength is depicted in Fig. 1. This effect has now been examined for cyclohexanol and cyclohexanone in their oxidations by manganese(III) sulphate and our results are also presented in Fig. 1.

The dependence of the oxidation rate on the concentration of formaldehyde was approximately first-order (Table 1b), and under conditions of constant ionic strength the rate was

¹ (a) Drummond and Waters, *J.*, 1953, 435; (b) Land and Waters, *J.*, 1958, 2129.

² Kemp and Waters, *Proc. Roy. Soc.*, 1963, *A*, 274, 480.

³ Littler, *J.*, 1962, 2190.

TABLE I.

Oxidation of formaldehyde by manganese(III) sulphate solution.

(a) Dependence of the pseudo-first-order rate constant on initial Mn(III) concentration.

Temp. 50.7°; [CH₂O] = 0.270M; [H₂SO₄] = 3.34M.

Mn(III) (M)	0.0055	0.0139	0.0277
Mn(II) (M)	0.211	0.205	0.194
10 ⁴ k ₁ (sec. ⁻¹)	14.8	16.6	17.1

(b) Formaldehyde-dependence of the oxidation rate.

Temp. 50.0°; [Mn^{III}] = 0.0135M; [Mn^{II}] = 0.200M; [H₂SO₄] = 2.025M.

CH ₂ O (M)	0.108	0.135	0.270	0.351	0.459	0.540
10 ⁴ k ₁ (sec. ⁻¹)	Pptn.	9.55	20.1	26.4	33.2	36.7
10 ⁴ k ₁ /[CH ₂ O] (l. mole ⁻¹ sec. ⁻¹)	—	70.6	74.5	75.2	72.4	67.8

(c) Acid-dependence of the rate at constant ionic strength.

Temp. 49.5°; [CH₂O] = 0.193M; [Mn^{III}] = 0.002065M; [Mn^{II}] = 0.0144M; ([H₂SO₄] + [NaHSO₄]) = 3.545M.

H ₂ SO ₄ (M)	0.294	1.10	1.92	2.73	3.54
H ⁺ (M) *	0.664	1.30	1.98	2.75	3.54
10 ⁴ k ₁ (sec. ⁻¹)	11.9	13.1	12.1	11.2	11.7

* Hydronium-ion concentrations were evaluated here and elsewhere in this paper with the aid of Ashurst and Higginson's values ⁴ for the ionisation of [HSO₄⁻].

(d) Effect, on the rate, of replacing bisulphate by perchlorate ions at constant acidity and ionic strength.

Temp. 47.8°; [CH₂O] = 0.270M; [Mn^{III}] = 0.00481M; [Mn^{II}] = 0.0338M; [HSO₄⁻] (associated with manganese species) = 0.082M; ([H₂SO₄] + [HClO₄]) = 3.685M.

H ₂ SO ₄ (M)	HClO ₄ (M)	Total HSO ₄ ⁻ (M)	10 ⁴ k (sec. ⁻¹), found	10 ⁴ k (sec. ⁻¹), calc.†	H ₂ SO ₄ (M)	HClO ₄ (M)	Total HSO ₄ ⁻ (M)	10 ⁴ k (sec. ⁻¹), found	10 ⁴ k (sec. ⁻¹), calc.‡
0.685	3.00	0.767	22.0	24.7	2.185	1.50	2.267	11.6	12.5
0.985	2.70	1.067	19.6	19.5	2.935	0.75	3.017	11.0	10.9
1.435	2.25	1.517	16.4	15.5	3.685	0	3.767	10.0	10.0
1.735	1.95	1.817	14.1	14.0					

† Rate calc. from: 10⁴k (sec.⁻¹) = 6.2 + 14.1/[HSO₄⁻].

(e) Effect, on the rate, of adding sodium perchlorate.

Temp. 48.0°; [CH₂O] = 0.216M; [Mn^{III}] = 0.00385M; [Mn^{II}] = 0.0270M; [H₂SO₄] = 1.748M; [HSO₄⁻] (associated with manganese species) = 0.066M.

NaClO ₄ (M)	0	0.8	1.6	2.4	3.2
Total ionic strength, μ (mole l. ⁻¹)	1.82	2.62	3.42	4.22	5.02
10 ⁴ k (sec. ⁻¹), found	15.6	14.1	13.6	12.0	11.5
10 ⁴ k (sec. ⁻¹), calc.‡	15.4	14.4	13.4	12.4	11.4

‡ Rate calc. from: 10⁴k (sec.⁻¹) = 17.7 - 1.26μ.

(f) Temperature-dependence of the oxidation rate.

[CH₂O] = 0.540M; [Mn^{III}] = 0.0135M; [Mn^{II}] = 0.200M; [H₂SO₄] = 2.025M.

Temp.	24.9°	25.0°	35.0°	40.6°	44.9°	51.5°	56.8°
10 ⁴ k (sec. ⁻¹)	1.23	1.10	4.87	11.1	18.6	40.1	74.5

TABLE 2.

Oxidation of cyclohexanol by manganese(III) sulphate solution.

(a) Dependence of the pseudo-first-order rate constant on initial manganese(III) concentration (method of initial rates).

Temp. 50.0°; [Cyclohexanol] = 0.0841M; [Mn^{II}] = 0.370M; [H₂SO₄] = 3.00M.

10 ³ [Mn ^{III}] (M)	2.42	4.84	7.28	13.1
-10 ⁷ Δ[Mn ^{III}]/Δt (mole l. ⁻¹ sec. ⁻¹)	3.62	7.84	11.8	19.2
-10 ⁴ {Δ[Mn ^{III}]/Δt}/[Mn ^{III}] (sec. ⁻¹)	1.50	1.61	1.62	1.59

(b) Temperature-dependence of the initial oxidation rate.

[Cyclohexanol] = 0.166M; [Mn^{III}] = 0.00410M; [Mn^{II}] = 0.167M; [H₂SO₄] = 1.97M.

Temp.	24.5°	36.15°	44.6°	49.6°	50.0°	54.05°
-10 ⁸ Δ[Mn ^{III}]/Δt (mole l. ⁻¹ sec. ⁻¹)	1.705	9.25	32.8	96.0	85.3	135

⁴ Ashurst and Higginson, *J.*, 1956, 343.

independent of acid concentration (Table 1c). Preliminary work had indicated that the overall effect of increasing the sulphuric acid content of the solutions, which is one method of lessening

TABLE 3.
Oxidation of cyclohexanone by manganese(III) sulphate solution.

Temperature-dependence of the initial oxidation rate.

[Cyclohexanone] = 0.0521M; [Mn^{III}] = 0.0135M; [Mn^{II}] = 0.200M; [H₂SO₄] = 3.525M.

Temp.	24.9°	31.1°	35.3°	40.6°	44.9°	51.1°	56.8°
$-10^6 \Delta[\text{Mn}^{\text{III}}]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) ...	10.2	19.6	29.7	46.4	68.6	104	154

the chance of precipitation of manganese dioxide, was to reduce the rates of oxidation of organic compounds by manganese(III) (cf. Table 5a for formic acid) and we ascribe this behaviour, at least in the case of formaldehyde, chiefly to a specific retarding effect of either HSO₄⁻ or, more

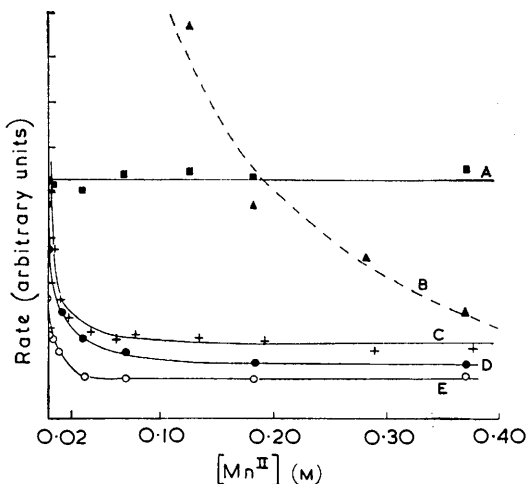


FIG. 1. Typical effects of manganese(II) ions on the rates of oxidation of organic compounds.

Curve:	A	B*	C	D	E
Substrate	Cyclohexanone	H·CO ₂ H with high [Mn ^{III}]	H·CO ₂ H with low [Mn ^{III}]	Cyclohexanol	CH ₂ O
Significance of 1 unit on rate axis	Initial $-d[\text{Oxidant}]/dt$ (10 ⁻⁷ mole l. ⁻¹ sec. ⁻¹)	k_3 (l. ² mole ⁻² sec. ⁻¹) for initial stages (0.1 l. ² mole ⁻² sec. ⁻¹)	Pseudo-first-order rate constant (10 ⁻⁴ sec. ⁻¹)	Initial $-d[\text{Oxidant}]/dt$ (10 ⁻⁷ mole l. ⁻¹ sec. ⁻¹)	Pseudo-first-order rate constant (10 ⁻⁴ sec. ⁻¹)
[Substrate] (M) ...	0.0521	1.09	2.185	0.0841	0.270
[H ₂ SO ₄] (M)	3.00	1.50	1.173	3.00	3.00
10 ⁴ [Mn ^{III}] (M)	72.8	72.8	12.44	72.8	72.8
Temp.	25.0	25.0	50.0	50.0	46.5
[Mn ^{II}] + [Zn ^{II}] (M)	0.373	0.373	0.390	0.373	0.373

* See also Table 5a.

probably, SO₄²⁻ ions. For formaldehyde Table 1d shows that the effect of replacing ClO₄⁻ by HSO₄⁻ ions may be expressed formally by the equation

$$-10^4 \frac{d[\text{Mn}^{\text{III}}]/dt}{[\text{Mn}^{\text{III}}]} = a + \frac{b}{[\text{HSO}_4^-]}, \tag{1}$$

where a and b are empirical constants, and this effect is, we consider, too great to be accounted for by incomplete dissociation of sulphuric acid to H^+ and HSO_4^- ions, particularly since the rate of this oxidation is independent of acidity (Table 1c).

A small overall retardation of the oxidation was also produced, however, when the ionic strength μ was increased simply by adding sodium perchlorate (Table 1e), and this effect may be expressed for the conditions of this Table by

$$-10^4 \frac{d[Mn^{III}]/dt \text{ (sec.}^{-1})}{[Mn^{III}]} = 17.7 - 1.26\mu. \quad (2)$$

The temperature-dependence of the oxidation of formaldehyde, cyclohexanol, and cyclohexanone by manganese(III) sulphate is shown in Tables 1f, 2b, and 3, respectively, and with other data in Table 6.

Oxidation of Formic Acid.—The rate of oxidation of formic acid was of combined first and third order with respect to manganese(III); evidence for this unusual behaviour is presented

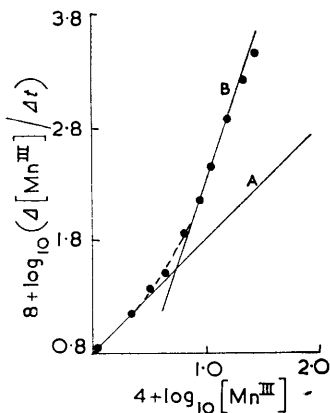


FIG. 2. Dependence of the initial rate of oxidation of formic acid on $[Mn^{III}]$.

Temp. 25.0° ; $[H\cdot CO_2H] = 2.185M$; $[Mn^{II}]_0 = 0.325M$; $[H_2SO_4] = 1.25M$. (A) Slope 1.01; (B) slope 2.97.

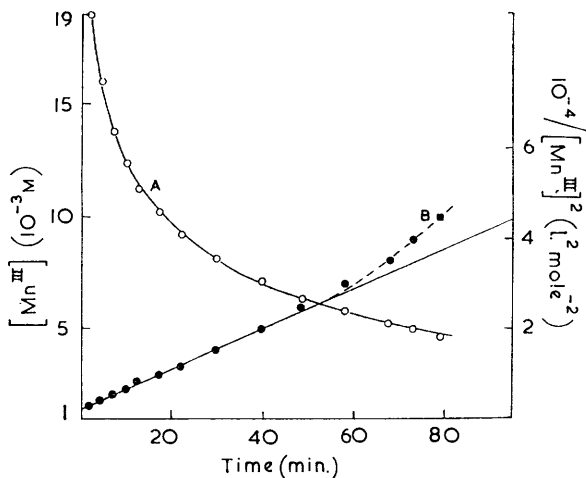


FIG. 3. Rate of oxidation of formic acid by manganese(III) sulphate in the high $[Mn^{III}]$ range: a typical "decay" of $[Mn^{III}]$.

(A) Change of $[Mn^{III}]$ (spectrophotometric measurement). (B) Plot of $1/[Mn^{III}]^2$. Initial $[Mn^{III}] = 0.0206M$; initial $[Mn^{II}] = 0.222M$; $[H_2SO_4] = 2.68M$; temp. 25.4° : measurements made in 1-cm. cells at 510μ .

in Figs. 2 and 3. Under the conditions of measurement for Fig. 2 the particular form of the manganese(III)-dependence was:

$$-d[Mn^{III}]/dt = 5 \times 10^{-5}[Mn^{III}] + 1.69[Mn^{III}]^3 \text{ (moles l.}^{-1} \text{ sec.}^{-1}). \quad (3)$$

When the manganese(II) concentration was initially so high that production of manganese(II) during the reaction had but a very slight autoretarding effect we obtained excellent third- and first-order decay rates for at least 70% of the reaction under conditions of high and low manganese(III) concentration, respectively. Dependence of the reaction rate on the concentrations of other species was measured for conditions which ensured the complete dominance of one of the two main reaction paths, and our results are presented in terms of two separate reactions.

(a) *Characteristics of the oxidation involving a first-order dependence on manganese(III).* In this concentration range the addition of manganous ions to the reaction medium affected the

rate in much the same way as we had encountered with formaldehyde and cyclohexanol (cf. Fig. 1).

The (formic acid)-dependence of this reaction was of the first order at the lowest substrate concentrations, but a deviation consistent with complex formation between substrate and oxidant was evident at higher concentrations. Tests of equation (4) are presented in Tables 4a and b.

$$\text{Rate} = k[\text{Substrate}]/(1 + K[\text{Substrate}]). \quad (4)$$

At 25° this expression gave only fair agreement with the experimental results, which indicated that the reaction became almost zero-order with respect to formic acid at concentrations above 3M, but at 50° (Table 4b) agreement with equation (4) was excellent for the whole range of formic acid concentration.

The acid-dependence of the oxidation rate for conditions of constant ionic strength was

TABLE 4.

Oxidation of formic acid by manganese(III) sulphate at low manganese(III) concentrations.

(a) *(Formic acid)-dependence of the initial oxidation rate.*

Temp. 25.0°, [Mn^{III}] = 0.000896M, [Mn^{II}] = 0.0777M, [H₂SO₄] = 0.818M.

H·CO ₂ H (M)	0.874	1.311	1.748	2.185	2.84	3.496	4.37	4.37
-10 ⁸ Δ[Mn ^{III}]/Δt (obs.) * ...	4.30	6.24	8.74	10.3	11.5	11.8	12.2	11.3
„ (calc.) *†	4.40	6.35	8.17	9.89	12.2	14.2	16.7	

* Mole l.⁻¹ sec.⁻¹. † Rate calc. from: -10⁸Δ[Mn^{III}]/Δt = 5.49[H·CO₂H]/(1 + 0.099[H·CO₂H]).

(b) *(Formic acid)-dependence of the oxidation rate.*

Temp. 50.2°; [Mn^{III}] = 0.00124M; [Mn^{II}] = 0.193M; [H₂SO₄] = 0.745M.

H·CO ₂ H (M)	0.175	0.328	0.656	1.093	2.18	3.28	4.37
10 ⁴ k ₁ (sec. ⁻¹),	2.68	4.85	8.75	12.2	21.5	23.8	27.3
„ calc. ‡	2.69	4.82	8.75	12.9	20.0	24.6	27.8

‡ Rate calc. from: 10⁴k₁ (sec.⁻¹) = 16.4[H·CO₂H]/(1 + 0.361[H·CO₂H]).

(c) *Acid-dependence of the rate at constant ionic strength.*

Temp. 50.1°; [Formic acid] = 0.874M; [Mn^{III}] = 0.001924M; [Mn^{II}] = 0.01345M; [H₂SO₄] + [NaHSO₄] = 3.632M.

H ₂ SO ₄ (M)	0.274	0.728	1.18	1.18	2.09	3.00	3.91
H ⁺ (M)	0.648	0.955	1.32	1.32	2.15	3.01	3.91
10 ⁴ k ₁ (sec. ⁻¹), obs.	7.18	6.72	5.80	6.21	5.32	4.70	4.45
„ calc. §	8.48	6.95	6.05	6.05	5.15	4.74	4.51

§ Rate calc. from: 10⁴k (sec.⁻¹) = 3.72 + 3.08/[H⁺].

(d) *Primary kinetic isotope effect.*

Temp. 50.0°; [Mn^{III}] = 0.0011M; [Mn^{II}] = 0.320M; [H₂SO₄] = 1.25M.

H·CO ₂ H (M)	H·CO ₂ D (M)	-10 ⁸ Δ[Mn ^{III}]/Δt (mole l. ⁻¹ sec. ⁻¹)
0.219	—	18.5, 18.9
—	0.228	8.76, 8.48

k_H/k_D = 2.2.

(d) No significant degree of complex formation exists between substrate and oxidant at the formic acid concentrations used in these measurements or those of Table 5e.

(e) *Temperature-dependence of the oxidation rate.*

[H·CO₂H] = 2.185M; [Mn^{III}] = 0.001244M; [Mn^{II}] = 0.390M; [H₂SO₄] = 1.173M.

Temp.	25.0°	35.35°	42.4°	50.0°	55.0°	61.6°
10 ⁴ k ₁ (sec. ⁻¹)	0.786	2.69	6.31	15.4	26.7	42.3

found to be of the form, Rate = a + b/[H⁺], (Table 4c). This dependence does not resemble that for the oxidation of formaldehyde (Table 1c) or of cyclohexanol by manganese(III) sulphate,

and it seems that oxidation of the formate anion plays a considerable part in the overall reaction, as it does in the oxidation of formic acid by permanganate.⁵

The primary kinetic isotope effect for the reaction was 2.2 at 50° (Table 4d); the temperature-dependence of the rate is recorded in Table 4e.

TABLE 5.

Oxidation of formic acid by manganese(III) sulphate at high manganese(III) concentrations.

(a) *Specific effect of manganese(II) ions on the third order rate constant* (see also Fig. 1).

Temp. 25.0°; [Mn^{III}] = 0.00728M; [H·CO₂H] = 1.09M; [MnSO₄] + [ZnSO₄] = 0.373M.

Mn ^{II} (initial) (M)	k ₃ in 1.50M-H ₂ SO ₄ (l. ² mole ⁻² sec. ⁻¹)	Rate × [Mn ^{II}]	k ₃ in 3.00M-H ₂ SO ₄ (l. ² mole ⁻² sec. ⁻¹)	Rate × [Mn ^{II}]
0	1767	—	155	—
0.00175	1133	1.98	83.3	0.146
0.00553	495	2.74	41.8	0.231
0.0131	205	2.59	14.4	0.189
0.0320	74.3	2.38	6.93	0.222
0.0510	27.0	1.38	2.10	0.107
0.0698	21.3	1.48	—	—
0.127	8.68	1.10	—	—
0.1835	4.68	0.86	—	—
0.284	3.55	1.01	—	—
0.373	2.35	0.88	—	—

(b) *(Formic acid)-dependence of the rate.*

Temp. 25.0°; [Mn^{III}] = 0.00962M; [Mn^{II}] = 0.0675M; [H₂SO₄] = 1.445M.

H·CO ₂ H (M)	0.1093	0.2185	0.3275	0.437	0.656	1.09	1.76	2.62	3.50	4.37
k ₃ (l. ² mole ⁻² sec. ⁻¹), obs. ...	5.43	11.1	16.5	19.3	24.0	33.8	43.0	43.0	42.3	43.8
„ „ calc.*	5.9	10.8	15.0	18.4	24.1	31.9	38.3	44.8	48.1	50.4

* Rate calc. from: $k_3 = 59.9[\text{H}\cdot\text{CO}_2\text{H}]/(1 + 0.957[\text{H}\cdot\text{CO}_2\text{H}])$.

(c) *(Formic acid)-dependence of the initial rate.*

Temp. 50.1°; [Mn^{III}] = 0.00962M; [Mn^{II}] = 0.113M; [H₂SO₄] = 2.79M.

H·CO ₂ H (M)	0.2185	0.437	0.874	1.31	1.75	2.185	2.62	3.495	4.37
10 ⁶ Δ[Mn ^{III}]/Δt (mole l. ⁻¹ sec. ⁻¹) obs. ...	6.58	12.4	17.9	21.0	23.9	25.8	28.5	29.7	31.5
1. ⁻¹ sec. ⁻¹) calc. † ...	6.67	11.4	17.6	21.5	24.1	26.1	27.5	29.6	31.1

† Rate calc. from: $10^6\Delta[\text{Mn}^{\text{III}}]/\Delta t = 37[\text{H}\cdot\text{CO}_2\text{H}]/(1 + 0.962[\text{H}\cdot\text{CO}_2\text{H}])$.

(d) *Acid-dependence of the rate at constant ionic strength.*

Temp. 25.0°; [H·CO₂H] = 0.794M; [Mn^{III}] = 0.0454M; [Mn^{II}] = 0.0708M; [H₂SO₄] + [NaHSO₄] = 3.50M.

H ₂ SO ₄ (M)	0.400	0.745	0.977	1.14	1.47	1.80	2.63	3.12	3.45
H ⁺ (M)	0.704	0.950	1.14	1.28	1.57	1.88	2.66	3.14	3.45
k ₃ (l. ² mole ⁻² sec. ⁻¹), obs. ...	5.58	4.35	3.98	3.50	2.83	2.63	2.31	2.13	2.00
„ „ calc. ‡ ...	5.48	4.36	4.08	3.53	3.09	2.78	2.30	2.12	2.04

‡ Rate calculated from expression $k_3 = 1.15 + 3.05/[\text{H}^+]$.

(e) *Primary kinetic isotope effect.*

Temp. 25.0°; [Mn^{III}] = 0.00728M; [Mn^{II}] = 0.051M; [Zn^{II}] = 0.322M; [H₂SO₄] = 1.5M.

[H·CO ₂ H] (M)	[D·CO ₂ H] (M)	-10 ⁷ Δ[Mn ^{III}]/Δt (mole l. ⁻¹ sec. ⁻¹)
0.219	—	10.9, 11.75
—	0.228	2.66, 2.56

$k_{\text{H}}/k_{\text{D}} = 4.3_4$.

(f) *Temperature-dependence of the third-order rate constant.*

[H·CO₂H] = 2.185M; [Mn^{III}] = 0.0185M; [Mn^{II}] = 0.0815M; [H₂SO₄] = 2.22M.

(This Table also illustrates the small increase in absorption with temperature of manganese(III) sulphate, of which due account was taken where appropriate.)

Temp.	25.6°	31.3°	35.4°	40.35°	45.0°	50°
ε at 5100 Å	108	110	112	113	116	—
k ₃ (l. ² moles ⁻² sec. ⁻¹)	10.95	20.8	33.5	58.8	86.5	Pptn.

⁵ Halpern and Taylor, *Discuss. Faraday Soc.*, 1960, **29**, 174.

(b) *Characteristics of the oxidation involving a third-order dependence on manganese(III) concentration.* The addition of manganous ions to the reaction medium in condition of constant ionic strength suppressed the rate of oxidation of formic acid far more than for the other reactions discussed in this paper. This retardation did not correspond exactly to a simple inverse dependence (Table 5a), for a plot of log rate against log $[\text{Mn}^{\text{II}}]$ exhibited a slope of -1.25 instead of -1.0 .

The (formic acid)-dependence of the reaction velocity resembled that for the oxidation involving a single manganese(III) species since at both 25° and 50° the agreement of the observed velocity with that calculated from an expression,

$$\text{Rate} = k[\text{Substrate}]/(1 + K[\text{Substrate}]),$$

was satisfactory (Tables 5b and c).

The acid-dependence was also of the same general form as that of the competing reaction (Table 5d), and the primary kinetic isotope effect, this time measured at 25° , had a mean value of 4.3 (Table 5e); attempts to measure this ratio at 50° were frustrated by precipitation of manganese dioxide. An energy of activation was computed from the temperature-dependence for this oxidation (Tables 5 and 6), but the unusual kinetics prevented a meaningful evaluation of any other thermodynamic parameters. It was evident, however, from the similarity of the ΔE^\ddagger values for the two paths, that the overwhelming dominance of the third-order reaction at high concentrations lay in the entropy factor.

DISCUSSION

The Reactions of the First Order with respect to Manganese(III).—The oxidation of formaldehyde by manganese(III) sulphate is kinetically similar to that of cyclohexanol. The formation of an initial complex between the reactants is not evident with formaldehyde concentrations below 0.5M, but is noticeable with even 0.03M-cyclohexanol.³ Though the actual rates of oxidation of the two compounds are similar the formaldehyde oxidation has a lower activation energy and a much lower positive activation entropy. A higher-order term in manganese(III) is just evident in the formaldehyde oxidation (Table 1a). Whilst this may be due to a side reaction involving manganese(IV) (see below) it is more probably due to a reaction involving a complex with two manganese(III) ions per formaldehyde molecule, as we have suggested² for the oxidation of formaldehyde by vanadium(V).

TABLE 6.

Parameters of the activation process for oxidation of some organic compounds by manganese(III) sulphate.

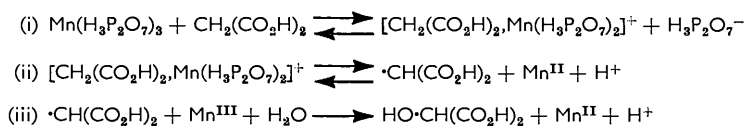
Substrate	$10^4 k_2$ at 298° (l. mole ⁻¹ sec. ⁻¹)	ΔF^\ddagger at 298° (kcal. mole ⁻¹)	ΔH^\ddagger (kcal. mole ⁻¹)	ΔS^\ddagger (e.u.)	$k_{\text{H}}/k_{\text{D}}$
Formaldehyde	2.17	22.4	24.6	+7	—
Cyclohexanol *	2.0	22.4	28.3	+20	1.6 (50°) (ref. 3)
Formic acid (low Mn^{III}) * ...	0.36	23.5	22.3	-4	2.2 (50°)
Formic acid (high Mn^{III}) ...	—	—	21.3	—	4.3 (25°)
Cyclohexanone	145	19.95	16.5	-12	4.1 (10.8°) †

* These parameters, which should be used for comparative purposes only, are evaluated from second-order rate constants for reactions involving substrate- Mn^{III} complex formation. All figures refer to rates measured at high $[\text{Mn}^{\text{II}}]$ where, as Fig. 1 indicates, all but one of these reactions are insensitive to the concentration of this ion. † Littler, *J.*, 1962, 832.

The oxidation of formic acid by very dilute solutions of manganese(III) sulphate also appears to follow a mechanism of the alcohol-oxidation type since the general kinetics, the Arrhenius parameters, and the magnitude of the primary kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 2.2$ at 50°) are similar for all three compounds (see Table 6). However, with formic acid

another reaction becomes dominant at high concentrations of manganese(III) and this needs separate consideration (see below).

Retardation of the Oxidation by Manganese(II).—At high concentrations of manganese(III) sulphate it becomes evident (see Fig. 1) that manganese(II) ions specifically retard oxidation of formic acid, formaldehyde, and cyclohexanol by manganese(III) though not that of cyclohexanone. This type of action was first described by Drummond and Waters⁶ for the oxidation of malonic acid by manganese(III) pyrophosphate and was, by them, ascribed to the reversibility of stage (ii) of the oxidation:

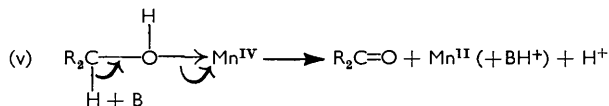


Abundant evidence for the transient existence of the intermediate free radical $\cdot\text{CH}(\text{CO}_2\text{H})_2$ was adduced from (a) uptake of oxygen, (b) induced polymerisation of vinyl cyanide, and, in particular, (c) the promotion of the oxidation of methanol and ethanol. A similar retardation was later noted by (Miss) Levesley and Waters⁷ for oxidation of α -hydroxy-acids by manganese(III) pyrophosphate which, however, was accelerated by addition of vinyl cyanide and did not promote the oxidation of alcohols. Still later Land and Waters^{1b} found that oxidation of allyl alcohol by manganese(III) pyrophosphate, which again did not promote the oxidation of methanol, had the kinetic features of Fig. 1, in that addition of manganese(II) soon reduced the oxidation rate to a minimum and at high concentrations appeared thereafter to enhance the velocity by way of a small, positive salt effect that could be produced equally by addition of zinc cations.

Though there are these resemblances between oxidation by manganese(III) pyrophosphate and sulphate, the latter reagent can be used only in solutions of high acidity and the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ sulphate system has a much higher redox potential than the corresponding pyrophosphate system; the latter, *per se*, does not effect the oxidation of saturated monohydric alcohols. The retardation of one-electron oxidations by added cations of lower valency seems to be a feature of oxidant systems containing manganese ions, for it has not been found amongst oxidations effected by vanadium(v), cobalt(III), or cerium(IV), which have similar redox potentials. Other explanations for the specific effect of manganese(II) on oxidations involving manganese(III) thus need consideration; the most probable of these involves the participation of an ion of manganese(IV), which could become stable in an aqueous medium of very high acidity [compare the oxidation of mercury(I) by manganese(III) recently studied by Rosseinsky⁸]:



Ions of manganese(IV) would undoubtedly have a much higher redox potential than manganese(III) and consequently only a small concentration of manganese(II) should effectively eliminate any oxidations of organic substrates by manganese(IV) in solutions of manganese(III) sulphate. This accords with the main observations noted in Fig. 1, and also with Land and Waters's observations; and the two-electron transfer scheme,



⁶ Drummond and Waters, *J.*, 1954, 2456.

⁷ Levesley and Waters, *J.*, 1955, 217.

⁸ Rosseinsky, *J.*, 1963, 1181.

of Merz, Stafford, and Waters⁹ is as appropriate for this oxidation as it is for the oxidation of alcohols by chromic acid.¹⁰ However, in advancing this alternative mechanism for the retarding effect of manganese(II) ions on oxidation by manganese(III) sulphate we do not suggest that a similar scheme should now be advocated for all oxidations effected, at low acidities, by manganese(III) pyrophosphate, for reactions (iv) and (v) do not easily explain all Drummond and Waters's observations⁶ for the malonic acid–manganese(III) pyrophosphate system. So little is known about compounds of manganese(IV) in solution that the question whether it should always behave as a two-electron oxidant [reaction (v)] is a moot point.

Oxidation of Formic Acid by Manganese(III) Sulphate at High Concentrations.—If oxidations by manganese(III) sulphate were directly effected by manganese(IV), then from equilibrium (iv) one would infer that the rate equation should be of the form,

$$-d[\text{Mn}^{\text{III}}]/dt = k[\text{Substrate}][\text{Mn}^{\text{III}}]^2/[\text{Mn}^{\text{II}}],$$

but the kinetics of oxidation of formic acid must clearly be represented by an equation having a $[\text{Mn}^{\text{III}}]^3$ term and not a $[\text{Mn}^{\text{III}}]^2$ term (compare Figs. 2 and 3). Tables (5e) and (6) show that the oxidation associated with this $[\text{Mn}^{\text{III}}]^3$ term exhibits a kinetic isotope effect of ~ 4.3 at 25° , which is in the range appropriate for a two-electron transfer,⁴ and certainly shows that H–C bond fission in formic acid is involved in the rate-determining process, an observation which would not accord with a reaction scheme involving a reversible step such as (ii). The kinetic isotope effect is less than that for the oxidation of formic acid by acid solutions of permanganate, and the view that HMnO_4 might be the true oxidant, consequent upon an equilibrium, $5\text{Mn}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{MnO}_4^- + 4\text{Mn}^{2+} + 8\text{H}^+$, does not accord at all with the kinetics. Now the (formic acid)-dependence of this oxidation (Tables 5b and c) shows that the oxidation involves the breakdown of a manganese–formic acid complex, with a stability constant, *ca.* 0.96 (see Tables 5b and c) greater than that observed at low manganese(III) concentrations (Tables 4a and b).

It is possible, therefore, that the reaction which becomes dominant at high concentrations of manganese(III) is an attack by manganese(IV) on a manganese(III)–formate complex, *e.g.*, $[\text{H}\cdot\text{CO}_2\text{Mn}]^{2+}$, or attack by manganese(III) on a manganese(IV)–formate complex. The objection to this is that it would appear to require electron movement away from a strongly electropositive manganese atom. Clearly, however, we must be dealing with a reaction complex that contains more than one manganese atom, but whether the oxidation involves one-electron or paired-electron shifts must be left open.

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⁹ Merz, Stafford, and Waters, *J.*, 1951, 638.

¹⁰ Waters, *Quart. Rev.*, 1958, **12**, 277.