

### 283. The Oxidation of Malonic Acid by Manganic Sulphate.

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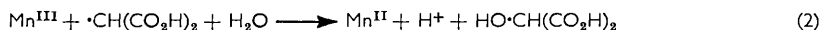
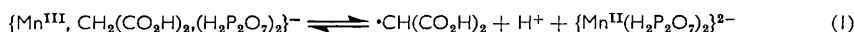
Kinetic studies of this reaction reveal that the singular features of the oxidation of malonic acid by manganic pyrophosphate <sup>1</sup> are largely reproduced in the case of the more powerful oxidiser. The significance of this observation is discussed in terms of the reaction involving a Mn<sup>III</sup>-Mn<sup>IV</sup> resonance hybrid.

ONE of us (W. A. W.) has investigated <sup>2</sup> the oxidation of many organic compounds by manganese(II) in the form of its pyrophosphate complex. In most cases the kinetics indicate that the species {Mn(H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>)<sub>3</sub>}<sup>3-</sup> loses one ligand and forms a complex with a molecule of the organic substrate, and there follows a one-electron abstraction process yielding an organic free radical and a manganese(II) species. With the oxidation <sup>1</sup> of malonic acid, however, a retardation of the reaction according to equation (A), is affected by increasing the prevailing manganese(II) concentration.

$$1(\Delta[\text{Mn}^{\text{III}}]/\Delta t) = a + b[\text{Mn}^{\text{II}}]. \quad (\text{A})$$

Although manganese(III) pyrophosphate scarcely attacks simple alcohols and non-enolising aldehydes, addition of malonic acid to a manganese(III)-alcohol mixture enables such oxidations to occur.

These observations were rationalised by the reaction scheme (1)–(2). To the radical  $\cdot\text{CH}(\text{CO}_2\text{H})_2$ , supposed to be a strong oxidising agent, was ascribed responsibility for the induced oxidation of alcohols.



Recent observations have indicated that some re-appraisal of this scheme is desirable. Thus: (i), the oxidation of formic acid by manganese(III) sulphate <sup>3</sup> proceeds in part according to the kinetics,

$$\Delta[\text{Mn}^{\text{III}}]/\Delta t = k \frac{K[\text{Formic acid}]}{(1 + K[\text{Formic acid}])} \cdot \frac{[\text{Mn}^{\text{III}}]^3}{[\text{Mn}^{\text{II}}]^{1.25}} \quad (\text{B})$$

and to explain this it has been necessary to suggest that ions of manganese(IV) are present in the strongly acid media. (ii) The oxidation of malonic acid by vanadium(v) sulphate <sup>4</sup> is very much slower than the manganese(III) pyrophosphate oxidation [indeed, manganese(II) ions catalyse <sup>4</sup> the vanadium(v) oxidation], although the normal order of reactivity towards organic compounds is the reverse of this. (iii) Rosseinsky <sup>5</sup> has found that the oxidation of mercurous ion by manganese(III) perchlorate involves as one of its kinetic terms,

$$-d[\text{Mn}^{\text{III}}]/dt = k[(\text{Hg}^{\text{I}})_2][\text{Mn}^{\text{III}}]^2/[\text{Mn}^{\text{II}}], \quad (\text{C})$$

and has explained his results in terms of the equilibrium



Accordingly, our present work attempts to discern if the kinetics observed in the oxidation of malonic acid by manganese(III) pyrophosphate are reproduced in the case of manganese(III) sulphate, for it is possible to account for retardations of manganese(III) oxidations by manganese(II) ions either by postulating reversible radical formation

<sup>1</sup> Drummond and Waters, *J.*, 1954, 2456.

<sup>2</sup> Land and Waters, *J.*, 1958, 2129.

<sup>3</sup> Kemp and Waters, *J.*, 1964, 339.

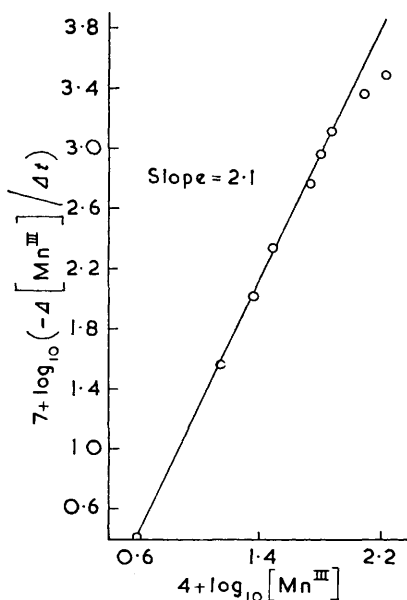
<sup>4</sup> Kemp and Waters, forthcoming publication.

<sup>5</sup> Rosseinsky, *J.*, 1963, 1181.

(equation 1 above) or by postulating that the active oxidising agent is a compound of manganese(IV), though the latter interpretation was regarded as improbable by Drummond and Waters.

## RESULTS

From measurements of the decrease in manganese(III) concentration during the oxidation of malonic acid the reaction order cannot easily be obtained. Variation of the initial oxidation rate with change of  $[\text{Mn}^{\text{III}}]$  was examined over a wide range of concentration, and our results, recorded in the Figure by a  $\log[\text{oxidant}]$  against  $\log(\Delta[\text{Mn}^{\text{III}}]/\Delta t)$  plot, reveal the reaction to be of the second order with respect to manganese ion concentration.



Demonstration of the second-order nature of the dependence on manganese(III) by means of a log-log plot.

Temp. 25.0°; [Malonic acid] 0.0169M;  $[\text{H}_2\text{SO}_4]$  2.75M;  $[\text{MnSO}_4]$  0.325M.

With some of the faster reactions in particular, the initial rates were not assessed with ease and we have used as a measure of the reaction speeds the slopes of the  $\log[\text{Mn}^{\text{III}}]$ -time plots for the first 30—40% of the reactions. This empirical practice is valid to within the accuracy of our experiments in view of our maintenance of constant initial  $[\text{Mn}^{\text{III}}]$  in determinations of dependences of the rate upon concentrations of other species.

The effect of introducing manganese(II) ions into the reaction medium is summarised

TABLE 1.

Specific effect of manganese(II) ions upon the reaction rate.

Temp. 25.1°; [Malonic acid] 0.0169M;  $[\text{H}_2\text{SO}_4]$  2.95M;  $[\text{Mn}^{\text{III}}]$  (initial)  $50 \times 10^{-4}$ M;  $\text{Mn}^{\text{II}}$  ions were gradually replaced by  $\text{Zn}^{\text{II}}$  ions.

$10^3 [\text{Mn}^{\text{II}}]$ (moles $l^{-1}$ )	3.64	13.1	32.0	51.0	69.8	127	183.5	284	373
$10^4 k_1$ (sec. <sup>-1</sup> ) (obs.)	305	207	193	150	103	76	65.5	45.7	32.5
$10^4 k_1$ (sec. <sup>-1</sup> ) (calc.) *	305	253	188	149	123	81	61	42.2	33.1

\* *I.e.*, calculated from the relation  $1/10^4 k_1 = 0.0030 + 0.073[\text{Mn}^{\text{II}}]$ .

TABLE 2.

Dependence of the reaction rate on malonic acid concentration.

Temp. 25.1°;  $[\text{Mn}^{\text{III}}]$   $72.8 \times 10^{-4}$ M;  $[\text{Mn}^{\text{II}}]$  0.373M;  $[\text{H}_2\text{SO}_4]$  2.95M.

$10^3$ [Malonic acid] (moles $l^{-1}$ )	8.46	16.9	42.3	84.6	127	169
$10^4 k_1$ (sec. <sup>-1</sup> ) (obs.)	27.8	43.6	86.5	117	140	159
$10^4 k_1$ (sec. <sup>-1</sup> ) (calc.) *	26.9	47.1	86.3	119	136	147

\* *I.e.*, calculated from the relation  $10^4 k_1$  (sec.<sup>-1</sup>) =  $3700[\text{Malonic acid}]/(1 + 19.3[\text{Malonic acid}])$ .

TABLE 3.

Dependence of the reaction rate on acidity.

Temp. 25.1°; [Malonic acid] 0.0113M; [Mn<sup>III</sup>] 47.2 × 10<sup>-4</sup>M; [Mn<sup>II</sup>] 0.094M; ([H<sub>2</sub>SO<sub>4</sub>] + [HSO<sub>4</sub><sup>-</sup>]) = 3.52M.

[H <sub>2</sub> SO <sub>4</sub> ] (moles l. <sup>-1</sup> )	[H <sup>+</sup> ] * (moles l. <sup>-1</sup> )	10 <sup>4</sup> k <sub>1</sub> (sec. <sup>-1</sup> ) (obs.)	10 <sup>4</sup> k <sub>1</sub> (sec. <sup>-1</sup> ) (calc.) †
0.276	0.656	73.2 77.1 83.3	77.1
0.504	0.809	71.1	72.0
0.657	1.08	71.8	69.2
1.038	1.245	63.3	64.3
1.42	1.585	60.5	61.2
1.80	1.94	55.8	59.2
2.56	2.66	55.3	56.7
3.32	3.39	54.8 57.8	55.3

\* Hydronium-ion concentrations were evaluated from the dissociation constant of HSO<sub>4</sub><sup>-</sup> given by Ashurst and Higginson. † *I.e.*, calculated from the relation 10<sup>4</sup>k<sub>1</sub> (sec.<sup>-1</sup>) = 50 + 17.8 [H<sup>+</sup>].

TABLE 4.

Dependence of the reaction rate on temperature.

Temp. ....	25.2	27.9	29.5	31.3	32.7	35.2	36.8
[Malonic acid] 0.0169M; [Mn <sup>III</sup> ] 96 × 10 <sup>-4</sup> M; [Mn <sup>II</sup> ] 0.393M; [H <sub>2</sub> SO <sub>4</sub> ] 3.30M.							
10 <sup>4</sup> k (sec. <sup>-1</sup> ) .....	68.3	77.4	89.2	100.7	112.5	143	145

Hence ΔE‡ = 13.2 ± 1.0 kcal./mole.

in Table 1. Observed rates compare reasonably well with those calculated from equation (A) after appropriate choice of values for *a* and *b*.

Increase in the substrate concentration affects the oxidation rate in a manner consistent with 1 : 1 complex formation (Table 2).

The reaction is only slightly sensitive to variation of the acid concentration (Table 3) and it is characterised by an apparent activation energy of about 13 kcal./mole (Table 4).

## DISCUSSION

The reproduction of the main kinetic features of the oxidation of malonic acid by manganese(III) pyrophosphate in the oxidation by manganese(III) sulphate indicates that both oxidations proceed by a common mechanism. Table 2 shows that a malonic acid-manganese(III) complex is again involved.

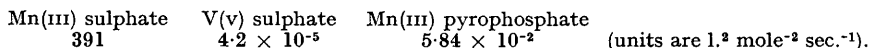
Two points emerge from the present study which are not explained by Drummond and Waters' scheme (1)–(2). There are: (i) The redox potential of the Mn(III)–Mn(II) couple is much higher in sulphuric acid<sup>6</sup> (1.51 v) than in pyrophosphoric<sup>7</sup> acid (1.15 v). The radical ·CH(CO<sub>2</sub>H)<sub>2</sub> should therefore be far less able to re-oxidise manganese(II) in the sulphate than in the pyrophosphate ion medium. (ii) The back reaction of equation (1), suggested to account for the strong retarding influence of manganese(II) ions, indicates that the reaction velocity should be similarly retarded by an increase of acidity. This acidity dependence could not be measured under the buffer-like conditions employed by Drummond and Waters, but our data (Table 3) indicate the retardation to be very slight and to be of the same order or magnitude as, for example, those encountered in one-electron oxidations of formic acid.<sup>3,4</sup>

We have noted before<sup>4</sup> the strong contrast between the oxidations of malonic acid by vanadium(v) and manganese(III), especially as regards the relative rates and the inability of either manganese(II) or vanadium(IV) ions to suppress the vanadium(v) oxidation. Use

<sup>6</sup> Grube and Metzger, *Z. Electrochem.*, 1923, **29**, 17.<sup>7</sup> Watters and Kolthoff, *J. Amer. Chem. Soc.*, 1948, **70**, 2455.

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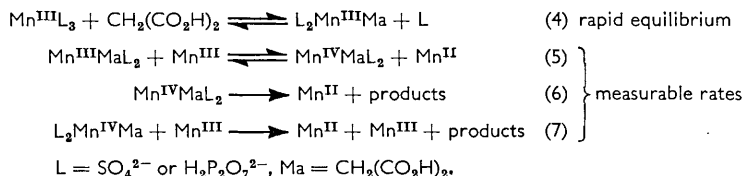
of activation energies for the vanadium(v) and manganese(III) sulphate oxidations enable us to compare third-order rate constants at 30°, the temperature employed by Drummond and Waters, after extrapolation of both sets of data of the manganese(III) oxidations to zero value of [Mn(II)].



The usual sequence of reactivities towards organic compounds such as alcohols, allylic alcohols, ketones, hydroxy-acids, enolising aldehydes, acyloins, etc., *i.e.*, manganese(III) sulphate > vanadium(v) sulphate > manganese(III) pyrophosphate fails abjectly for malonic acid, and we can reconcile the extreme slowness of the vanadium(v) attack with its normal reactivity only by suggesting a mechanism unique to manganese(III) which can also account for the free-radical phenomena.

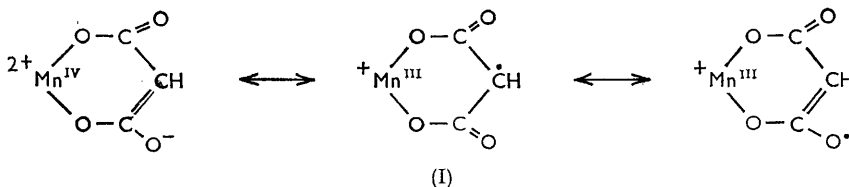
Rosseinsky's<sup>6</sup> study of the Mn(III)—Hg(I) reaction indicates that for reductants preferring to give up electrons in pairs rather than singly, *e.g.*, the mercury(I) dimer, sufficient manganese(IV) is present in solutions of manganese(III) at 50° by virtue of the equilibrium (3) to enable such two-electron transfers to take place; Lingane and Selim<sup>8</sup> give a value of  $K_{298}$  for equilibrium (3) of *ca.*  $10^{-3}$  for a 4.5M-sulphuric acid medium.

For the oxidations of malonic acid by manganese(III) we can write



Equation (4) can be derived from either equations (5) and (6) or equations (5) and (7).

The reactive intermediate producing the effects observed by Drummond and Waters may be the  $\text{L}_2\text{Mn}^{\text{IV}}\text{Ma}$  complex, for this can behave as a free radical by virtue of the interaction of the  $t_{2g}$  orbitals of the metal ion, which possesses three unpaired electrons, with the  $\pi$ -system of the malonate ligand which will probably be in the enol form. Thus the "resonance hybrids" of the  $\text{L}_2\text{Mn}^{\text{IV}}\text{Ma}$  complex may be expressed:



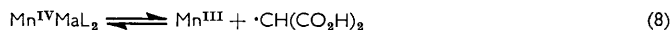
(We thank Dr. J. S. Littler of this laboratory for this suggestion.)

The main reaction (6) corresponds to an intramolecular or solvolytic two-electron decomposition of the  $\text{Mn}^{\text{IV}}\text{L}_2\text{Ma}$  complex, whilst the tendency of the reaction to display an order in manganese(III) higher than second at highest manganese(III) concentrations, observed by Drummond and Waters in the manganese(III) pyrophosphate work, may result from step (7), *i.e.*, an attack by manganese(III) upon the manganese(IV) complex. This step has a precedent in the manganese(III) sulphate oxidation of formic acid.<sup>3</sup> The radical reactions and the induced oxidations correspond to attacks on the free-radical hybrid (I), which could be sterically hindered by substitution at the *meso*-carbon atom of malonic acid. This could explain Drummond and Waters' finding that ethyl- and

<sup>8</sup> Lingane and Selim, *Acta Chim. Analyt.*, 1959, **21**, 536.

benzyl-malonic acids are oxidised in a "normal" manner by manganese(III) pyrophosphate, *i.e.*, no retardation by the manganese(II) ions occurs and induced oxidations of alcohols are not observable.

The resonance of the complex (I) implies that manganese(III) is in the low-spin form, for only then is no change in multiplicity involved. For this reason one cannot envisage similar resonance in either a vanadium(v)—or even a manganese(III)—malonic acid complex.



Equations (8) and (2) would allow for the possibility of the dissociation of  $\text{Mn}^{\text{IV}}\text{L}_2\text{Ma}$  into  $\text{Mn}^{\text{II}}$  and a free radical, not containing manganese, although no advantage is gained in reconciling the various kinetic data by involving them.

The general reaction sequence (4)—(6), unlike (1)—(2) does not require strong acid-retardation in the manganese(III) sulphate oxidation.

#### EXPERIMENTAL

Malonic acid was recrystallised from a benzene-ethanol and had m. p. 135.5—136°.

Reaction rates were measured spectrophotometrically, utilising the point of maximum absorption of manganese(III) sulphate at 510 m $\mu$ . No measures were taken to exclude oxygen from reaction mixtures; at very low ( $<10^{-3}\text{M}$ ) concentrations of manganese(III) an initial extremely rapid reduction of manganese(III) was observed which consumed about  $5-6 \times 10^{-4}$  moles of oxidant. Thereafter the "normal" reaction set in at a rate about one-twentieth that of the presumed "oxygen" reaction.<sup>1</sup> We consider therefore that our rate measurements correspond to anærobic conditions.

Dependences of the rate upon various factors were ascertained under conditions of high concentrations of manganous ion for only then is autoretardation due to accumulation of this ion eliminated.

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