

607. *The Catalysis by Manganous Ions of Oxidations by Aqueous Chromic Acid.*

By T. J. KEMP and WILLIAM A. WATERS.

Manganous ions enhance the rates of oxidation of several organic compounds by aqueous chromic acid at acidities which are far too low for the occurrence of appreciable direct oxidation of manganous ions by chromic acid. The catalysis is characterised by a tendency for the oxidation to appear to be of zero order with respect to $[\text{Cr}^{\text{VI}}]$; detailed testing with α -hydroxyisobutyric acid indicates however that the true relationship should be a one-third order with respect to $[\text{HCrO}_4^-]$. With progressive manganous ion catalysis the kinetic isotope effect for the oxidations of mandelic and deuterio-mandelic acid falls towards that found for direct oxidation by manganic sulphate.

A general interpretation of this catalysis is given: there is a fast oxidation of an organic complex of manganese(II) to a corresponding complex of manganese(III), following which there is a slow, rate-determining, breakdown of the manganese(III) complex.

THE well-known effect of manganous ions in diminishing the rates of oxidation of alcohols and aldehydes by chromic acid has been of diagnostic theoretical importance in establishing the mechanisms of oxidation of these substances.¹⁻³ Much less attention however has been paid to the findings that the chromic acid oxidations of oxalic acid^{4,5} and of certain α -hydroxy-carboxylic acids^{6,7} are positively catalysed by manganous ions. This catalysis, which we have examined kinetically, now appears to be more directly related to valency states of manganese than of chromium, for several other oxidations are known in which manganese ions can act as "potential mediators" or positive catalysts.

The role of manganese(II) in catalysing the oxidations by acid permanganate of tartaric,⁸ malonic,⁹ and oxalic^{10,11} acids is fairly well understood: these acids are relatively inert to two-electron oxidants but are quite sensitive to one-electron oxidants such as manganese(III) which is formed by the interaction of Mn^{2+} and MnO_4^- ions. However, when two-electron shifts are favoured, catalysis may be due to manganese(IV). Schaffer¹² has

¹ Westheimer, *Chem. Rev.*, 1949, **45**, 419.

² Waters, *Quart. Rev.*, 1958, **12**, 277.

³ Kemp and Waters, *Proc. Roy. Soc.*, 1962, *A*, **274**, 480.

⁴ Dhar, *J.*, 1917, **111**, 707.

⁵ Chakravarty and Ghosh, *J. Indian Chem. Soc.*, 1957, **34**, 841.

⁶ Chatterjee and Gyani, *J. Indian Chem. Soc.*, 1958, **36**, 605.

⁷ Gyani and Prasad, *J. Indian Chem. Soc.*, 1962, **39**, 765.

⁸ Bhale, Sant, and Bafna, *J. Sci. Ind. Res. (India)*, 1956, **15**, *B*, 45.

⁹ Drummond and Waters, *J.*, 1954, 2456.

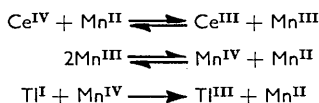
¹⁰ Launer and Yost, *J. Amer. Chem. Soc.*, 1934, **56**, 2571.

¹¹ Malcolm and Noyes, *J. Amer. Chem. Soc.*, 1952, **74**, 2769.

¹² Schaffer, *J. Amer. Chem. Soc.*, 1933, **55**, 2169.

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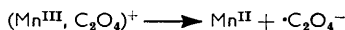
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whereby the two-electron oxidation of Ti^{I} can be effected in a single step without involving the high-energy intermediate Ti^{II} . The catalysis by manganese(II) of the oxidations of oxalic and malonic acids by vanadium(V) illustrates¹³ still another feature of manganese chemistry, for it depends on the fact that manganese can readily form complex ions in which the ligand groups reduce the redox potential of the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ couple considerably below that for the system $\text{Mn}^{3+}, \text{aq}/\text{Mn}^{2+}, \text{aq}$.

Catalysis by manganese(II) of chromic acid oxidations may be observed under various distinct circumstances. In concentrated sulphuric acid ($> 6\text{M}$) chromic acid and manganous sulphate interact to produce some manganese(III).^{6,14,15} Though the standard redox potentials of $\text{Cr}^{\text{VI}}/\text{Cr}^{\text{III}}$ (1.3 v) and $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ (1.5 v) couples indicate that Cr^{VI} should not oxidise Mn^{II} , sulphate complexing of manganese(III) stabilises this ion sufficiently to allow of some equilibration. In accord with this we have recently¹⁶ noted the retarding effect of sulphuric acid on oxidations effected by manganic sulphate. Chatterjee and Gyani⁶ and Gyani and Prasad⁷ have studied the manganese catalysis of the chromic acid oxidations of lactic and citric acids under these conditions; with lactic acid the breakdown of a lactic acid-manganese(III) complex is evidently the rate-controlling process.

Some catalysed oxidations occur under conditions in which manganese(III) is not present in visibly detectable amounts. For instance Bobtelsky and Glasner¹⁷ who studied the manganous ion catalysed oxidation of bromide anions to bromine by chromic acid in sulphuric acid found that the slow reaction was of the first order with respect to both $[\text{Mn}^{\text{II}}]$ and $[\text{Cr}^{\text{VI}}]$ but was independent of $[\text{Br}^-]$. They ascribed the slow reaction to the oxidation of Mn^{II} by Cr^{VI} and suggested that the Mn^{III} ion was immediately reduced again by the bromide. We have found that this occurs even in 2.4M sulphuric acid. Again, Dhar⁴ found that the oxidation of oxalic acid by chromic acid can be catalysed by manganous sulphate even in the absence of sulphuric acid. The uncatalysed reaction is of the first order with respect to $[\text{Cr}^{\text{VI}}]$ but it becomes of almost zero order in $[\text{Cr}^{\text{VI}}]$ in the presence of manganous ions. These results have been confirmed by Chakravarty and Ghosh⁵ who showed that the manganese-catalysed reaction had a much more favourable entropy of activation than a higher activation energy. They can be interpreted from the work of Taube¹⁸ on the catalysis by manganese(III) of the oxidation of oxalic acid by halogens, for here the rate-controlling reaction is the decomposition of a mono-oxalate chelate of manganese(III), *i.e.*,



This reaction which is also important in the permanganate oxidation of oxalic acid¹¹ has an activation energy of 18.3 kcal./mole which is approximately that found by the Indian workers.

Our results with several organic acids have elucidated more fully the nature of this catalysis in dilute sulphuric acid solutions.

Results.—Data concerning the manganese ion catalysis of oxidation of (\pm)-mandelic, α -hydroxyisobutyric, and malonic acids and of cyclohexanone by chromic acid are presented in Figs. 1—3. From Fig. 1, after correction for the manganese-independent path, it is

¹³ Kemp and Waters, *J.*, 3101.

¹⁴ Chatterjee and Gyani, *J. Indian Chem. Soc.*, 1957, **34**, 721.

¹⁵ Chakravarty and Ghosh, *Proc. Nat. Acad. Sci. India*, 1957, **26A** (Pt I), 41.

¹⁶ Kemp and Waters, *J.*, 1964, **339**.

¹⁷ Bobtelsky and Glasner, *J.*, 1948, **1376**.

¹⁸ Taube, *J. Amer. Chem. Soc.*, 1947, **69**, 1418.

FIG. 1. Effect of Mn^{II} upon the initial rates of oxidation of some organic substrates by Cr^{VI} .

Curve	Substance	Concentration (moles l^{-1})	T°
A	(±)-Mandelic acid	0.0234	25.8
B	Cyclohexanone	0.0429	51.5
C	α -Hydroxyisobutyric acid	0.0289	25.8

$[H_2SO_4] = 1.43M$, $[Cr^{VI}] = 15.8 \times 10^{-4}M$,
 $[MnSO_4] + [ZnSO_4] = 0.496M$.

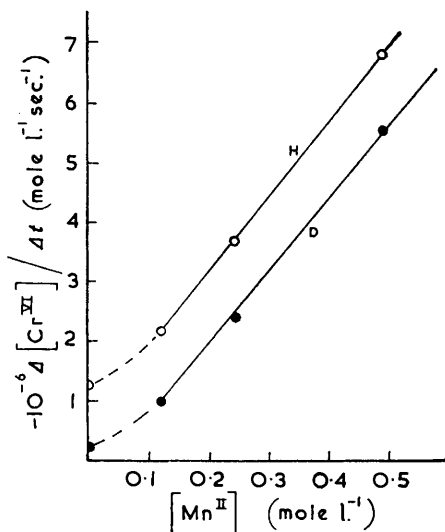
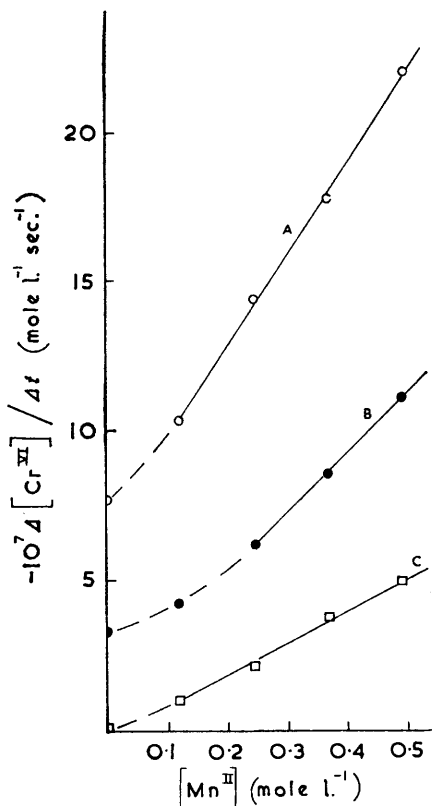


FIG. 2. Effect of Mn^{II} upon the initial rates of oxidation of mandelic and $[\alpha\text{-}^2H_1]$ mandelic acid at 41.3°.

$[Ph \cdot CH(OH) \cdot CO_2H] = 0.01735M$.
 $[Ph \cdot CD(OH) \cdot CO_2H] = 0.01645M$.
 $[Cr^{VI}] = 19.5 \times 10^{-4}M$.
 $[MnSO_4] + [ZnSO_4] = 0.490M$.
 $[H_2SO_4] = 1.41M$.

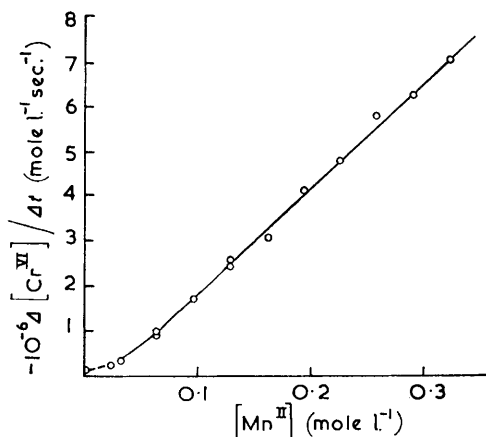


FIG. 3. Effect of Mn^{II} upon the initial rate of oxidation of malonic acid by Cr^{VI} at 27.0°.

$[Malonic\ acid] = 0.0650M$.
 $[Cr^{VI}] = 20.8 \times 10^{-4}M$.
 $[H_2SO_4] = 1.875M$.
 $[MnSO_4] + [ZnSO_4] = 0.325M$.

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evident that the rates of oxidation of (\pm)-mandelic and α -hydroxyisobutyric acids by the Cr^{VI} — Mn^{II} couple are in the ratio 2.9 : 1. For the straightforward oxidations of these two acids by chromic acid the ratio is 300 : 1 and for their oxidation by manganic sulphate¹⁹ it is 2.3 : 1. Fig. 2 shows that for the oxidations of mandelic and [α - 2H_1]mandelic acids, $\text{Ph}\cdot\text{CD}(\text{OH})\cdot\text{CO}_2\text{H}$, the primary kinetic isotope effect depends on the concentration of manganous ions.

In all our experiments we took a large excess of the organic substrate and found that the rate of consumption of chromium(vi) was exponential in the absence of manganous sulphate, but showed almost a linear time dependence at high manganese concentrations. The oxidations however are not true zero-order reactions with respect to [Cr^{VI}] since an increase in the initial concentration of chromic acid resulted in an increase of the apparent zero-order rate constants [Table I(a)] and with α -hydroxyisobutyric acid a plot of $\log [\text{Cr}^{\text{VI}}]$ against $\log k_0$ plot had a slope of 0.25. Calculations of (HCrO_4^-) concentrations enabled us to plot $\log [\text{HCrO}_4^-]$ against $\log k_0$, and for this the slope was 0.30 ± 0.04 .

With α -hydroxyisobutyric acid at our highest manganese sulphate concentration the reaction was no longer of first order with respect to the organic substrate, but showed Michaelis–Menten kinetics [Table I(b)], *i.e.*,

$$\text{Rate} = a[\text{Substrate}]/(1 + b[\text{Substrate}])$$

With the addition of manganese ions the activation energy falls from 16.9 (ref. 19) to 15.6 kcal./mole [Table I(c)].

With malonic acid the catalysed oxidation has a short induction period of relatively slow oxidation which decreases as the concentration of malonic acid is increased. [Table 2(b)]. For both catalysed and uncatalysed reactions the rate is approximately of first order with respect to malonic acid [Table 2(a) and (b)] and to manganese(ii) (Fig. 3). Moreover the manganese-catalysed reaction has a lower activation energy [Tables 2(c) and 4].

In Table 3 we have compared the rates of reduction of chromic acid by our substrates in the presence of manganese ions with data for the direct reduction of Cr^{VI} by Mn^{II} as measured by bromide anion oxidation.¹⁷ Our figures cover a wider concentration range than has been examined hitherto and, together with the energy data of Table 4, give a comprehensive picture of the whole catalysis:

TABLE 1.

Oxidation of α -hydroxyisobutyric acid by chromic acid in the presence of manganous sulphate

(a) Dependence of the apparent zero-order rate upon [HCrO_4^-] at 49.5°.

[Hydroxy-acid] = 0.0244M; [MnSO_4] = 0.284M; [H_2SO_4] = 1.09M

$10^4 [\text{Cr}^{\text{VI}}]$ (moles l. ⁻¹)	$10^4 [\text{HCrO}_4^-]^a$	$\sqrt[3]{[\text{HCrO}_4^-]}$	$-\frac{10^7 \Delta[\text{Cr}^{\text{VI}}]}{\Delta t}$	$\frac{10^7 \Delta[\text{Cr}^{\text{VI}}]/\Delta t}{\sqrt[3]{[\text{HCrO}_4^-]}}$
6.03	5.45	0.0815	10.1	124
9.06	7.88	0.0922	10.1	109
12.05	10.0	0.100	10.0	100
18.1	14.0	0.112	10.5	94
24.1	17.8	0.121	11.1	92
33.2	22.8	0.132	12.45	94
45.2	28.8	0.142	14.6	103
60.4	35.5	0.153	14.8	97
75.5	41.3	0.161	16.55	103
90.5	46.8	0.167	17.35	104
			15.2	91

^a Calc. from $[\text{HCrO}_4^-]^2/[\text{Cr}_2\text{O}_7^{2-}] = 0.01$ at 50°.20

¹⁹ Kemp and Waters, *J.*, 1964, 1192.

²⁰ Best, Littler, and Waters, *J.*, 1962, 822.

TABLE 1.—(Continued.)

(b) Dependence of the initial oxidation rate upon substrate concentration at 51.8°.

[MnSO₄] = 0.496M, [Cr^{VI}] = 15.8 × 10⁻⁴M, [H₂SO₄] = 1.43M

10 ³ [Hydroxy-acid] (moles l. ⁻¹)	0	7.24	14.45	21.7	28.9
-10 ⁷ Δ [Cr ^{VI}]/Δt (moles l. ⁻¹ sec. ⁻¹) (obs.)	0	24.3	33.4	38.9	41.5, 42.4
-10 ⁷ Δ [Cr ^{VI}]/Δt (moles l. ⁻¹ sec. ⁻¹) (calc.) ^b	0	23.9	33.5	38.8	41.9

^b Calculated from the relation:
-10⁷Δ [Cr^{VI}]/Δt = 5780 [Hydroxy-acid]/(1 + 103[Hydroxy-acid])

(c) Temperature dependence of the initial oxidation rate.

[Hydroxy-acid] = 0.0289M, [MnSO₄] = 0.496M, [Cr^{VI}] = 15.8 × 10⁻⁴M, [H₂SO₄] = 1.43M

Temp.	21.6°	25.8°	29.5°	36.0°	41.7°	51.8°
-10 ⁷ Δ [Cr ^{VI}]/Δt (moles l. ⁻¹ sec. ⁻¹)	3.57	4.95	6.91	12.4	19.6	42.4, 41.5

Hence E‡ = 15.6 kcal./mole.

DISCUSSION

Whilst the manganese(II) catalysed oxidation of bromide ions is a first-order reaction with respect to chromic acid and a zero-order reaction with respect to bromide, the catalysed oxidations of the organic acids, and of cyclohexanone are almost of zero order with respect to chromium(VI) and almost of first order with regard to the organic substrate. With α-hydroxyisobutyric acid which we studied in greatest detail the reaction is evidently dependent on [HCrO₄⁻][‡], of first order with respect to the manganese(II) and exhibits Michaelis-Menten kinetics with respect to the organic acid. This behaviour we take to be

TABLE 2.

Oxidation of malonic acid by chromic acid in the presence and absence of Manganese(II) ions.

Dependence of the initial oxidation rate upon substrate concentration.

(a) Uncatalysed

[Cr^{VI}] = 20.8 × 10⁻⁴M, [HClO₄] = 2.50M, T = 27.0°

[Malonic acid] (moles l. ⁻¹)	0.1625	0.227	0.325	0.650	0.975	1.30
-10 ⁷ Δ [Cr ^{VI}]/Δt (moles l. ⁻¹ sec. ⁻¹)	19.4	28.7	38.7	87.3	147	192
$\frac{-10^5\Delta [\text{Cr}^{\text{VI}}]/\Delta t}{[\text{Malonic acid}]}$	1.2	1.3	1.2	1.3	1.5	1.5

(b) Catalysed

[Cr^{VI}] = 20.8 × 10⁻⁴M, [MnSO₄] = 0.325M, [H₂SO₄] = 1.875M; a small correction for the effect of the uncatalysed oxidation was applied

10 ³ [Malonic acid] (moles l. ⁻¹)	6.50	13.0	26.0	39.0	52.0	65.0
-10 ⁷ Δ [Cr ^{VI}]/Δt (moles l. ⁻¹ sec. ⁻¹)	7.85	14.9	30.1	42.9	56.6	68.8
Induction time (min.)	5.5	4.0	2.5	2	1.5	1
$\frac{-10^4\Delta [\text{Cr}^{\text{VI}}]/\Delta t}{[\text{Malonic acid}]}$	1.3	1.2	1.2	1.1	1.1	1.1

(c) Dependence of the initial rates of oxidation for both catalysed and uncatalysed reactions upon temperature.

Uncatalysed. [Malonic acid] = 0.650M, [H₂SO₄] = 1.875M, [Cr^{VI}] = 20.8 × 10⁻⁴M.
Catalysed. [Malonic acid] = 0.0131M, [MnSO₄] = 0.325M; [Cr^{VI}] and [H₂SO₄] as above.

Temp.	$\frac{-10^8\Delta [\text{Cr}^{\text{VI}}]/\Delta t}{[\text{Malonic acid}]}$ (uncatalysed path)	$\frac{-10^4\Delta [\text{Cr}^{\text{VI}}]/\Delta t}{[\text{Malonic acid}]}$ (catalysed) *
26.8°	1.48	1.07
36.5	2.67	1.72
43.5	3.91	2.33
50.3	5.92	3.11
57.8	8.12	4.19

* Corrected for effect of uncatalysed path.

Hence E‡ (uncatalysed path) = 11.2 kcal./mole
E‡ (catalysed path) = 8.75 kcal./mole

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TABLE 3.
Relative rates of oxidations by a chromic acid-manganous sulphate mixture
at 36.7°.

[Substrate] (moles l. ⁻¹)	[Mn ^{II}] (moles l. ⁻¹)	$\frac{-10^7 \Delta [\text{Cr}^{\text{VI}}]}{\Delta t}$ (total) (moles l. ⁻¹ sec. ⁻¹)	$\frac{-10^7 \Delta [\text{Cr}^{\text{VI}}]}{\Delta t}$ (catalysed *) (moles l. ⁻¹ sec. ⁻¹)
Br ⁻	0.032	0.248	4.2
"	0.064	"	4.6
"	0.096	"	4.4
"	0.160	"	4.4
"	0.240	"	3.9
"	0.400	"	3.5
Oxalic acid	0.0623	0	3.80
"	"	0.00416	29.1
"	"	0.0104	68.2
"	"	0.0208	131
"	"	0.0416	309
"	"	0.0624	475
"	"	0.0832	585
"	"	0.104	683, (835)
"	"	0.125	847
"	"	0.1455	845
"	"	0.1665	944
"	"	0.187	1160
"	"	0.208	1135
Malonic acid	0.208	0	16.5
"	"	0.104	216
"	"	0.208	500
α -Hydroxyisobutyric acid	0.00895	0	0.30
"	"	0.104	6.06
"	"	0.208	13.9

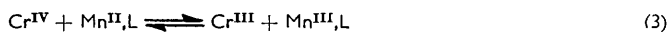
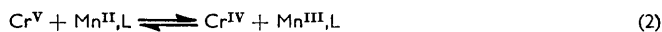
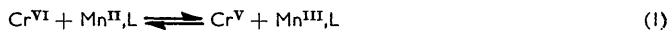
* Corrected for the uncatalysed path.

TABLE 4.
Collected activation energies.

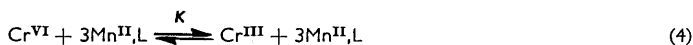
Substrate	Oxidant	E^\ddagger (kcal./mole)	Ref.
Mn ^{II}	Cr ^{VI}	11.0	17
α -Hydroxyisobutyric acid	Cr ^{VI}	16.9	19
"	Mn ^{III} sulphate	20.0	19
"	Cr ^{VI} -Mn ^{II}	15.6	—
Malonic acid	Cr ^{VI}	11.2	—
"	Mn ^{III} sulphate	13	22
"	Cr ^{VI} -Mn ^{II}	8.75	—
Oxalic acid	Cr ^{VI}	12	4, 5
"	Mn ^{III}	18.3	18
"	Cr ^{VI} -Mn ^{II}	18	4, 5

typical of all our organic substrates. It indicates that we must be dealing with oxidations of 1 : 1 organic complexes of manganese.

The one-third order reaction with respect to $[\text{HCrO}_4^-]$ can be rationalised by postulating the occurrence of the following equilibria, where (Mn, L) denotes a complex ion of manganese



If all these reactions were faster than an irreversible, subsequent oxidative step, then we may write



$$\text{or } [\text{Mn}^{\text{III}}, \text{L}] = K[\text{Mn}^{\text{II}}, \text{L}] [\text{Cr}^{\text{VI}}]^\ddagger [\text{Cr}^{\text{III}}]^\ddagger$$

and our observed kinetics can correspond to oxidations involving the slow breakdown of manganic complexes, *i.e.*,

$$-d[\text{Cr}^{\text{VI}}]/dt = -d[\text{Mn}^{\text{III}},\text{L}]/dt = kK\ddagger[\text{Cr}^{\text{VI}}]\ddagger [\text{Mn}^{\text{II}},\text{L}]/[\text{Cr}^{\text{III}}]\ddagger$$

which we, and others, have already studied, though under different conditions of acidity, etc., for the organic acids which we have now examined.^{9,11,16,19,21,22}

The postulate that the complexing of manganese cations can lower the redox potential of $(\text{Mn}^{\text{III}},\text{L})/(\text{Mn}^{\text{II}},\text{L})$ sufficiently to allow the slight formation of $(\text{Mn}^{\text{III}},\text{L})$ by the forward reaction (1) needs little elaboration since it is common in the chemistry of the cations of transition metals. For the oxidation of bromide anions with which there is very little complexing of Mn^{II} , the forward reactions (2) and (3) and the oxidation (5) must all occur



much more rapidly than (1), so as to give the kinetic behaviour discovered by Bobtelsky and Glasner. Table 3 however shows that with organic ligands the oxidation rate can be much greater than that of bromide; with them the forward reaction (1) can evidently be quite fast. With malonic acid the slight induction period may perhaps be associated with this reaction. All previous studies¹⁻³ of oxidations of organic compounds by chromium(vi) indicate that both Cr^{V} and Cr^{IV} are more powerful oxidants than (HCrO_4^-) and hence it is quite rational to suppose that equations (2) and (3) represent rapid equilibria.

Reactions such as (6) or similar reactions of Cr^{V} or Cr^{IV} cannot be occurring significantly,



for if so then the reaction order with respect to chromium(vi) would be much greater than $\frac{1}{3}$.

The view that the rate-determining reaction is a breakdown of a complex $(\text{Mn}^{\text{III}},\text{L})$ receives support from the comparative study of the oxidations of mandelic and deuterio-mandelic acid, for the kinetic isotope effect $k_{\text{H}}/k_{\text{D}}$ falls as $[\text{Mn}^{\text{II}}]$ increases (Fig. 2) and with high $[\text{Mn}^{\text{II}}]$ approaches the value of 1.1 found (at 23°) for the oxidation of mandelic acid by manganic sulphate.¹⁹

Table 4 indicates that the activation energies of these catalysed reactions depend on the nature of the $(\text{Mn}^{\text{III}},\text{L})$ complex which is decomposing. Thus for oxalic acid the activation energy corresponds to that measured by Taube¹⁸ for the decomposition of a manganic-oxalate, but comparisons with manganic sulphate oxidations^{16,19,22} cannot be made since in the latter case there must also be stabilisation of manganese(III) by sulphate complexing.

EXPERIMENTAL

We have described¹⁹ the preparation of $[\alpha\text{-}^2\text{H}_1]$ mandelic acid. Oxidant solutions were prepared from AnalaR chromium trioxide and manganous sulphate. Our reaction rates were determined spectrophotometrically by observing the disappearance of absorption due to chromium(vi) at 350 m μ . Under our conditions no change of absorption of light due to the formation of ions of manganese(III) could be observed. When necessary for the maintenance of constant ionic strengths manganous ions were replaced by zinc ions.

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²¹ Levesley and Waters, *J.*, 1955, 217.

²² Kemp and Waters, *J.*, 1964, 1489.