A Kinetic Study of the Oxidation of Lactic Acid by Vanadium (V)

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The kinetics of oxidation of lactic acid by quinquevalent vanadium is found to be of first order with respect to both vanadium(v) and lactic acid. The Arrhenius equation is found to be valid for the reaction between 25° and 35°. The values for the energy of activation, entropy of activation, and frequency factor are found to be 16·4 kcal., -13.70 cal./MA°, and 6.687 × 10⁹ sec⁻¹ respectively. These experimental findings are consistent with the postulate that the rate-determining step in the reaction involves the first order disproportionation of a co-ordination complex between lactic acid and vanadium(v), affording products through free-radical formation.

A review of the existing literature reveals that the kinetics of oxidation of α-hydroxy acids by quinquevalent vanadium has been almost neglected, though West and Skoog[1] have shown that lactic acid is quantitatively oxidised by acidic vanadium(v) solution. The present investigation is therefore undertaken to elucidate the kinetics of lactic acid oxidation by vanadium(v).

EXPERIMENTAL

The chemicals used were either of AnalaR or E. Merck's G.R. quality. Equal volumes (50 ml) of ammonium metavanadate (in aq. H_2SO_4) and lactic acid solutions, both of known concentrations, were brought to the temperature of the thermostat and then mixed. The course of the reaction was followed by withdrawing 10-ml portions of the reaction mixture at definite intervals of time, chilling by ice to check the reaction, and by estimating the amount of the unchanged oxidant volumetrically by a standard Mohr's salt solution, using 3 to 5 drops of 0.066M N-phenylanthranilic acid[1] as an indicator. The requisite quantity of sodium sulphate was added to acidic vanadium (v) solution to maintain the ionic strength of the solution constant.

DISCUSSION

The reaction follows a simple kinetic order provided that the molar concentration of vanadium(v) in the given concentration of H_2SO_4 (in which the active species of vanadic acid[2,3] is well known) is not greater than that of lactic acid.

1. *Anal. Chem.*, 1959, **31**, 583.
2. Lasdle and Cobble, *J. Phys. Chem.*, 1955, **59**, 519.
3. Rossotti and Rossotti, *Acta Chem. Scand.*, 1956, **10**, 957.

The reaction has been found to be of first order with respect to vanadium(v). The values of the first-order rate constant at different lactic acid concentrations and temperatures are recorded in Table I

TABLE I

$$[V^v] = 0.01 M. \quad [H_2SO_4] = 0.5 M$$

Lactic acid.	$10^4 k_1$ sec^{-1} at		
	25°.	30°.	35°.
0.5000 M	3.44	5.07	9.00
0.2500	1.88	3.23	4.31
0.1250	1.05	1.21	2.26
0.0625	0.48	0.79	1.32

That the reaction is also of first order with respect to lactic acid is shown by the fairly constant values of the quotients obtained when k_1 is divided by lactic acid concentration.

TABLE II

Constancy of the quotient k_1/[lactic acid] at 35°.

$$[V^v] = 0.01 M. \quad [H_2SO_4] = 0.5 M.$$

[Lactic acid] (M)	..	0.500	0.250	0.125	0.062
$10^4 k_1$ sec^{-1}	..	· 9.000	4.310	2.260	1.320
k_1/[acid]	..	0.018	0.017	0.018	0.020

Thus the total order of the reaction comes out to 2 (unity with respect to each reactant). Fairly constant values are obtained for the second order rate constant when the reactants are taken in equimolar quantities, as shown in Table III.

TABLE III

[Lactic acid] $= .01 M.$ Other conditions same as in Table II.

Time (sec.)	..	0	900	5400	9000	10,980	12,780
$(a-x)$ (ml)	..	9.4	9.2	8.5	8.0	7.7	7.3
x (ml)	..	0.0	0.2	0.9	1.4	1.7	2.1
$k_2 \times 10^6$ (litre mole^{-1} sec^{-1})	..	..	2.57	2.09	2.07	2.14	2.40

Average $10^6 k_2 = 2.25$ litre mole^{-1} sec^{-1}.

The rate of the reaction is found to vary with hydrogen-ion concentration, as is evident from Table IV.

TABLE IV

$$10^2 (V^v) = 0.89 M. \quad [\text{Lactic acid}] = 0.25 M. \quad \text{Temp.} = 35°.$$

(H$^+$) (mole litre)	..	0.25	0.50	0.75	1.00
$10^4 k_1$ sec^{-1}	..	4.80	7.40	10.05	12.70

It is observed that in the given range of the concentration of H_2SO_4, the reaction is independent of bisulphate-ion concentration, so that there seems no probability of formation of sulphato complexes of vanadium.

No primary salt effect has been observed on the reaction velocity by addition of ammonium sulphate, sodium sulphate, and ammonium chloride, as shown in Table V

TABLE V

Effect of neutral salts on the reaction velocity.

10^3 [V^v] = 6.66M. 10 [Lactic acid]=1.666M. 10 [H_2SO_4] = 3.33M. Temp.=35°.

Salt conc.	10 k_1 sec^{-1}.		
	*Am. sulphate.	Am. chloride.	Sodium sulphate.
0.0000M •	4.62	4.62	4.62
0.0333	4.53	4.75	4.67
0.0166	4.64	4.67	4.47

The Arrhenius equation is found to be valid between 25° and 35°. The values for the energy of activation, frequency factor, and entropy of activation are found to be 16.4 kcal., 6.687×10^9 sec^{-1}, and -13.70 cal./MA°.

An important fact is revealed by the negative entropy of activation[4] and frequency factor of the order less than 10^{10} sec^{-1}, which, besides unimolecular nature of the reaction, clearly indicate some stable activated complex formation and also suggest that the free radical is involved in the reaction mechanism.

The variation of rate with respect to lactic acid concentration can also be expressed as:

$$\frac{-d[V^v]}{dt} = \frac{k' K [Acid] [V^v]}{1 + K [Acid]}$$

where K and k' are the equilibrium and decomposition constants for the formation and decomposition of the intermediate, respectively (showing that the equilibrium is in favour of the intermediate complex). Their values are obtained by the linear relationship observed by the plot of the reciprocal of rate constant against the reciprocal of lactic acid concentration. The solpe of the curve provides the value of $1/K$ as 0.055.

For complete oxidation (carried out at about 60°) 1 mM of lactic acid has been found to consume nearly 4 m.e. of vanadate, corresponding to the formation of equimolar amounts of acetic acid and carbon dioxide:

$$CH_3CH(OH)COOH + 4VO_2^+ + 4H^+ = CH_3COOH + CO_2 + 4VO^{2+} + 3H_2O.$$
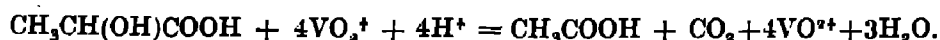
That the oxidation of lactic acid[5,6] involves formation of free radical has been confirmed by the polymerisation and mercuric chloride reduction test[7].

4. Glasstone, "Text Book of Physical Chemistry", Macmillan and Co., Ltd., London, 2nd ed., 1960, p. 1110.
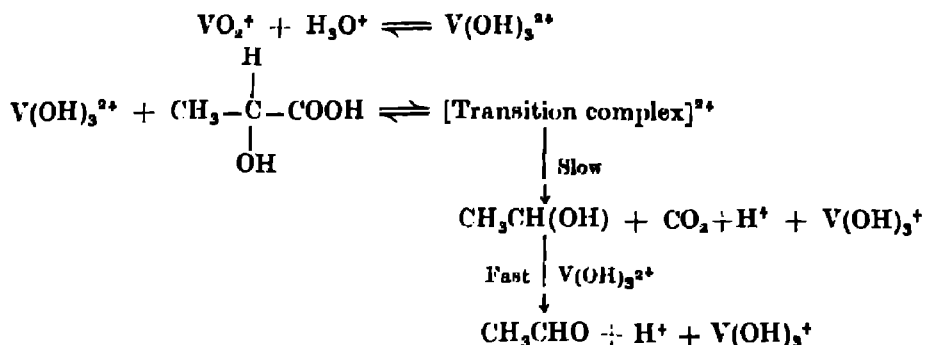5. Lovesley and Waters, J. Chem. Soc., 1955, 217.
6. Littler and Waters, ibid., 1950, 1299.
7. Drummond and Waters, ibid., 1953, 2836.

Table IV shows that the rate of the reaction varies with H^+-ion concentration. It has also been observed that the second order rate constant depends on H^+-ion concentration. So it leads to the conclusion that the pervanadyl ion as such is not involved in the rate-determining step. It seems probable therefore that ionic species of pentavalent vanadium, formed by the reaction of pervandyl ion with H^+ ion, is involved.

Further, the complex formation of monohydric alcohols[8] with trihydroxy pervanadyl ion (in acid medium) and also of lactic acid by vanadic acid[9] lead to the same conclusion.

The foregoing information therefore suggests the following reaction mechanism:

$$VO_2^+ + H_3O^+ \rightleftharpoons V(OH)_3^{2+}$$

$$V(OH)_3^{2+} + CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-COOH \rightleftharpoons [Transition\ complex]^{2+}$$

$$\downarrow Slow$$

$$CH_3CH(OH) + CO_2 + H^+ + V(OH)_3^+$$

$$Fast \downarrow V(OH)_3^{2+}$$

$$CH_3CHO + H^+ + V(OH)_3^+$$

The presence of acetaldehyde in the reaction mixture was confirmed by the usual tests. It has already been shown that lactic acid on complete oxidation furnishes acetic acid through the intermediate formation of acetaldehyde.

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8. Littler and Waters, *J. Chem. Soc.*, 1959, 4046.
9. Mullick *et al.*, this *Journal*, 1963, 40, 137.