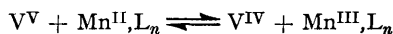


591. *Oxidations of Organic Compounds with Quinquevalent Vanadium. Part XIV.¹ Catalysis of the Oxidations of Malonic and Oxalic Acids by Manganous Ions.*

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

Manganous ions markedly catalyse the oxidations of malonic and oxalic acids by vanadium(v), but vanadium(iv) retards these reactions, which have very low activation energies. The catalysis is ascribed to equilibria



in which the malonic or oxalic acids function as the ligands, L. Moreover, the species $\text{Mn}^{\text{III}},\text{L}_n$ which is involved in the subsequent reaction is not produced in spectroscopically detectable concentrations.

No instance of the catalysis by manganous ions of any oxidation effected by quinquevalent vanadium had been reported until we noted briefly in Part XIII¹ that the oxidation of malonic acid, far from being retarded by manganous ions (as is the case for its oxidations by the sulphate¹ and pyrophosphate² complexes of Mn^{III}), is strongly accelerated by this species. We have now studied this catalysis in detail, employing our standard spectrophotometric techniques¹ and making comparisons only between reaction mixtures of the same ionic strength, using for this purpose zinc ions to balance manganous and vanadyl ions in our solutions. Manganous-ion catalysis is also exhibited, with similar but less marked features, in the oxidation of oxalic acid by vanadium(v). Neither oxidation resembles the catalysis by bromide anions³ of the vanadium(v) oxidations of organic compounds.

RESULTS

The general features of the manganous-ion catalysis are depicted by Figs. 1 and 2. Table 1(a) shows that the oxidation of malonic acid has a dependence on $[\text{Mn}^{\text{II}}]$ consistent

¹ Part XIII, Kemp and Waters, *J.*, 1964, 1610.

² Drummond and Waters, *J.*, 1954, 2456.

³ Julian and Waters, *J.*, 1962, 818.

with Michaelis-Menten kinetics, so that the fast, reversible formation of a manganese complex with one molecule of the oxidisable substrate must precede the rate-determining oxidation. Fig. 3 shows, however, that the oxalic acid reaction is strictly of the first order until a limiting

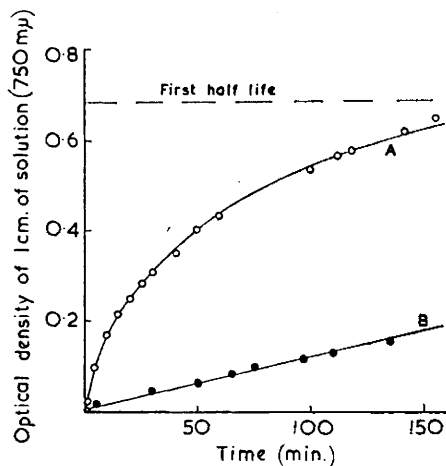


FIG. 1. The effect of Mn^{II} ions upon the rate of appearance of V^{IV} in the oxidation of malonic acid by vanadium(V) sulphate. $[\text{Malonic acid}] = 0.338\text{M}$; $[\text{V}^{\text{V}}] = 0.0725\text{M}$; $[\text{H}_2\text{SO}_4] = 1.66\text{M}$; $T = 57.0^\circ$.

Curve A, $[\text{MnSO}_4] = 0.260\text{M}$.

Curve B, $[\text{ZnSO}_4] = 0.260\text{M}$.

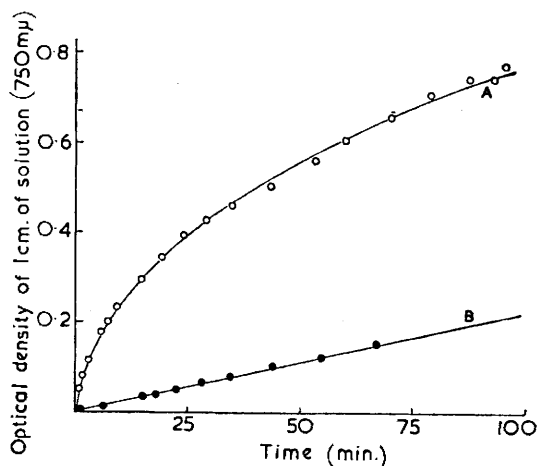


FIG. 2. The effect of Mn^{II} ions upon the rate of appearance of V^{IV} in the oxidation of oxalic acid by vanadium(V) sulphate. $[\text{Oxalic acid}] = 0.264\text{M}$; $[\text{V}^{\text{V}}] = 0.0707\text{M}$; $[\text{H}_2\text{SO}_4] = 1.61\text{M}$; $T = 25.0^\circ$.

Curve A, $[\text{MnSO}_4] = 0.203\text{M}$.

Curve B, $[\text{ZnSO}_4] = 0.203\text{M}$.

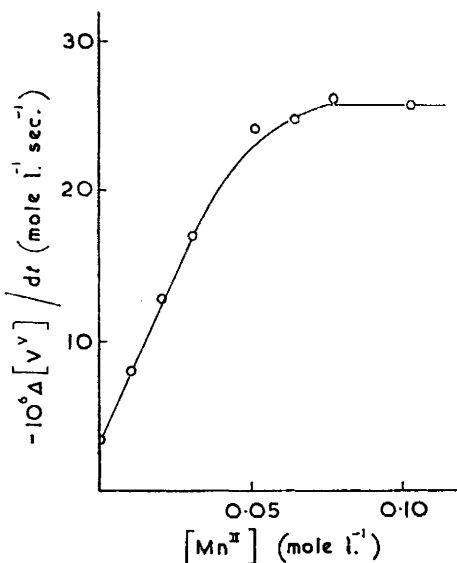
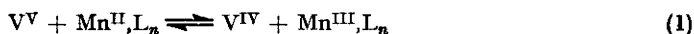


FIG. 3. Effect on the initial rate of oxidation of oxalic acid by vanadium(V) sulphate of adding increasing amounts of manganese(II) sulphate. $[\text{Oxalic acid}] = 0.156\text{M}$; $[\text{V}^{\text{V}}] = 0.0725\text{M}$; $[\text{H}_2\text{SO}_4] = 2.56\text{M}$; $[\text{MnSO}_4] + [\text{ZnSO}_4] = 0.104\text{M}$; $T = 25.4^\circ$.

concentration of Mn^{II} is reached, whereafter the reaction becomes of zeroth order with respect to $[\text{Mn}^{\text{II}}]$.

Tables 1(b) and 2(a) show that vanadyl ions (V^{IV}) markedly reduced the catalysed-oxidation rates, and this is consistent with the occurrence of a slow equilibrium



(L_n denotes ligand groups one of which must be the oxidisable substrate)

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that yields a manganese(III) species capable of oxidising the organic substrate rapidly. Increase in $[V^V]$ produces a linear increase in oxidation rate for oxalic acid [Table 2(b)] but the corresponding increase for malonic acid [Table 1(c)] is more consistent with a 1 : 1 complex formation. For each of these reactions the substrate-dependence follows Michaelis-Menten kinetics, [Tables 1(d) and 2(c)]. The temperature-dependences of the two reactions are shown in Tables 1(e) and 2(d). They indicate that for the Mn^{II} -catalysed oxidations of malonic and oxalic acids the activation energies drop to 6.9 and 4.7 kcal. mole⁻¹ from values of 19.7¹ and 19.2 kcal. mole⁻¹ respectively for their oxidations by vanadium(V) alone or of 13 and 18.3 kcal. mole⁻¹ for their oxidations by manganic sulphate.^{3,4} Table 2d also shows that cobaltous ions have no catalytic activity.

Neither vanadium(V) nor vanadium(IV) ions absorb light strongly at 510 $m\mu$, the wavelength maximum for absorption by manganese(III), but observations made at this wavelength with half-oxidised solutions of both malonic and oxalic acids showed that manganese(III) was

TABLE I.

The oxidation of malonic acid by V^V in the presence of Mn^{II} ions.

(a) *Dependence of the initial oxidation rate upon catalyst concentration.*

$[Malonic\ acid] = 0.338M$; $[V^V] = 0.0725M$; $([ZnSO_4] + [MnSO_4]) = 0.260M$; $[H_2SO_4] = 1.655M$;
 $T = 47.1^\circ$

$[Mn^{II}]$ (mole l. ⁻¹)	$-10^7\Delta[V^V]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (obs.)	$-10^7\Delta[V^V]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (calc.) ^a	$[Mn^{II}]$ (mole l. ⁻¹)	$-10^7\Delta[V^V]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (obs.)	$-10^7\Delta[V^V]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (calc.) ^a
0	5.03	5.0	0.0520	57.5	65.3
0.0026	9.90	9.84	0.104	90.9	102
0.0052	14.75	14.5	0.156	120	122
0.0104	22.3	23.0	0.208	143	134
0.0182	35.8	34.4	0.260	170	143
0.0260	42.5	44.4			

^a *I.e.*, calculated from the relation $-10^7\Delta[V^V]/\Delta t = 5 + 1910[Mn^{II}]/(1 + 10[Mn^{II}])$.

(b) *Effect of V^{IV} ions upon the initial rate of disappearance of V^V .*^b

$[ZnSO_4] + [VOSO_4] = 0.0733M$; $[MnSO_4] = 0.203M$; $[V^V] = 0.0707M$; $[Malonic\ acid] = 0.264M$;
 $[H_2SO_4] = 1.61M$; $T = 59.8^\circ$

$10^8[V^{IV}]$ (mole l. ⁻¹)	$-10^7\Delta[V^V]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (corr. total rate) ^c	$-10^7\Delta[V^V]/\Delta t$ (calc.) ^d	$10^8[V^{IV}]$ (mole l. ⁻¹)	$-10^7\Delta[V^V]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (corr. total rate) ^c	$-10^7\Delta[V^V]/\Delta t$ (calc.) ^d
0	83	133 ^e	14.6	23	27
1.46	85	96	21.9	22	19
4.39	74	61	29.3	13.1	14.9
7.33	51	45	44.0	11.1	10.3
10.25	42	35	73.3	3.4	6.4

^b Instead of following our usual practice of measuring the increase in V^{IV} absorption at 750 $m\mu$ we observed at 370 $m\mu$ the absorption of V^V in a 2-mm. cell of reaction solution. At this wavelength V^{IV} absorbs very slightly whilst V^V has an ϵ value of 53.8. ^c Corrected for the $[Mn^{II}]$ -independent reaction: $-10^7\Delta[V^V]/dt = 6$. ^d Calculated from the relation, $-10^7\Delta[V^V]/\Delta t = 1/(0.0075 + 2.03[V^{IV}])$. ^e This would be an ideal value for an oxidation which did not itself produce V^{IV} .

(c) *Dependence of the initial oxidation rate upon $[V^V]$.*

$[Malonic\ acid] = 0.1725M$; $[MnSO_4] = 0.332M$; $[VO_2HSO_4] + [NaHSO_4] + [NH_4HSO_4] = 0.247M$;
 $[H_2SO_4] = 1.03M$; $T = 47.1^\circ$

$10^8[V^V]$ (mole l. ⁻¹)	$-10^7\Delta[V^V]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (corr. obs. rate) ^e	$-10^7\Delta[V^V]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (calc. rate) ^f	$10^8[V^V]$ (mole l. ⁻¹)	$-10^7\Delta[V^V]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (corr. obs. rate) ^e	$-10^7\Delta[V^V]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (calc. rate) ^f
6.18	7.0	8.5	80.3	79.6	80
12.3	17.5	17	92.5	85.0	87
24.7	31.0	31	111	98.0	98
43.3	46.3	50	123.5	104	105
61.8	63.3	66			

^e As in previous Table. ^f Calculated from the relation $-10^7\Delta[V^V]/\Delta t = 1430[V^V]/(1 + 5.57[V^V])$.

⁴ Taube, *J. Amer. Chem. Soc.*, 1947, **69**, 1418.

TABLE 1. (Continued.)

(d) Dependence of the initial oxidation rate upon substrate concentration.

$$[\text{V}^{\text{V}}] = 0.145\text{M}; [\text{MnSO}_4] = 0.260\text{M}; [\text{H}_2\text{SO}_4] = 0.310\text{M}; T = 56.9^\circ$$

$10^2[\text{Malonic acid}]$ (mole l. ⁻¹)	$-10^7\Delta[\text{V}^{\text{V}}]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (obs. total rate)	$-10^7\Delta[\text{V}^{\text{V}}]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (corr. rate) ^c	$-10^7\Delta[\text{V}^{\text{V}}]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (calc. rate) ^d
3.38	2.29	27.0	25
6.77	49.5	44.3	44
13.5	73.8	63.4	71
23.7	114.5	96.1	97
33.8	145	119	113

^c Corrected as for preceding Tables. ^d Calculated from the relation,

$$-10^7\Delta[\text{V}^{\text{V}}]/\Delta t = 850[\text{Malonic acid}]/(1 + 4.59[\text{Malonic acid}]).$$

(e) Temperature-dependences of the initial rates of oxidation of malonic acid by vanadium (v) in the presence and absence of manganous ions.

$$[\text{Malonic acid}] = 0.520\text{M}; [\text{V}^{\text{V}}] = 0.1015\text{M}; [\text{H}_2\text{SO}_4] = 1.72\text{M}; [\text{MnSO}_4] + [\text{ZnSO}_4] = 0.156\text{M}$$

T°	$-10^7\Delta[\text{V}^{\text{V}}]/\Delta t$ ^a (mole l. ⁻¹ sec. ⁻¹) in absence of Mn^{II}	$-10^7\Delta[\text{V}^{\text{V}}]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹); extra increment due to Mn^{II}	$k_{\text{Mn}^{\text{II}}}/k_{\text{uncat}}$
25.1	—	87.2	—
25.4	1.35	90.0	64.5
27.1	1.87 ⁱ	—	—
30.8	2.34	110	47.1
36.7	5.15	156	30.3
42.8	8.55	165	19.3
50.2	20.6	231	11.2
55.6	31.3	273	8.7
60.55	47.3	306	6.5

These data yield for the uncatalysed and catalysed paths respectively ΔE^\ddagger values of 19.7 and 6.9 kcal. mole⁻¹.^a These figures from ref. 1 are included for comparison. ⁱ ZnSO_4 was replaced by an equivalent quantity of CoSO_4 .

TABLE 2.

The oxidation of oxalic acid by V(v) in the presence of Mn^{II} ions.(a) Effect of V^{IV} ions upon the initial rate of appearance of V^{IV} .

$$[\text{ZnSO}_4] + [\text{VOSO}_4] = 0.0732\text{M}; [\text{MnSO}_4] = 0.203\text{M}; [\text{V}^{\text{V}}] = 0.0707\text{M}; [\text{oxalic acid}] = 0.264\text{M};$$

$$[\text{H}_2\text{SO}_4] = 1.61\text{M}; T = 25.0^\circ$$

$10^3[\text{V}^{\text{IV}}]$ (mole l. ⁻¹)	$-10^6\Delta[\text{V}^{\text{V}}]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (obs. total rate)	$-10^6\Delta[\text{V}^{\text{V}}]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (corr. rate) ^a	$-10^6\Delta[\text{V}^{\text{V}}]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) (calc. rate) ^b
0	28	26	47
5.85	15.5	13.4	13.1
10.25	11.0	8.92	8.5
14.6	8.19	6.13	6.3
21.9	6.08	4.02	4.4
29.3	5.46	3.40	3.4

Corrected for $[\text{Mn}^{\text{II}}]$ -independent path. ^b Calculated from the expression

$$-10^6\Delta[\text{V}^{\text{V}}]/\Delta t = 1/(0.021 + 9.45[\text{V}^{\text{IV}}]) \text{ (mole l.⁻¹ sec.⁻¹)}.$$

(b) Dependence of the initial oxidation rate upon $[\text{V}^{\text{V}}]$.

$$[\text{MnSO}_4] = 0.104\text{M}; [\text{Oxalic acid}] = 0.0779\text{M}; [\text{H}_2\text{SO}_4] = 2.63\text{M}; [\text{V}^{\text{V}}] + [\text{Na}^+] + [\text{NH}_4^+] = 0.218\text{M};$$

$$T = 25.0^\circ$$

$10^2[\text{V}^{\text{V}}]$ (mole l. ⁻¹)	$-10^6\Delta[\text{V}^{\text{V}}]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) ^a	$\frac{-10^5\Delta[\text{V}^{\text{V}}]/\Delta t}{[\text{V}^{\text{V}}]}$	$10^2[\text{V}^{\text{V}}]$ (mole l. ⁻¹)	$-10^6\Delta[\text{V}^{\text{V}}]/\Delta t$ (mole l. ⁻¹ sec. ⁻¹) ^a	$\frac{-10^5\Delta[\text{V}^{\text{V}}]/\Delta t}{[\text{V}^{\text{V}}]}$
1.09	7.5	68	7.25	41	56
2.17	15	69	8.70	61	70
3.63	22	61	10.9	75	69
5.80	29	50			

^a As in preceding Table.

TABLE 2. (Continued.)

(c) *Dependence of the initial oxidation rate upon concentration of substrate.*

[V ^V] = 0.0725M; [MnSO ₄] = 0.104M; [H ₂ SO ₄] = 2.56M; T = 25.4°					
10 ³ [Oxalic acid] (mole l. ⁻¹)	-10 ⁶ Δ[V ^V]/Δt (mole l. ⁻¹ sec. ⁻¹) (obs.) ^a	-10 ⁶ Δ[V ^V]/Δt (mole l. ⁻¹ sec. ⁻¹) (calc.) ^c	10 ³ [Oxalic acid] (mole l. ⁻¹)	-10 ⁶ Δ[V ^V]/Δt (mole l. ⁻¹ sec. ⁻¹) (obs.) ^a	-10 ⁶ Δ[V ^V]/Δt (mole l. ⁻¹ sec. ⁻¹) (calc.) ^c
7.8	5.66	5.3	93.5	22.4	21
15.6	9.05	8.9	124.6	24.2	22
31.2	12.5	13	156	22.4	23
60.8	16.7	18			

^a As in preceding Tables. ^c Calculated from the relation

$$-10^6\Delta[V^V]/\Delta t = 833 [\text{Oxalic acid}]/(1 + 30 [\text{Oxalic acid}]).$$

(d) *Temperature dependences of initial rates of oxidation of oxalic acid by vanadium(v) in the presence and absence of manganous ions.*[Oxalic acid] = 0.156M; [V^V] = 0.1015M; [H₂SO₄] = 2.56M; [MnSO₄] + [ZnSO₄] = 0.104M

T°	-10 ⁶ Δ[V ^V]/Δt (mole l. ⁻¹ sec. ⁻¹) in absence of Mn ^{II}	-10 ⁶ Δ[V ^V]/Δt (mole l. ⁻¹ sec. ⁻¹) extra increment due to Mn ^{II}	k _{Mn^{II}} /k _{uncat.}
25.4	3.23	22.4	6.94
30.0	6.40	30.5	4.77
30.0 ^a	6.46	—	—
34.8	10.05	34.95	3.47
41.0	20.55	31.15	1.52
46.85	34.9	37.0	1.06
52.4	51.8	48.2	0.93

These data yield for the uncatalysed and catalysed paths, respectively, ΔE[‡] values of 1.92 and 4.7 kcal./mole.

^a ZnSO₄ was replaced by an equivalent quantity of CoSO₄.

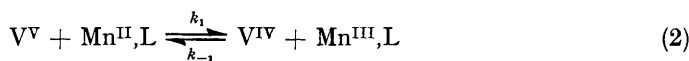
not present in detectable amounts. Again, concentrated mixtures of V^V and Mn^{II}, even after storage at 60° for several hours, produced no detectable quantities of either Mn^{III} or V^{IV} ions. Thus the balance of equilibrium (1) must be very markedly to the left.

DISCUSSION

The marked lowering of the activation energies of the reactions catalysed by manganous ion, below those for attack by either [V(OH)₃]²⁺ or Mn³⁺ ions in strong mineral acid, together with the retarding effect of vanadyl ions, show that the balance of the equilibrium in equation (1), to which the catalysis is evidently due, depends on the fact that the two substrates—malonic and oxalic acids—can both form chelate complexes with manganous ions in which the redox potential for Mn^{III}/Mn^{II} is decidedly less than for Mn³⁺,aq/Mn²⁺,aq. If such complexing was not involved then the catalytic efficiency of the manganous ions should be the same for both reactions, and, moreover, other oxidations of organic compounds by vanadium(v), *e.g.*, that of cyclohexanone,⁵ should exhibit similar catalysis; but this is not the case.

Again the special kinetic features of the uncatalysed oxidations of malonic and oxalic acids by vanadium(v) disappear, *i.e.*, the [V^V]² term in the malonic acid oxidation¹ and the [oxalic acid]² term in the oxalic acid oxidation.⁶

For both reactions the slow oxidative process may involve the transfer of an electron to vanadium(v) from a chelate compound of manganese(II), followed by a much faster breakdown of the manganese(III) complex, for this never attains a spectroscopically detectable concentration. For the sequence

⁵ Littler, *J.*, 1962, 832.⁶ Jones and Waters, *J.*, 1961, 4757.

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the steady-state concentration of the species $(\text{Mn}^{\text{III}}, \text{L})$, *i.e.*,

$$k_1[\text{V}^{\text{V}}][\text{Mn}^{\text{II}}, \text{L}]/(k_2 + k_{-1}[\text{V}^{\text{IV}}]) \text{ is minute if } k_2 \gg k_1$$

Also
$$+d[\text{V}^{\text{IV}}]/dt = k_1[\text{V}^{\text{V}}][\text{Mn}^{\text{II}}, \text{L}] \times 1/(1 + k_{-1}/k_2[\text{V}^{\text{IV}}])$$

which accords with our kinetic findings, and can explain why the apparent activation energy for the catalysed oxidation of oxalic acid (4.7 kcal. mole⁻¹) is much less than that for the direct reaction between manganese(III) and oxalic acid (18.3 kcal. mole⁻¹).⁴

Catalysis by manganese(II) would of course reach an upper limit when the maximum concentration of complexed ion has been formed. The maximum reached in the oxidation of oxalic acid (Fig. 3) might be explained in this way.

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