126. Oxidations of Organic Compounds with Quinquevalent Vanadium. Part VII.[1] The Kinetic Resemblance between the Oxidations of some α-Hydroxy-acids and that of Pinacol and of its Monomethyl Ether.

By J. R. Jones, William A. Waters, and (in part) J. S. Littler.

Lactic, malic, and mandelic acid are oxidised by vanadium(v) according to the reaction:

$$\mathrm{R{\cdot}CH(OH){\cdot}CO_2H + 2V^{V} \longrightarrow R{\cdot}CHO + H_2O + CO_2 + 2V^{IV}}$$

at a rate given by

$$-\mathrm{d}[\mathrm{V^V}]/\mathrm{d}t = k[\text{Hydroxy-acid}][\mathrm{V^V}](1 + ah_0)$$

where h_0 is the Hammett acidity function. This rate equation also holds for oxidation of pinacol in perchloric acid solutions of constant ionic strength, but the rate of oxidation of pinacol monomethyl ether depends on the acid concentration. The reason for this difference is discussed.

Levesley and Waters [2] showed that in many respects the oxidations of α-hydroxy-acids by manganic pyrophosphate resemble that of pinacol. We have now examined the oxidation of lactic, malic, and mandelic acid by quinquevalent vanadium in perchloric acid solution and again find that the oxidations involve C–C bond fission and are kinetically similar to that of pinacol. All three α-hydroxy-acids quickly consume 2 equivalents of vanadium(v), as required by the reaction:

$$\mathrm{R{\cdot}CH(OH){\cdot}CO_2H + 2V^{V} \longrightarrow R{\cdot}CHO + H_2O + CO_2 + 2V^{IV}}$$

and the aldehydic products are thereafter oxidised more gradually. Both lactic and malic acid yield some acetaldehyde, and mandelic acid gives benzaldehyde.

Kinetic measurements carried out in perchloric acid–sodium perchlorate mixtures of constant ionic strength are summarised in the Tables which follow. They show that the oxidations are all of first order with respect both to vanadium(v) and to the α-hydroxy-acid. In contrast to the oxidations effected by manganic pyrophosphate,[2,3] no kinetic evidence for initial complex formation between the vanadium and the α-hydroxy-acid could be discerned, but this is not surprising since oxidation of cyclohexanol [4] by vanadium(v), in which complex formation is involved, shows no deviation from first-order kinetics with respect to the alcohol. The addition of manganous ions had no effect on the rate of the reaction (cf. ref. 2).

The α-hydroxy-acids resemble pinacol in being oxidised by quinquevalent vanadium at a rate that can be expressed by equation (*A*)

$$-\mathrm{d}[\mathrm{V^V}]/\mathrm{d}t = k[\text{Substrate}][\text{Vanadium(v)}](1 + ah_0) \quad . \quad . \quad . \quad . \quad (A)$$

where h_0 is the appropriate value of the Hammett acidity function.

This type of acidity-dependence for the oxidation rate of pinacol was suggested by Littler and Waters [5] who however did not control the ionic strengths of their solutions and used sulphuric acid, which itself forms complexes with vanadium(v). Table 2(*d*) shows that the oxidation of pinacol in perchloric acid at constant ionic strength follows equation (*A*) but Table **3** shows that the rate of oxidation of pinacol monomethyl ether has dependence on the acidity concentration, $C_{\mathrm{H_3O^+}}$. Comparison of Table 1(*a*) with 1(*b*) and of Table 1(*c*) with 1(*d*) shows that the positive ionic-strength effect is considerable in

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[1] Part VI, *J.*, 1960, 2773.
[2] Levesley and Waters, *J.*, 1955, 217.
[3] Drummond and Waters, *J.*, 1953, 2836.
[4] Littler and Waters, *J.*, 1959, 4046.
[5] Littler and Waters, *J.*, 1959, 1299.

this type of oxidation. This accords with the view that the reacting species is a doubly charged cation (III).

TABLE 1. *Oxidation of α-hydroxy-acids by vanadium*(V): *reaction order with respect to the α-hydroxy-acid.*

(*a*) Lactic acid in 1·0N-perchloric acid; ionic strength, *S* = 3M.

Hydroxy-acid (N)	0·110	0·219	0·274	0·329	0·384	0·439
k (10^{-4} sec.$^{-1}$)	1·18	2·62	3·27	4·03	4·73	5·25
10^4k/[Acid]	10·8	11·1	12·2	12·3	12·3	12·0

(*b*) Lactic acid in 3·0N-perchloric acid; ionic strength *S* = 3M.

Hydroxy-acid (N)	0·086	0·161	0·240	0·320	0·400
k (10^{-4} sec.$^{-1}$)	3·77	7·60	11·1	15·8	19·0
10^4k/[Acid]	47·1	47·5	46·3	49·4	47·5

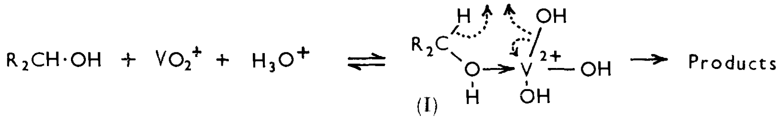
(*c*) Malic acid in 1·0N-perchloric acid; no added salt.

Hydroxy-acid (N)	0·078	0·156	0·233	0·311	0·389
k (10^{-4} sec.$^{-1}$)	1·05	2·17	3·30	4·53	5·60
10^4k/[Acid]	13·5	13·9	14·2	14·6	14·4

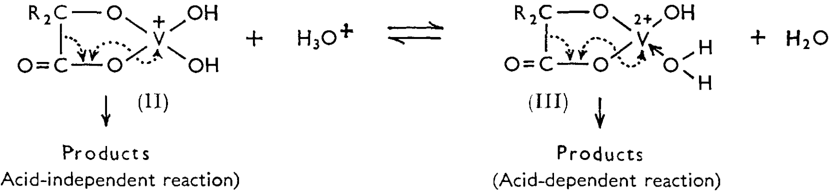
(*d*) Malic acid in 3·0N-perchloric acid; no added salt.

Hydroxy-acid (N)	0·078	0·156	0·233	0·311	0·389
k (10^{-4} sec.$^{-1}$)	4·22	10·0	14·4	19·5	24·0
10^4k/[Acid]	54·1	64·1	61·8	62·7	61·7

Now the oxidations of cyclohexanol and of those secondary α-glycols which are attacked at C–H bonds[6] have been found to be linearly dependent on hydrogen-ion concentration, $C_{H_3O^+}$, and not on the Hammett function, h_0. For the alcohol oxidation it has been suggested[4] that the reactive complex has a structure (I) in which both a monohydric alcohol molecule and a hydrated proton are co-ordinated to the VO_2^+ cation.



However, in the oxidation of both the pinacol and the α-hydroxy-acid the complexes (II) and (III), which can undergo C–C fission, need not contain an extra water molecule, for the protonated structure (III) postulated for the acid-catalysed reaction can be built up from VO_2^+, a substrate molecule, and a proton.



If this is so, Hammett's original theories[7] of the differing kinetic significance of h_0 and $C_{H_3O^+}$ satisfactorily explain why the rate of acid-dependent oxidation of hydroxy-acids and of pinacol follows h_0 rather than $[H_3O^+]$, and why the rate of oxidation of pinacol monomethyl ether follows $[H_3O^+]$ and not h_0, for the latter would form a complex of type (IV) (cf. I). This is in agreement with the stereochemical evidence of Part IV[8] and the kinetic data of Part V.[6]

We suggest that the reversible formation of complexes (II—IV) precedes the rate-determining, concerted electron redistribution which, in converting vanadium(V) into

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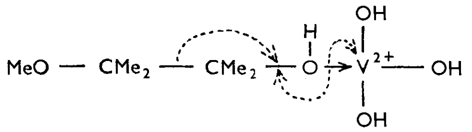
[6] Littler and Waters, *J.*, 1960, 2767.

[7] Hammett, " Physical Organic Chemistry," Chap. ix, McGraw-Hill Publ. Co., New York, 1940.

[8] Littler, Mallet, and Waters, *J.*, 1960, 2761.

vanadium(IV), effects C–C fission giving radicals, $R_2C(OH)\cdot$ or $R_2C(OMe)\cdot$, which are then rapidly oxidised further.



(IV)

In support of our view that α-hydroxy-acids form soluble complexes with quinquevalent vanadium we have observed that, though the gradual acidification of aqueous ammonium metavanadate with solutions of lactic, malic, acetic, and monochloroacetic acid leads in all cases to the separation of a brown precipitate (V_2O_5 polymer), the latter is easily soluble in an excess of each of the hydroxy-acids but is not dissolved by further aqueous acetic or monochloroacetic acid, though the latter has a pK_a similar to those of the hydroxy-acids. These solutions of vanadium(V) in an excess of lactic or malic acids do very slowly ($k \approx 0{\cdot}1 \times 10^{-4}$ sec.$^{-1}$ at 25°) reduce ammonium vanadate without the addition of any mineral acid: they could contain low concentrations of charged complexes (II).

EXPERIMENTAL AND RESULTS

Materials.—Lactic acid was of " AnalaR " grade; (±)-malic acid was crystallised from ethyl acetate to m. p. 128°, and (±)-mandelic acid from benzene to m. p. 118°. The concentrations of these acids in distilled water at the thermostat temperature were determined by titration with sodium hydroxide. Pinacol monomethyl ether (cf. Part V [6]) was purified by vapour-phase chromatography through Apiezon grease on Embacil at 100° and was obtained free from pinacol dimethyl ether.

Mixtures of " AnalaR " ammonium metavanadate, perchloric acid (Harrington's 60%, diluted to 8·0M), and sodium perchlorate (Hopkin and Williams, recrystallised grade, in 8·0M-solution) of constant ionic strength were warmed to 25° ± 0·1° in a thermostat and to these was added the aqueous hydroxy-acid. The titrimetric procedure was that of Parts I and II.[5,9] The oxidations of pinacol monomethyl ether were carried out (by J. S. L.) at 50° ± 0·1° and followed spectrophotometrically, as in Part V.[6]

TABLE 2. *Dependence of oxidation rate on acidity; ionic strength S = 5M.*

(*a*) Lactic acid (0·186M)

$HClO_4$		k (10^{-4} sec.$^{-1}$)	
(N)	h_0	Found	Calc.
0·5	12·9	2·42	2·37
1·0	28·2	3·30	3·77
1·5	47·9	5·8	5·56
2·0	69·2	7·3	7·50
2·5	100·0	10·5	10·3
3·0	138	13·8	13·8
4·0	282	25·7	26·9

Calc., $k = 1{\cdot}2 + 0{\cdot}091h_0$

(*b*) Malic acid (0·194M)

$HClO_4$		k (10^{-4} sec.$^{-1}$)	
(N)	h_0	Found	Calc.
0·5	12·9	3·17	3·11
1·0	28·2	4·58	4·77
1·8	60·3	8·05	8·3
2·6	105	13·5	13·1
3·4	186	21·2	21·0
3·8	246	28·3	28·5
4·6	427	51·7	48·2

Calc., $k = 1{\cdot}7 + 0{\cdot}109h_0$

(*c*) Mandelic acid (0·151M)

$HClO_4$		k (10^{-4} sec.$^{-1}$)	
(N)	h_0	Found	Calc.
0·5	12·9	57·0	56·9
0·7	19·0	60·8	60·6
1·0	28·2	67·5	66·2
1·4	42·7	75·5	75·1
1·8	60·3	83·3	85·8
2·2	79·4	98·2	97·5
2·6	105	109	113

Calc., $k = 49{\cdot}0 + 0{\cdot}611h_0$

Pinacol (0·125M)

$HClO_4$		k (10^{-4} sec.$^{-1}$)	
(N)	h_0	Found	Calc.
0·5	12·9	43·5	43·3
1·0	28·2	51·7	48·1
1·8	60·3	55·7	56·2
2·6	105	70·8	67·6
3·4	186	87·8	88·1
4·2	324	112	123
(5·0	589	165 ± 10	191)

Calc., $k = 41{\cdot}0 + 0{\cdot}253h_0$

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[9] Littler and Waters, *J.*, 1959, 3014.

In all oxidations the organic substrate was in large excess and the logarithmic plots of titre changes indicated a strict first-order decrease in vanadium(v) concentration for over 85% of the reaction: the initial concentration of vanadium(v) was 0·050N.

TABLE 3. *Oxidation of pinacol monomethyl ether* (0·111M) *at* 50°.

$HClO_4$ (N)	1·0	1·8	2·6	3·4	4·2	5·0
k (10^{-4} sec.$^{-1}$)	(1·52)	3·53	4·8	6·31	7·75	9·55
$10^4k/[H^+]$	(1·52)	1·96	1·85	1·86	1·85	1·91

Weighted mean value: $k = (1{\cdot}63 \pm 0{\cdot}02) \times 10^{-3} . [H_3O^+][\text{Ether}]$.

The values of h_0 cited in Table 2 were obtained from Paul and Long's review [10] and refer to mixtures of perchloric acid and sodium perchlorate of ionic strength $S = 6$. Values for $S = 5$ are not available but should be directly proportional to those given, except possibly in 5M-perchloric acid to which no sodium perchlorate had been added.

Stoicheiometry and Oxidation Products.—Lactic, malic, and mandelic acids all consumed 2 equivalents of vanadium(v) within a few hours in 2M-sulphuric acid at 25°, but the oxidation continued slowly thereafter. After a week the equivalents of vanadium(v) consumed were: lactic acid 4·75; malic acid 3·84; mandelic acid 2·60 (increasing to 2·9 after 1 month). West and Skoog [11] found that mandelic acid consumed up to 3·9 mols. of vanadium(v) at higher concentrations of sulphuric acid.

Oxidised solutions of lactic and malic acid were shown to contain acetaldehyde by isolating the latter as its dimedone derivative, m. p. and mixed m. p. 139°. After prolonged oxidation, lactic acid solutions also gave a positive chromotropic acid test for formic acid. Mandelic acid solutions, on oxidation, soon smelt of benzaldehyde; this was characterised as its 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 235°.

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[10] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.
[11] West and Skoog, *Analyt. Chem.*, 1959, **31**, 583.