Stages in Oxidations of Organic Compounds by Potassium Permanganate. Part V. Oxidations of Some α-Hydroxy-acids by Manganic Pyrophosphate.*

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Oxidation of α-hydroxy-acids by manganic pyrophosphate involves the reversible formation of a cyclic complex which then breaks down with loss of carbon dioxide and formation of a free radical. Further extensive oxidation follows, tartaric and malic acids being degraded to carbon dioxide and formic acid.

Manganous ions retard the rate of oxidation.

THE kinetic investigations described by Drummond and Waters (Parts III and IV *) have now been extended to the manganic pyrophosphate oxidations of simple α-hydroxy-acids. Whilst (+)-tartaric, *meso*tartaric, and DL-malic acids have been studied more particularly, racemic, lactic, and glycollic acids have been examined sufficiently to show that they are oxidised by the same mechanism, and it has been shown that β-hydroxybutyric acid is hardly attacked.

In many respects the oxidations of tartaric and malic acids resemble that of pinacol (Part III), though the nature of its oxidation products and the absence of a comparable oxidation with dimethyl tartrate clearly show that tartaric acid does not behave merely

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* Parts III and IV, *J.*, 1953, 3119; 1954, 2456.

as a 1 : 2-glycol. The initial reactions are strictly of first order with respect to [Mn^{III}] (Table 2), and the variation of rate with respect to acid concentration can be expressed as $-\text{d}[\text{Mn}^{\text{III}}]/\text{d}t = k[\text{Acid}]/(a + [\text{Acid}])$ (Figs. 1 and 2; Tables 3—5). Again the oxidation rate is retarded to about half its value by the addition of vinyl cyanide, which polymerises. The free radicals which are formed can reduce mercuric chloride but do not combine with oxygen or promote oxidation of ethanol or *iso*propanol (contrast the oxidation of malonic acid; Part IV). However the rates of oxidation of the α-hydroxy-acids are retarded by the addition of manganous sulphate, according to the equation $1/(\text{d}[\text{Mn}^{\text{III}}]/\text{d}t) = k(1 + b)/[\text{Mn}^{\text{II}}]$ (Tables 6 and 7), though the extent of this retardation does not reach an upper limit, as noticed in the oxidation of pyruvic acid (Part VI, in the press).

In all cases the evolution of carbon dioxide sets in immediately and continues at a steady rate as the oxidation proceeds. This evolution of gas is not entirely eliminated by the addition of vinyl cyanide and consequently some carbon dioxide must be formed by the initial oxidation step. When oxidation is prolonged in the presence of an excess of manganic pyrophosphate very extensive oxidation occurs. Carbon dioxide and formic acid are formed from both tartaric and malic acid in amounts approximating to the equations :

FIG. 1.

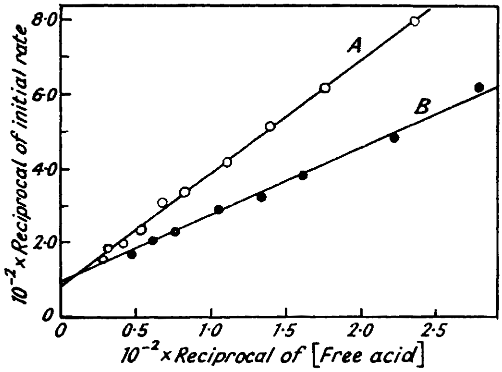


FIG. 2.

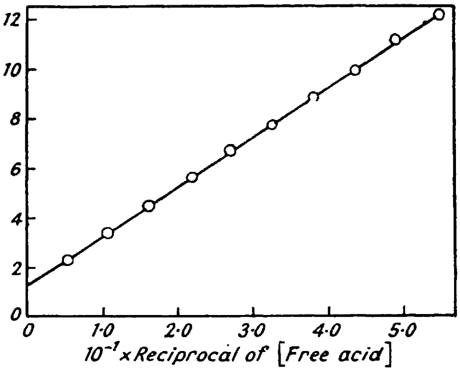


FIG. 1. *Oxidations of* (+)- *and of* meso-*tartaric acid.*

Reciprocal rate relations between oxidation rate and concentration of *free* organic acid. Initial [Mn^{II}], $4{\cdot}9 \times 10^{-3}$M; [Pyrophosphate], 0·29M. Temp., 35°; pH, 1·9.

Line A. (+)-*Tartaric acid* : *initial* [Mn^{III}], $1{\cdot}9 \times 10^{-2}$M.
Line B. meso*Tartaric acid* : *initial* [Mn^{III}], $1{\cdot}82 \times 10^{-2}$M.

FIG. 2. *Oxidation of* DL-*malic acid.*

Reciprocal rate relation between oxidation rate and concentration of *free* malic acid. Initial [Mn^{II}], $4{\cdot}9 \times 10^{-3}$M; initial [Mn^{III}], $1{\cdot}80 \times 10^{-2}$M; [Pyrophosphate], 0·29M. Temp. 35°; pH, 1·9.

$$\text{HO}_2\text{C}{\cdot}[\text{CH(OH)}]_2{\cdot}\text{CO}_2\text{H} + 8\text{Mn}^{\text{III}} + 2\text{H}_2\text{O} = 3\text{CO}_2 + \text{H}{\cdot}\text{CO}_2\text{H} + 8\text{Mn}^{\text{II}} + 8\text{H}^+$$

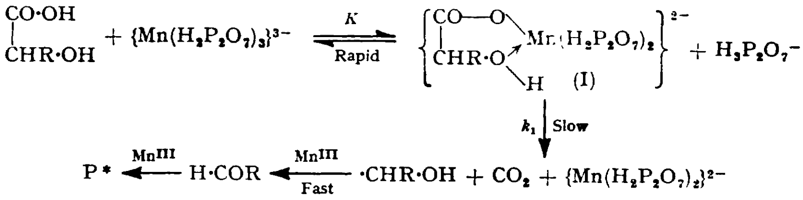
(Found : 7·7 equiv. of Mn^{III}; ratio $\text{CO}_2/\text{Mn}^{\text{III}} = 3/7{\cdot}3$)

$$\text{HO}_2\text{C}{\cdot}\text{CH(OH)}{\cdot}\text{CH}_2{\cdot}\text{CO}_2\text{H} + 10\text{Mn}^{\text{III}} + 3\text{H}_2\text{O} = 3\text{CO}_2 + \text{H}{\cdot}\text{CO}_2\text{H} + 10\text{Mn}^{\text{II}} + 10\text{H}^+$$

(Found : ratio $\text{CO}_2/\text{Mn}^{\text{III}} = 3/8{\cdot}9$)

whilst lactic acid consumes 7·1 equivalents of Mn^{III} per mole and so is not converted, *via* pyruvic acid, just into carbon dioxide and acetic acid (4 equiv. of Mn^{III}).

Except for the retardation due to manganous ions the kinetics of the oxidations of these α-hydroxy-acids are sufficiently similar to that of pinacol (*loc. cit.*) to indicate that a similar mechanism involving the fast, initial, reversible formation of a chelated manganic complex is involved, and indeed with tartaric acid the immediate change in colour of the solution at pH 1—2 (pink ⟶ brown) clearly shows the occurrence of this complex formation. The general oxidation scheme is therefore considered to be as annexed.



From tartaric acid the final oxidation probably has the sequence :

$$HO_2C{\cdot}CH(OH){\cdot}CHO \longrightarrow HO{\cdot}CH(CO_2H)_2 \longrightarrow 2CO_2 + H{\cdot}CO_2H \quad \text{(cf. Part IV)}$$

and from malic acid :

$$HO_2C{\cdot}CH_2{\cdot}CHO \longrightarrow HO_2C{\cdot}CH(OH){\cdot}CHO \longrightarrow 2CO_2 + H{\cdot}CO_2H$$

For the initial rate of oxidation the above scheme would lead to the rate equation below, which satisfies the appropriate kinetic measurements,

$$\frac{1}{-\,\mathrm{d}[\mathrm{Mn^{III}}]/\mathrm{d}t} = \frac{1}{nk_1[\mathrm{Mn^{III}}]}\left(\frac{[(H_2P_2O_7)^{-2}]}{K[\mathrm{Acid}]} + 1\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

where $[\mathrm{Mn^{III}}]$ = total manganic salt taken (moles), n = number of equivalents of $\mathrm{Mn^{III}}$ consumed rapidly per mole of hydroxy-acid (>2), [Acid] = concentration of *free* hydroxy-acid (moles), and $[H_2P_2O_7]$ = concentration of pyrophosphate *not* involved in complex formation (the salt is always present in large excess). The reaction scheme, and its derived equation (*A*), need modification however to account for the retarding action of added manganous salt. A possible explanation of this is the reversible formation of an organomanganous salt complex which reduces the amount of free acid in the solution, *i.e.* :

$$R{\cdot}CH(OH){\cdot}CO_2H + \{Mn(H_2P_2O_7)\}^{2-} \overset{K'}{\rightleftharpoons} \{Mn^{II}(HO{\cdot}CHR{\cdot}CO_2),(H_2P_2O_7)\}^{-} + (H_3P_2O_7)^{-}$$

(compare the formation of copper tartrate) ; for, provided that the equilibrium constant (K') for this reaction is small the addition of the manganous salt should reduce the amount of free hydroxy-acid in proportion to $1/(1 + K'[\mathrm{Mn^{II}}])$.

Postulation that the initial oxidation step [manganic complex (I) ⟶ radical, R·CH(OH)•] may be reversible does not accord with the experimental observations. In the first place the kinetics of the oxidations of α-hydroxy-acids are not at all similar to those for malonic acid (Part IV), as the oxidation rate is decreased rather than increased by addition of vinyl cyanide, and in the second place the free radical formed has reducing, and not oxidising, properties.

By the use of equation (*A*) the values of $K/[H_2P_2O_7]$ in Table 1, indicative of the equilibrium constant for the formation of the manganic complex (I), and of nk_1, indicative of its rate of degradation, have been computed from the results shown in Figs. 1 and 2.

TABLE 1. *Oxidations of α-hydroxy-acids with manganic pyrophosphate.*

Temp., 35°; pH, 1·9; total pyrophosphate = 0·29M. Initial $[\mathrm{Mn^{II}}] = 4{\cdot}9 \times 10^{-3}$M.

Acid	$K/[(H_2P_2O_7)]$ (M^{-1})	nk_1 (hr.$^{-1}$)
(+)-Tartaric	23	6·8
*meso*Tartaric	49	6·4
dl-Malic	6·3	4·4

Racemic acid was oxidised at exactly the same rate as (+)-tartaric acid. It can be seen that though *meso*tartaric acid is oxidised about twice as fast as (+)-tartaric acid almost the whole difference can be ascribed to the different equilibrium constant for the complex formation, whilst malic acid, which has one potential chelating group only, combines with $\mathrm{Mn^{III}}$ to much less than half the extent of the tartaric acids.

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* P = Products of aldehyde oxidation (cf. *J.*, 1953, 440).

TABLE 2. *Variation of initial oxidation rate with initial* [Mn^{III}].

Initial [acid], 1·90 × 10^{-2}M; initial [Mn^{II}], 4·9 × 10^{-3}M; 35°.

(+)-Tartaric acid [Pyrophosphate], 0·29M pH, 1·9			DL-Malic acid [Pyrophosphate], 0·197M pH 1·6		
[Mn^{III}] (10^{-3} mole l.$^{-1}$)	Init. Rate (10^{-3} mole l.$^{-1}$ hr.$^{-1}$)	$\frac{\text{Init. Rate}}{\text{Init. [Mn}^{III}]}$ (× 10)	[Mn^{III}] (10^{-3} mole l.$^{-1}$)	Init. Rate (10^{-3} mole l.$^{-1}$ hr.$^{-1}$)	$\frac{\text{Init. Rate}}{\text{Init. [Mn}^{III}]}$ (× 10)
18·6	4·30	2·32	18·0	1·07	59·4
17·3	3·94	2·28	16·8	0·961	57·2
16·1	3·85	2·39	15·6	0·908	58·2
14·9	3·39	2·33	14·4	0·846	58·7
13·6	3·24	2·38	13·2	0·772	58·5
8·7	3·15	2·53	12·0	0·708	59·0
6·2	1·37	2·21	10·8	0·656	60·7
3·7	0·77	2·08	4·8	0·283	59·0

TABLE 3. *Data for the calculated results shown in Fig. 1A. Oxidation of (+)-tartaric acid.* pH, 1·9; *Temp.* 35°.

Initial concns.: [Mn^{III}] 1·90 × 10^{-2}M; [Mn^{II}], 4·9 × 10^{-3}M; [Pyrophosphate], 0·29M.

Init. total acid (10^{-2} mole l.$^{-1}$)	Free acid (calc.) (10^{-2} mole l.$^{-1}$)	Init. rate [10^{-3} mole (Mn^{III}) l.$^{-1}$ hr.$^{-1}$]	1/(10^2. Rate)	1/[10^2 (Free acid)]
4·95	4·03	6·45	1·55	0·248
3·96	3·15	5·41	1·85	0·317
3·07	2·39	4·98	2·01	0·418
2·47	1·89	4·23	2·36	0·530
1·98	1·49	3·28	3·10	0·671
1·64	1·22	2·99	3·34	0·822
1·24	0·91	2·39	4·19	1·104
0·99	0·72	1·95	5·13	1·397
0·79	0·57	1·63	6·15	1·761
0·59	0·42	1·25	7·97	2·364

TABLE 4. *Data for the calculated results shown in Fig. 1B. Oxidation of* meso*tartaric acid.* pH, 1·9; *temp.*, 35°.

Initial concns.: [Mn^{III}], 1·82 × 10^{-2}M; [Mn^{II}], 4·9 × 10^{-3}M; [Pyrophosphate], 0·29M.

Init. total acid (10^{-2} mole l.$^{-1}$)	Free acid (calc.) (10^{-2} mole l.$^{-1}$)	Init. rate [10^{-3} mole (Mn^{III}) l.$^{-1}$ hr.$^{-1}$]	1/(10^2. Rate)	1/[10^2 (Free acid)]
2·98	2·12	5·74	1·74	0·47
2·38	1·64	4·88	2·05	0·61
1·96	1·32	4·31	2·32	0·76
1·49	0·96	3·44	2·91	1·04
1·19	0·75	3·08	3·25	1·33
0·99	0·62	2·62	3·82	1·61
0·74	0·45	2·08	4·82	2·22
0·59	0·36	1·62	6·17	2·78

TABLE 5. *Data for the calculated results shown in Fig. 2. Oxidation of* DL-*malic acid.* pH, 1·9; *temp.* 35°.

Initial concns.: [Mn^{III}], 1·80 × 10^{-2}M; [Mn^{II}], 4·9 × 10^{-3}M; [Pyrophosphate], 0·29M.

Init. total acid (10^{-2} mole l.$^{-1}$)	Free acid (calc.) (10^{-2} mole l.$^{-1}$)	Init. rate [10^{-3} mole (Mn^{III}) l.$^{-1}$ hr.$^{-1}$]	1/(10^2. Rate)	1/[10 (Free acid)]
20·00	19·05	4·35	2·3	0·53
10·00	9·36	2·94	3·4	1·07
6·67	6·19	2·22	4·5	1·62
5·00	4·70	1·79	5·6	2·20
4·00	3·68	1·49	6·7	2·71
3·33	3·07	1·30	7·7	3·26
2·86	2·61	1·14	8·8	3·82
2·50	2·29	1·02	9·9	4·37
2·22	2·04	0·90	11·1	4·90
2·00	1·83	0·83	12·1	5·47

TABLE 6. *Variation of initial rate with initial* [Mn^{II}] *for the oxidation of* (+)*-tartaric acid.* pH, 1·9; *temp.* 35°.

Initial concns.: [Mn^{III}], 1·90 × 10^{-2}M; [Pyrophosphate], 0·29M; [Tartaric acid], 9·50 × 10^{-3}M.

Init. [Mn^{II}] (10^{-3} mole l.$^{-1}$)	Init. rate [10^{-3} mole (Mn^{III}) l.$^{-1}$ hr.$^{-1}$)]	1/[10^{-2} (Init. rate)]	$\left(\frac{1}{\text{Rate}_e} - \frac{1}{\text{Rate}_0}\right) \cdot \frac{1}{10^4[\text{Mn}^{II}]}$
4·87	2·66	3·76	5·44
4·38	2·77	3·62	5·73
3·90	3·08	3·25	5·49
3·41	3·36	2·98	5·48
1·95	4·27	2·34	6·31
0·97	6·26	1·60	5·03
0·00	9·03	1·11	—

TABLE 7. *Variation of initial rate with initial* [Mn^{II}] *for the oxidation of* DL*-malic acid.* pH, 1·3; *temp.* 35°.

Initial concns.: [Mn^{III}], 1·60 × 10^{-2}M; [Pyrophosphate], 0·175M; [Malic acid], 3·12 × 10^{-2}M.

Init. [Mn^{II}] (10^{-3} mole l.$^{-1}$)	Init. rate [10^{-3} mole (Mn^{III}) l.$^{-1}$ hr.$^{-1}$)]	1/[10^{-2} (Init. rate)]	$\left(\frac{1}{\text{Rate}_e} - \frac{1}{\text{Rate}_0}\right) \cdot \frac{1}{10^4[\text{Mn}^{II}]}$
7·99	1·11	9·01	5·32
7·19	1·17	8·55	5·27
6·39	1·23	8·13	5·27
5·59	1·29	7·75	5·35
4·79	1·37	7·30	5·30
3·99	1·45	6·90	5·36
3·19	1·53	6·54	5·58
2·39	1·62	6·17	5·90
0·00	2·10	4·76	—

The first column of Tables 6 and 7 gives the amount of manganous sulphate added to each reaction mixture.

EXPERIMENTAL

Materials.—Calcium *meso*tartrate, prepared from (+)-tartaric acid (*Org. Synth.*, Coll. Vol. I, 2nd Edn., p. 497), was treated with a slight excess of 4N-sulphuric acid and after filtration the strength of the free *meso*tartaric acid in the solution (K_1 = 7·8 × 10^{-4}; K_2 = 1·6 × 10^{-5}) was determined by alkali-titration with, successively, methyl-red (pK 5·1) and thymol-blue (pK 1·7). Small amounts of calcium salts were shown to have no effect on the oxidation rates.

Racemic acid (*op. cit.*) was crystallised from water; DL-malic acid, m. p. 128—129°, was crystallised from ethyl acetate; solutions of (+)-tartaric acid and of lactic acid were prepared from " AnalaR " materials.

Measurements.—The volumetric measurements were carried out as described in Part III; carbon dioxide evolution was measured in Warburg respirometers, solutions saturated with carbon dioxide being used. The induced polymerisations of vinyl cyanide and the reductions of mercuric chloride were conducted in Thunberg tubes (see *J.*, 1953, 2836). The results are tabulated.

Oxidation Products.—The chromotropic acid reaction (Feigl, " Spot Tests," Elsevier, Amsterdam, 1947, p. 395) was used to establish the formation of formic acid from both tartaric and malic acid.

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