Oxidation of Malic Acid by Vanadium(V) in Sulphuric Acid Medium: A Kinetic and Mechanistic Investigation

CLAUDIO MARCOS ZIGLIO and KEIKO TAKASHIMA*

Departamento de Química, Universidade Estadual de Londrina, caixa postal 6001, 86051–970, Londrina, PR, Brazil

Abstract

The oxidation kinetics of malic acid by vanadium(V) in aqueous sulphuric acid was investigated at 303 K by monitoring the appearance of vanadium(IV) at 760 nm. The reaction showed first-order behavior with respect to vanadium(V), malic acid, and hydrogen ion concentration, respectively, regardless of the ionic strength. The reaction rate is enhanced by an increase in ionic strength and a decrease of the dielectric constant of the medium by addition of methanol. The activation parameters were estimated by varying the temperature in the range of 293 K to 313 K. An oxidation mechanism is proposed, involving different vanadium(V) species produced in the presence of sulphuric acid. © 1995 John Wiley & Sons, Inc.

Introduction

The oxidation kinetics of hydroxyacids by different oxidants [1-5] has been extensively studied. The oxidation mechanism of α -hydroxyacids, a bifunctional compound, by vanadium(V) may occur through two general routes: as alcohols [6], or undergoing oxidative decarboxilation [7]. Nevertheless, relatively few studies have concerned themselves with the nature of the oxidizing species in these systems. In the present study, we report the oxidation rate of malic acid by vanadium(V) in sulphuric acid under variable and constant ionic strength conditions. The active oxidizing species of vanadium(V) are also postulated by comparison with the results obtained in perchloric acid [8].

In our previous study, the oxidation rate of malic acid was shown to display fractionary dependence on the hydrogen ion concentration while the variation of the ionic strength, by the addition of sodium perchlorate solution, had essentially no effect on the rate. On the other hand, in the present case, the reaction rate is observed to be enhanced in a sulphuric acid solution, with no control of ionic strength or with ionic strength control. It is also shown that within experimental error the reaction steps obey first-order kinetics with respect to the hydrogen ion concentration, indicating that a different mechanism is operative in this medium involving the participation of other active species of vanadium(V).

^{*}To whom correspondence should be addressed.

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Experimental

Materials

The solution of vanadium(V), V(V), was prepared by dissolving ammonium metavanadate, NH₄VO₃ (Merck, p.a.) in an appropriate amount of sulphuric acid, as described previously [8,9]. The ionic strength was controlled by the addition of a concentrated sodium bisulphate (Reagen, p.a.) solution. The malic acid, HMA, (Sigma, purity >98%) was used without further purification. All the solutions were prepared with deionized water just before the experiment, and all other reagents were of analytical grade.

Kinetic Procedure

The kinetic measurements were performed, by automatic acquisition (Microquímica, MQI12/8PCC) monitoring the appearance of vanadium(IV), V(IV), as vanadyl ion at 760 nm using a Varian spectrophotometer model DMS-80, with a 1.0 cm pathlength cell and provided with a cuvette holder thermostated at 303.0 K (±0.1 K). These reactions were investigated under pseudo-first-order conditions maintaining a large excess of malic acid over V(V), and following them during four or five half-lives. The pseudo-first-order rate constants, k_{obs} , were calculated from the slopes of the linear plots (correlation coefficient, r > 0,9970, standard deviation, $s \leq 3.79 \times 10^{-4}$) of $\ln[V(V)]$ against time, and were reproducible within $\pm 5\%$ of each other. The linearity of these plots indicates that any product formed during the reaction does not interfere in the rate. The pseudo-first-order rate constant calculation was carried out using a personal computer coupled to the spectrophotometer. The measurements were carried out in duplicates and, when necessary, in triplicates.

Reaction Stoichiometry and Product Analysis

A reaction mixture of 3.0 ml containing an excess of V(V) (0.20 moles) over HMA $(2.0 \times 10^{-3} \text{ moles})$ in acidic medium (2.5 mol dm⁻³) was thermostated at 313 K. The CO₂ evolved using six hours of reaction time was measured by using a Warburg respirometer (B. Braun, model V-85). The residual amount of the oxidant showed that 1.0 mol of HMA liberated 2.0 (± 0.2) moles of CO₂.

The reaction mixture was allowed to stand at room temperature for several hours under the conditions normally used for kinetic measurements in order to determine the other products. The presence of aldehyde and/or ketone was characterized by reaction with 2,4-dinitrophenylhydrazine [10]. The differentiation was carried out through the use of Tollens reagent [10]. The reaction was positive for aldehyde. The absence of formaldehyde was tested using chromotropic acid [11]. The presence of acetaldehyde was deduced from the formation of 2.0 moles of carbon dioxide. The overall reaction for malic acid oxidation may be represented by the following equation

 $HOOCCH_2CH(OH)COOH + 2V(V) \longrightarrow CH_3COH + 2CO_2 + 2V(IV)$

Free Radical Test

The reaction between V(V) and HMA was carried out under kinetic conditions in the presence of recrystallized acrylamide solution (25%). When the reaction mixture was allowed to stand for several hours, a viscous solution was obtained. Control reactions in which either V(V) or HMA were excluded demonstrated the absence of polymerization.

Results

Effect of Reactants Concentration

The oxidation rate increases with an increase of the excess malic acid concentration, [HMA], while maintaining constant the initial concentrations of V(V), [V(V)]₀, and sulphuric acid, [H₂SO₄]₀, as shown in the Table I (r > 0.9972 and $s \le 2.87 \times 10^{-4}$) whether the reaction is carried out at constant ionic strength or with no control over the ionic strength. Individual plots of $\ln[V(V)]$ as a function of time for different initial concentrations of malic acid, [HMA]₀, show excellent linearity (r > 0.9970 and $s \le 3.79 \times 10^{-4}$). The order with respect to [HMA] is approximately 1 and it was determined from the slope of the linear plot of $\ln k_{obs}$ against $\ln [HMA]_0$ (r > 0.9978 and $s \le 0.0367$). The variation of [V(V)]₀ from 0.005 to 0.025 mol dm⁻³ increased the rate constant by about 35% (r = 0.9962 and $s = 5.74 \times 10^{-4}$) in solutions with no control of ionic strength, and by about 38% (r = 0.9949 and $s = 1.2 \times 10^{-4}$) at constant ionic strength as indicated in Table II.

TABLE 1.	Pseudo-first-order rate constants for th	ne oxidation of	malic acid	by $V(V)$ with	n no control (of ionic
strength,	and at constant ionic strength.* [V(V)]	$= 1.00 \times 10^{-2}$	mol dm ⁻³ ,	$[H_2SO_4] = 1$	1.00 mol dm	⁻³ , and
T = 303]	К.					

$I/ \text{ mol } \text{dm}^{-3}$	[HMA]/mol dm ⁻³	$k_{ m obs}/10^{-3}~{ m s}^{-1}$
a	0.50	2.60
a	0.75	3.68
а	1.00	4.70
а	1.25	5.64
a	1.50	6.43
2.00	0.50	3.52
2.00	0.75	5.85
2.00	1.00	7.43
2.00	1.25	9.60
2.00	1.50	12.17

*Constant ionic strength was achieved by using NaHSO₄ as an added electrolyte.

^a The initial ionic strength is $1.00 \text{ mol } \text{dm}^{-3}$, but changes in the course of the reaction.

$I/ \text{ mol } dm^{-3}$	$[V(V)]/10^{-2} \text{ mol } dm^{-3}$	$k_{ m obs}/10^{-3}~{ m s}^{-1}$
a	0.50	4.26
а	1.00	4.70
a	1.50	4.96
а	2.00	5.30
a	2.50	5.75
2.00	0.50	6.75
2.00	1.00	7.43
2.00	1.50	7.85
2.00	2.00	8.77
2.00	2.50	9.32

TABLE II. Pseudo-first-order rate constants for the reduction of vanadium(V) at 303 K with no control of ionic strength, and at constant ionic strength.* [HMA] = 1.00 mol dm⁻³, [H₂SO₄] = 1.00 mol dm⁻³.

*Constant ionic strength was achieved by using NaHSO₄ as an added electrolyte.

^a There is a small variation in the initial ionic strength due to the initial [V(V)], which changes in the course of the reaction.

Effect of Hydrogen Ion Concentration

An enhancement in the oxidation rate was observed with an increase of the hydrogen ion concentration, $[H^+]$, through the addition of sulphuric acid, maintaining the same initial reactants concentrations. The pseudo-first-order rate constants at 303 K, with no control of ionic strength and at constant ionic strength, are presented in Table III. The reaction order with respect to the hydrogen ion concentration was estimated from the plot of $\ln k_{obs}$ against $\ln [H^+]$, derived from $[H_2SO_4]$. The reaction order for both the variations was approximately 1 (r > 0.9911 and $s \le 0.026$).

Effect of Ionic Strength

The ionic strength was changed through the addition of a concentrated solution of sodium bisulphate (5.0 mol dm⁻³) in the reactant solution. The pseudo-first-order rate constant increased more than two-fold in the range of 1.25 to 2.75 mol dm⁻³ (Table IV). The plot of log k_{obs} as a function of the square root of the ionic strength at 303 K gives a product of ionic charges, z_+z_- of 0.73 (r = 0.9921 and s = 0.020).

$I/ \text{ mol } dm^{-3}$	$[\mathrm{H_2SO_4}]/\mathrm{mol}~\mathrm{dm}^{-3}$	$k_{ m obs}/10^{-3}~{ m s}^{-1}$
0.51	0.50	2.68
0.76	0.75	3.66
1.01	1.00	4.70
1.26	1.25	5.98
1.51	1.50	7.60
2.00	0.50	4.35
2.00	0.75	5.82
2.00	1.00	7.43
2.00	1.25	9.05
2.00	1.50	11.90

TABLE III. Effect of the sulphuric acid concentration on the pseudo-first-order rate constants at 303 K with no control of ionic strength, and at constant ionic strength. $[V(V)] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ and $[HMA] = 1.0 \text{ mol dm}^{-3}$.

 $k_{\rm obs}/10^{-3}~{
m s}^{-1}$ $I/ \text{ mol } \text{dm}^{-3}$ 1.254.561.506.071.756.43 2.007.432.258.76 2.5010.482.7511.73

TABLE IV. Effect of the ionic strength^{*} on the pseudo-first-order rate constants at 303 K. $[V(V)] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $[HMA] = 1.0 \text{ mol dm}^{-3}$ and $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$.

* Ionic strength was achieved by using NaHSO₄ as an added electrolyte.

Effect of Solvent

The oxidation rate was investigated in solutions containing different proportions of methanol and water. The decrease of the dielectric constant by the addition of methanol resulted in a rate increase (Table V). Control experiment showed a negligible oxidation of methanol by V(V).

Effect of Temperature

The oxidation rate was measured by varying the temperatures from 293 to 313 K and maintaining constant all the other experimental conditions. These results are given in Table VI (r > 0.9970 and $s \le 3.79 \times 10^{-4}$). The Arrhenius plots (Fig. 1, r > 0.9981 and $s \le 0.059$) of the apparent second order rate constant, k', obtained from Table VI as a function reciprocal of absolute temperature, 1/T, yield the activation parameters (Table VII).

Discussion

The principal observations concerning the malic acid oxidation by vanadium(V), in sulphuric acid medium, may be summarized as follows. The reaction rate was found to be linearly proportional to the concentrations of the oxidant, of malic acid and of the hydrogen ion, respectively, under constant or variable ionic strength. We assumed that sulphuric acid behaves as a strong monobasic acid, for the purpose of hydrogen and/or bisulphate ions.

TABLE V. Pseudo-first-order rate constants for the malic acid oxidation in binary aqueous mixtures of methanol at 303 K. $[V(V)] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ and $[HMA] = 1.00 \text{ mol dm}^{-3}$ and $[H_2SO_4] = 1.00 \text{ mol dm}^{-3}$.

[MeOH]/%	$k_{ m obs}/10^{-3}~{ m s}^{-1}$
0	4.70
10	5.16
15	6.21
20	6.72
25	7.56
30	8.62

T/K				$k_{ m obs}/10^{-3}~{ m s}^{-1}$				
	$I/{ m mol}~{ m dm}^{-3}$	[HMA]/mol dm ⁻³	0.50	0.75	1.00	1.25	1.50	
293	а		0.75	1.22	1.56	2.14	2.78	
298	a		1.57	2.22	3.07	3.88	4.67	
303	а		2.60	3.68	4.70	5.64	6.43	
308	а		3.30	4.79	5.86	7.26	8.83	
313	а		4.63	6.71	8.97	9.98	11.82	
293	2.00		1.89	2.85	4.25	5.60	7.12	
298	2.00		2.81	3.97	5.66	6.90	8.78	
303	2.00		3.52	5.85	7.43	9.60	12.17	
308	2.00		5.39	8.18	10.31	13.35	16.49	
313	2.00		7.21	10.11	13.25	16.39	19.23	

TABLE VI. Effect of temperature on the malic acid oxidation with no control of ionic strength, and at constant ionic strength.* $[V(V)] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ and $[HMA] = 0.50 - 1.50 \text{ mol dm}^{-3}$ and $[H_2SO_4] = 1.00 \text{ mol dm}^{-3}$.

*Constant ionic strength was achieved by using NaHSO₄ as an added electrolyte.

^a The initial ionic strength is 1.00 mol dm^{-3} , but changes in the course of the reaction.

It has been established that, V(V) in acidic solution (>0.005 mol dm⁻³) exists as pervanadyl ion, VO₂⁺, which is believed to exist in the hydrated form, V(OH)₄⁺. In more concentrated solution, the protonated form, V(OH)₃²⁺, is more reactive [12].

(1)
$$\operatorname{VO}_2^+ + 2 \operatorname{H}_2 O \xrightarrow{K_1} \operatorname{V(OH)}_4^+$$

(2)
$$V(OH)_4^+ + H^+ \rightleftharpoons V(OH)_3^{2+} + H_2O$$



Figure 1. Plot of $\ln k'$ vs. T^{-1} for $[V(V)] = 1.00 \times 10^{-2} \text{ mol } \text{dm}^{-3}$, $[H_2SO_4] = 1.00 \text{ mol } \text{dm}^{-3}$, and $[HMA] = 0.50 - 1.50 \text{ mol } \text{dm}^{-3}$ at 303 K. (\blacksquare) no control of the ionic strength and (\bullet) constant ionic strength ($I = 2.00 \text{ mol } \text{dm}^{-3}$).

$I/ \text{ mol dm}^{-3}$	$E^{\neq}/\mathrm{kJ} \mathrm{mol}^{-1}$	$\Delta H^{\neq}/\mathrm{kJ} \mathrm{mol}^{-1}$	$\Delta G^{\neq}/\mathrm{kJ} \mathrm{mol}^{-1}$	$\Delta S^{\neq}/\mathrm{J} \mathrm{\ mol}^{-1} K^{-1}$
а	47.0	44.5	87.5	-144
2.00	34.7	32.2	85.5	-179

TABLE VII. Arrhenius parameters for the malic acid oxidation by vanadium(V) calculated from the values of the apparent second order rate constant, $k' \pmod{10^{-1} \text{ dm}^3 \text{ s}^{-1}}$ obtained from Table VI.

^a The initial ionic strength is $1.00 \text{ mol } \text{dm}^{-3}$, but changes in the course of the reaction.

In the previous article [8], we proposed that $V(OH)_3^{2+}$ was the active species for the oxidation of malic acid in a perchloric acid solution. The K_2 value was determined to be about 2.0. On the other hand, the reaction rate doubled in sulphuric acid solutions, in the same range of 0.50 to 1.50 mol dm⁻³ regardless of ionic strength control (Table I). An increase of the reaction rate was also observed with the V(V) concentration varying from 0.50×10^{-2} to 2.5×10^{-2} mol dm⁻³ (Table II). Upon addition of sodium bisulphate, the rate increased almost three-fold (Table III). These increases in the rate can be attributed to the formation of different active species produced by the interaction between hydrated vanadium(V) and bisulphate group [13] before reaction with the malic acid, according to the following scheme

(3)
$$V(OH)_3^{2+} + HSO_4^- \xrightarrow{K_3} V(OH)_3 HSO_4^+$$

when the ionic strength is not maintained constant. The fact that the reaction rate is faster under controlled ionic strength conditions is probably due to another reactive species postulated to be $V(OH)_2(HSO_4)_2^+$

(3')
$$V(OH)_3^{2+} + H^+ + 2HSO_4^- \xrightarrow{K_{3'}} V(OH)_2(HSO_4)_2^+ + H_2O$$

The oxidation rate was enhanced by more than two-fold, when the ionic strength was changed from 1.25 to 2.75 mol dm⁻³ at 303 K (Table IV). The ionic charge product, z_+z_- of 0.73 was obtained from the Debye–Hückel limiting-law [14]. This result suggests that the vanadium(V) reacts almost predominantly with malic acid in the protonated form

(4)
$$HOOCCH_2CH(OH)COOH + H^+ \rightleftharpoons HOOCCH_2CH(OH)C^+OOH_2$$

Thus, the protonated malic acid reacts with $V(OH)_3HSO_4^+$ or $V(OH)_2(HSO_4)_2^+$ to yield a V(V)-HMA complex, $[X^{*2+}]$ or $[Y^{*2+}]$, in solutions without or with ionic strength control respectively, according to the following schemes

(5)
$$V(OH)_3HSO_4^+ + HOOCCH_2CH(OH)C^+OOH_2 \xrightarrow{K_5} [X^{*2+}]$$

(5')
$$V(OH)_2(HSO_4)_2^+ + HOOCCH_2CH(OH)C^+OOH_2 \xrightarrow{K_{5'}} [Y^{*2+}]$$

The activated species, $[Y^{*2+}]$, has a larger volume due to the V(V) species, $V(OH)_2(HSO_4)_2^+$, with two HSO_4^- groups, producing a less stable species with the protonated hydroxyacid. Both the intermediate complexes, $[X^{*2+}]$ and $[Y^{*2+}]$, would subsequently decompose to give a free radical, carbon dioxide and a mol of V(IV), such as $V(OH)(HSO_4)_2^+$ and $V(OH)_2HSO_4^+$, according to k_6 , with no control of ionic strength, and with k_6' , at constant ionic strength, in the rate-determining step.

It has been shown earlier that most reactions involving V(V) proceed via a freeradical mechanism [15]. In this investigation, the addition of acrylamide to the reaction mixture was shown to yield a polymeric product indicating that V(V)

(6)
$$[X^{*2+}] \xrightarrow{k_6} \text{HOOCCH}_2\text{CH}(\text{OH}) \xrightarrow{C} + \text{CO}_2 + \text{V}(\text{OH})_2\text{HSO}_4^+ + \text{H}^+ + \text{H}_2\text{O} \xrightarrow{I}_{OH}$$

(6')
$$[Y^{*2+}] \xrightarrow{k_6'} \text{HOOCCH}_2\text{CH}(\text{OH})\overset{H}{\text{C}} + \text{CO}_2 + \text{V}(\text{OH})(\text{HSO}_4)_2^+ + \text{H}^+ + \text{H}_2\text{O}$$

OH

behaves as a one-equivalent oxidant. Thus, the conversion of V(V) into V(IV) yields the free radical HOOCCH₂CH(OH)CH(OH)· in the rate determining step, which is subsequently and rapidly oxidized to produce another mol of V(IV), carbon dioxide and acetaldehyde. In this manner, in the absence of ionic strength control,

(7)
$$\begin{array}{c} HOOCCH_2CH(OH)C + V(OH)_3HSO_4^+ \xrightarrow{k_7} CH_3COH \\ OH \\ + CO_2 + V(OH)_2HSO_4^+ + H_2O \end{array}$$

with a similar way at constant ionic strength.

The solvent effect on the reaction rate was studied by varying the binary mixture of methanol-water in different compositions (Table V). The linear plot of $\ln k_{obs}$ as a function of the reciprocal of dielectric constant, 1/D, [16] of the methanol-water mixture at 303 K [17] gave a straight line with a positive slope (r = 0.9902 and s = 0.036) showing that the decrease in the solvent polarity favoured the reaction. Thus, the transition state is either less polar than the reactants [16], or the solvent is providing more hydrogen bonding which can stabilize the activated complex, and in this manner, decrease the next step in the reaction rate.

The negative values for the overall entropies of activation of the oxidation pathways are expected because there is a charge increase of the reactive vanadium(V) species [18], and thus restricting the movement of water molecules. When the ionic strength is kept constant the value is more negative $(-179 \text{ J mol}^{-1} \text{ K}^{-1})$, because these species are little affected by the medium acidity, as opposed to the situation where there is not control of ionic strength $(-144 \text{ J mol}^{-1} \text{ K}^{-1})$. The small values of enthalpies of activation (44.5 and 32.2 kJ mol⁻¹) suggest that the oxidation is controlled by entropy. The lower values of the activation energy indicate considerable ease for oxidation, in comparison with that obtained in the previous study (77.8 kJ mol⁻¹) [8]. Furthermore, the values of ΔH^{\neq} as a function of ΔS^{\neq} , in both media, can be correlated linearly (Fig. 2, r = 0.9998 and s = 0.6871) and results in an isokinetic relationship [19]. This behavior suggests that, regardless of the value of the entropy of activation, the C—C bond rupture occurs in the rate determining step, as described in the malic acid oxidation in perchloric acid medium [8]. This is similar to the mechanism of the pinacol oxidation by chromic acid, suggested by Chang and Westheimer [20].



Figure 2. Plot of ΔH^{\neq} as a function of ΔS^{\neq} of the malic acid oxidation in the media of perchloric acid and sulphuric acid.

Considering the first five steps involving K_1 , K_2 , K_3 , K_4 , and K_5 as preequilibria ones, and the rate-determining one as k_6 , the above mechanisms for the oxidation with no ionic strength control, leads to

(8)
$$-\frac{d[V(V)]}{dt} = k_6 K_1 K_2 K_3 K_4 K_5 [VO_2^+] [HMA] [H^+]$$

where

(9)
$$k_{\rm obs} = k_6 K_1 K_2 K_3 K_4 K_5 [{\rm HMA}] [{\rm H}^+].$$

For the reactions with ionic strength control, the reaction rate is given by

(10)
$$-\frac{d[V(V)]}{dt} = k_6' K_1 K_3' K_4 K_5 [VO_2^+] [HMA] [H^+]$$

where k_6' is the rate constant for the rate-determining step, and

(11)
$$k_{\rm obs} = k_6' K_1 K_3' K_4 K_5 [\rm HMA] [\rm H^+].$$

Both eqs., (8) and (10), are in agreement with the experimental rate law that the reactions are first-order with respect to vanadium (V), malic acid, and hydrogen ion concentrations. Substituting the values of Table III for [HMA] = 1.0 mol dm⁻³ in equations (9) and (11), the product $k_6K_1K_2K_3K_4K_5$ is calculated to be 4.86×10^{-3} mol⁻¹ dm⁻³ s⁻¹ (r = 0.9942 and $s = 2.40 \times 10^{-4}$) and $k_6'K_1K_3'K_4K_5$ to be 7.33×10^{-3} mol⁻¹ dm³ s⁻¹ (r = 0.9898 and $s = 4.81 \times 10^{-4}$).

In conclusion, the formation of different oxidizing species of vanadium(V), in the presence of sulphuric acid and bisulphate ions, accounts for the faster oxidation of malic acid in comparison with that in perchloric acid medium through the rupture of the C—C bond in the rate determining step regardless of the ionic strength of the solution.

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