Kinetic and Mechanistic Aspects for the Tartaric Acid Oxidation by Vanadium(V) in Sulfuric Acid Medium

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ABSTRACT: Tartaric acid oxidation by vanadium(V) in sulfuric acid medium was investigated spectrophotometrically at 760 nm and 30°C by appearance of the vanadium(IV), as vanadyl. The reaction rate was determined under pseudo-first-order conditions with an excess of hydroxyacid over the oxidant concentration. The oxidation showed a first-order dependence with respect to vanadium(V) concentration and fractional orders with respect to tartaric acid and sulfuric acid concentrations, with no control and with constant ionic strength. The reaction rate is enhanced by an increase of ionic strength, and slightly reduced by a decrease of the dielectric constant of the medium. The activation parameters were calculated based on the rate constants determined in the 293 to 313 K interval. The proposed oxidation mechanisms and the derived rate laws are consistent with the experimental rate laws. © 1998 John Wiley & Sons, Inc. Int J Chem Kinet: **30**: 55–61, 1998.

INTRODUCTION

The kinetics of α -hydroxyacids oxidation through several oxidants has been investigated [1–4] and recently reviewed by Wells [5]. Being bifunctional compounds, their oxidation can proceed by many possible routes. While oxidation of hydroxyacids by one-electron oxidants generally take place through one of the several possible initial radical formation steps [6], two electrons oxidants usually promote oxidation either by an ionic mechanism involving transfer of an α -hydrogen or by concerted oxidative decarboxylation involving cleavage of a C—C bond [7]. The choice of the mechanism route would thus depend on several factors, such as the structure of the substrates and the nature and the oxidizing capacity of the oxidant, the reaction conditions, and the actual products isolated. Nevertheless, relatively few studies have concerned themselves with the nature of the oxidizing species in these systems [8,9] because apparently the kinetic behavior of hydroxyacids oxidations are well-established.

In our earlier study [10-12] we have reported that different mechanisms are operative with the participation of some different active species of vanadium(V). The oxidation rate of malic acid by vanadium(V) was greater in sulfuric acid medium with

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ionic strength control and showed first-order behavior with respect to oxidant, substrate, and hydrogen ion concentrations with or without control of the ionic strength [10]. However, when this oxidation was performed in perchloric acid medium, the rate constant remained practically constant with increase of the ionic strength. The rate law showed a first-order behavior with respect to the oxidant and malic acid concentrations and a fractional-order with respect to the hydrogen ion concentration and a similar mechanism was proposed with or without control of ionic strength [12]. On the other hand, when lactic acid was oxidized in a sulfuric acid medium, a larger rate was observed with ionic strength control, and the plot of $\ln k_{obs}$ vs. In [H⁺] displayed an inflexion in both conditions, indicating two different orders in the investigated hydrogen ion concentrations range [11]. The variation of the reaction-order was more significant when the ionic strength was not controlled, showing a behavior of approximately first- and second-orders, respectively. We attributed these changes not only to the nature of the vanadium(V), but also to the oxidizing capacity promoted by the increase of the hydrogen ion concentration. In continuation with our studies, we report herein the results of the oxidation of tartaric acid by vanadium(V) in sulfuric acid medium under variable and constant ionic strength conditions.

EXPERIMENTAL

The solution of vanadium(V), V(V), was prepared and the ionic strength was controlled as described previously [10,11]. The tartaric acid, HTA, (Merck, purity 99.5%) was used after recrystallization with water.

The pseudo-first-order rate constants, k_{obs} were calculated from the slopes of the linear plots (correlation coefficient, $r \ge 0.9988$, standard deviation, $s \le 2.2 \times 10^{-4}$) of ln[V(V)] against time, and were reproducible within $\pm 5\%$. The kinetic measurements were performed monitoring the appearance of vanadium(IV), V(IV), at 760 nm with a Varian spectrophotometer model DMS-80 at 303.0 K (± 0.1 K). The measurements were carried out in duplicate and, when necessary, in triplicate.

The oxidation of tartaric acid by V(V) induced the polymerization of a solution of recrystallized acrylamide (25%) under kinetic conditions. Control experiments in which either V(V) or HTA were excluded demonstrated the absence of polymerization.

The product analysis was carried out under kinetic conditions. The presence of aldehyde and/or ketone was characterized by the reaction with 2,4-dinitro-

phenylhydrazine, and the Tollens reagent displayed to be positive for aldehyde [13]. The production of formaldehyde was verified by means of the Hantzsch reaction through the addition of reagents containing acetylacetone and ammonium salt [14]. The stoichiometry was determined as described early [11]. A yield of 2.0 (± 0.2) moles of CO₂ for each mol of HTA was obtained in a Warburg respirometer (B. Braun, model V-85) at 313 K. The overall reaction for tartaric acid oxidation may be represented by the following equation

HOOCCH(OH)CH(OH)COOH + 2 V(V) \longrightarrow 2 HCOH + 2 CO₂ + 2 V(IV) + 2 H⁺

RESULTS

Effect of Reactants Concentration

An enhancement in the oxidation rate was observed with an increase of the excess tartaric acid concentration, [HTA], when the initial concentrations of V(V), $[V(V)]_0$, and sulfuric acid, $[H_2SO_4]_0$, were maintained constant at 303 K as shown in Table I ($r \ge$ 0.9962 and $s \le 0.0797$). This was independent of whether the reaction took place at constant or with no control of the ionic strength. Individual plots of ln [V(V)] as a function of time for different initial concentrations of tartaric acid, $[HTA]_0$, display satisfactory linearity ($r \ge 0.9988$ and $s \le 2.20 \times 10^{-4}$) at

Table I Pseudo-First-Order Rate Constants for the Oxidation of Tartaric Acid by V(V) with No Control of Ionic Strength (I), and at Constant Ionic Strength.^a $|V(V) = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$, $|H_2SO_4| = 0.15 \text{ mol dm}^{-3}$, and T = 303 K

I/mol dm ⁻³	[HTA]/mol dm ⁻³	$\frac{k_{\rm obs}/10^{-3} \ {\rm s}^{-1}}{1.03}$ 1.30		
b	0.50	1.03		
b	0.75	1.30		
b	1.00	1.51		
b	1.25	1.74		
b	1.50	1.96		
1.10	0.50	2.25		
1.10	0.75	2.87		
1.10	1.00	3.34		
1.10	1.25	3.89		
1.10	1.50	4.24		

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

 $^{\rm b}\,Initial$ ionic strength is 0.16 mol dm $^{-3},$ but changes in the course of the reaction.

Table IIPseudo-First-Order Rate Constants for theReduction of Vanadium(V) at 303 K with No Control ofIonic Strength (I), and at Constant Ionic Strength.a $[HTA] = 1.00 \text{ mol } dm^{-3}$ and $[H_2SO_4] = 0.15 \text{ mol } dm^{-3}$

I/mol dm ⁻³	$[V(V)]/10^{-2} \text{ mol } dm^{-3}$	$k_{\rm obs}/10^{-3} {\rm ~s^{-1}}$	
b	0.50	1.35	
b	1.00	1.51	
b	1.50	1.66	
b	2.00	1.86	
b	2.50	1.98	
1.10	0.50	3.00	
1.10	1.00	3.34	
1.10	1.50	3.51	
1.10	2.00	3.72	
1.10	2.50	3.98	

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

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

303 K, and the order with respect to [HTA] is around 0.5 ($r \ge 0.9902$ and $s \le 0.0301$). The variation of $[V(V)]_0$ from 0.50×10^{-2} to 2.5×10^{-2} mol dm⁻³ increased the rate constant by about 47% (r = 0.9978 and s = 0.0193) in solutions with no control of ionic strength, and by about 33% (r = 0.9993 and s = 0.0166) at constant ionic strength as indicated in Table II.

Effect of Hydrogen Ion Concentration

Maintaining the same initial reactants concentrations, $[V(V)]_0$ and $[HTA]_0$, the oxidation rate increased with the increase of the hydrogen ion concentration, $[H^+]$, through the addition of sulfuric acid. The pseudo-first-order rate constants at 303 K, are presented in Table III. The reaction-order for the reaction without ionic strength control was 0.60 (r = 0.9946 and s = 0.0699) and with control, 0.28 (r = 0.9959 and s = 0.0439).

Effect of Ionic Strength

The kinetic experiments were performed changing the ionic strength by the addition of a concentrated solution of sodium bisulfate (5.0 mol dm⁻³) in the reactant solution. The pseudo-first-order rate constant increased by approximately four-fold in the range of 0.16 to 2.00 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 [15,16] gives a product of the ionic charges, z_+z_- of 0.56 (r = 0.9976 and s = 0.0164).

Table III Effect of the Sulfuric Acid Concentration on the Pseudo-First-Order Rate Constants at 303 K with No Control of Ionic Strength (1), and at Constant Ionic Strength.^a $[V(V)] = 1.00 \times 10^{-2}$ mol dm⁻³ and [HTA] = 1.00 mol dm⁻³

I/mol dm ⁻³	$[H_2SO_4]/mol dm^{-3}$	$k_{\rm obs}/10^{-3} {\rm ~s^{-1}}$
0.06	0.05	0.91
0.11	0.10	1.21
0.16	0.15	1.51
0.26	0.25	2.31
0.41	0.40	3.30
0.56	0.55	3.87
0.71	0.70	4.15
0.86	0.85	4.51
1.01	1.00	5.11
1.10	0.05	2.56
1.10	0.10	2.87
1.10	0.15	3.34
1.10	0.25	3.58
1.10	0.40	4.16
1.10	0.55	4.63
1.10	0.70	4.98
1.10	0.85	5.58
1.10	1.00	5.85

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

Effect of Solvent

The solvent composition was varied by adding methanol to aqueous medium (0–40% v/v). The oxidation rate decreased with the increase of methanol content (Table V). Plots of ln k_{obs} vs. reciprocal of dielectric constant of the medium, $1/\epsilon$ [17] resulted in straight lines ($r \ge 0.9065$, $s \le 0.05045$). Control experiments showed a negligible oxidation of methanol by V(V).

Table IV Effect of the lonic Strength (I) on the Pseudo-First-Order Rate Constants at 303 K. $[V(V)] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[HTA] = 1.00 \text{ mol dm}^{-3}$, and $[H_2SO_4] = 0.15 \text{ mol dm}^{-3}$

I/mol dm ⁻³	$k_{\rm obs}/10^{-3}~{ m s}^{-1}$
0.16	1.51
0.20	1.54
0.50	2.23
0.80	2.75
1.10	3.34
1.40	3.88
1.70	4.86
2.00	5.86

 $^{\rm a}\,Ionic$ strength was achieved by using $\rm NaHSO_4$ as an added electrolyte.

$[HTA] = 1.00 \text{ mol } dm^{-3}$, and $[H_2SO_4] = 0.15 \text{ mol } dm^{-3}$				
I/mol dm ⁻³	[MeOH]/%	$k_{\rm obs}/10^{-3} {\rm ~s^{-1}}$		
b	0	1.51		
b	20	1.36		
b	25	1.26		
b	30	1.26		
b	35	1.30		
b	40	1.09		
1.10	0	3.34		
1.10	20	3.06		
1.10	25	2.79		
1.10	30	2.84		
1.10	35	2.84		
1.10	40	2.70		

Table V Pseudo-First-Order Rate Constants for the Tartaric Acid Oxidation in Binary Aqueous Mixtures of Methanol with No Control and at Constant Ionic Strength (1)^a at 303 K. $[V(V)] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$, [HTA] = 1.00 mol dm⁻³, and [H-SO₄] = 0.15 mol dm⁻³

 $^{\rm a}$ Initial ionic strength is 0.16 mol dm $^{-3},$ but changes in the course of the reaction.

 $^{\rm b}\mbox{Ionic}$ strength was achieved by using $\rm NaHSO_4$ as an added electrolyte.

Effect of Temperature

The oxidation rate was measured by varying the temperature from 293 to 313 K, maintaining constant all the other experimental conditions. These results are given in Table VI ($r \ge 0.9988$ and $s \le 2.20 \times 10^{-4}$) and the reaction order with respect to [HTA] was remained around 0.5. The Arrhenius plots (Fig. 1, $r \ge 0.9961$ and $s \le 0.08132$) were constructed from ln k' (the apparent second-order rate constants, obtained from Table VI) vs. the reciprocal absolute tem-



Figure 1 Plot of $\ln k'$ vs. T^{-1} for $[V(V)] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.15 \text{ mol dm}^{-3}$, and $[HTA] = 0.50-1.50 \text{ mol dm}^{-3}$. (**I**) No control of the ionic strength and (**O**) constant ionic strength (I = 1.10 mol dm}^{-3}).

perature. The activation parameters are displayed in Table VII.

DISCUSSION

The reaction rate was found to be linearly proportional to the concentration of the oxidant, and to have a fractional dependence on the concentrations of both tartaric acid and hydrogen ion under constant and variable ionic strengths. We assumed that sulfuric acid

Table VI Effect of Temperature on the Tartaric Acid Oxidation with No Control of Ionic Strength (I), and at Constant Ionic Strength.^a $[V(V)] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[HTA] = 0.50-1.50 \text{ mol dm}^{-3}$, and $[H_2SO_4] = 0.15 \text{ mol dm}^{-3}$

			$k_{\rm obs}/10^{-3}~{ m s}^{-1}$				
T/K	I/mol dm ⁻³	[HTA]/mol dm ⁻³	0.50	0.75	1.00	1.25	1.50
293	b		0.44	0.57	0.64	0.70	0.78
298	b		0.66	0.75	0.87	1.02	1.13
303	b		1.03	1.30	1.51	1.74	1.96
308	b		1.60	1.85	2.34	2.86	3.20
313	b		3.55	4.28	4.86	5.22	5.88
293	1.10		0.85	1.12	1.25	1.48	1.62
298	1.10		1.43	1.89	2.08	2.43	2.75
303	1.10		2.25	2.87	3.34	3.89	4.24
308	1.10		3.83	4.56	5.24	6.12	6.61
313	1.10		5.10	6.06	6.86	7.69	8.69

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

^b Initial ionic strength is 0.16 mol dm⁻³, but changes in the course of the reaction.

Table VII Activation Parameters for the Tartaric Acid Oxidation by Vanadium(V) Calculated from the Values of the Apparent Second-Order Rate Constant, $k' \pmod{V}$ (mol⁻¹ dm³ s⁻¹) obtained from Table VI

I/mol cm ⁻³	$E_{\rm a}/{\rm kJ}~{\rm mol^{-1}}$	$\Delta H^{\neq}/\mathrm{kJ}~\mathrm{mol}^{-1}$	$\Delta S^{\neq}/J \text{ mol}^{-1} K^{-1}$	
a	77.1	74.6	-57	
1.10	59.3	56.8	-110	

^a Initial ionic strength is 0.16 mol dm⁻³, but changes in the course of the reaction.

behaves as a strong monobasic acid for the purpose of hydrogen and/or bisulfate ions.

The oxidation of tartaric acid, HTA, by vanadium(V), V(V), takes place more rapidly in comparison with lactic acid [11] and malic acid [10] indicating that electron withdrawing substituents at the α -position increased the oxidation rate. This was experimentally verified through the use of a smaller concentration of sulfuric acid in the kinetic measurements.

In the previous article [11] we assumed that the pervanadyl ion, VO₂⁺, obtained in acidic solution ([H⁺] > 0.005 mol dm⁻³) exists in the hydrated form, V(OH)₄⁺ [9,18]. In more concentrated solution, the protonated form, V(OH)₃²⁺ is more reactive. The observed increase in the reaction rate with the V(V) concentration varying from 0.50×10^{-2} to 2.50×10^{-2} mol dm⁻³, regardless of the ionic strength in the sulfuric acid medium (Table II), and with the addition of sodium bisulfate, varying the ionic strength from 0.16 to 2.00 mol dm⁻³ by approximately four-fold (Table IV), can be attributed to the formation of different species produced by the interaction between hydrated vanadium (V) and the bisulfate group before the reaction with tartaric acid, according to the following scheme

$$V(OH)_3^{2+} + HSO_4^{-} \xrightarrow{K_1} V(OH)_3 HSO_4^{+}$$
 (1)

for the reactions with no control of ionic strength, where $K_1 = k_1/k_1$ and

$$V(OH)_{3}^{2+} + H^{+} + 2HSO_{4}^{-} \underbrace{\overleftarrow{K_{l'}}}_{V(OH)_{2}(HSO_{4})_{2}^{+}} + H_{2}O \quad (1')$$

under controlled ionic strength conditions. On the other hand, when $[H^+]$ was varied from 0.05 to 1.00 mol dm⁻³ (Table III), the variation range of the rate constants with no control of ionic strength was greater in comparison with those at constant ionic strength and both showed the trend to a limit value. This yields an order of 0.60 with respect to $[H^+]$ for the former, and 0.28 at constant ionic strength.

This oxidation and the earlier ones [10-12] have

presented a linear dependence on the plot of log k_{obs} against the square root of until 2.75 mol dm⁻³ for the ionic strength [10,12]. This means that the primary salt effect [15] is surprisingly applicable to the ionic strength upper 0.05 mol dm⁻³. The reasons that lead to this behavior are unknown yet. In this reaction the ionic charge product, z_+z_- , of 0.56 was obtained by the variation of the ionic strength from 0.16 to 2.00 mol dm⁻³ (Table IV). From this value alone, it is difficult to suggest that the vanadium(V) reacts with tartaric acid either as the protonated form or in the molecular form. Furthermore, the plots of $\ln k_{obs}$ against the reciprocal of the dielectric constant of methanolwater composition [17], with no control or constant ionic strength, give straight lines. This suggests an iondipole interaction under the assumption that HTA behaves as a dipole in methanol, whereas positive ionic species of V(V) may be considered active in the reaction. The less polar solvents have a greater loss in freedom in becoming frozen to the ions than the more polar solvents, hence the lower rates of reaction in less polar solvents [19]. The increase in the reaction rate of the mixture with smaller proportion of methanol indicates that the activated complex radial term in the Born expression [20] is less than the sum of the reagents radii in the solution with low dielectric constant and, thus favors the production of species with higher dipole moments.

The negative values of the entropy of activation (Table VII) are indicative of the formation of more rigid activated complexes than the reagents, due to the approach of like charges which undergo electrostriction with the solvent molecules [20]. A more negative value $(-110 \text{ J mol}^{-1} \text{ } K^{-1})$ and therefore a lower frequency factor (3.0 \times 10⁸ mol⁻¹ dm³ s⁻¹) was found for fixed ionic strength conditions. This may suggest that the number of HSO_4^- groups in the vanadium(V) species increases the activated complex stability by comparison with a less negative value obtained in the medium without ionic strength control ($-57 \text{ J} \text{ mol}^{-1}$) K^{-1}), where the oxidant has only one HSO₄⁻ group, leading to the higher activation energy (77.1 kJ mol⁻¹). Furthermore, it is possible to suggest that the oxidation is controlled by entropy at constant ionic strength, and by enthalpy (74.6 kJ mol K^{-1}) without ionic control. In addition to these facts, the fractionalorders with respect to [HTA] and [H⁺] suggest an equilibrium for the oxidation with no control of ionic strength according to

$$V(OH)_{3}HSO_{4}^{+} + H^{+}$$

+ HOOCCH(OH)CH(OH)COOH $\xleftarrow{K_{2}} (X^{*2+})$ (2)

and,

$$V(OH)_{2}(HSO_{4})_{2^{+}} + H^{+}$$

+ HOOCCH(OH)CH(OH)COOH $\xleftarrow{K_{2^{-}}} (Y^{*2^{+}})$
(2')

with control of ionic strength. It has been shown earlier that most reactions involving V(V) proceed via a free-radical mechanism [18]. In this investigation the addition of acrylamide to the reaction mixture has also been shown to yield the formation of a polymeric product indicating that V(V) behaves as an one-equivalent oxidant. Thus, these activated species, (X^{*2+}) and (Y^{*2+}) , are decomposed to give the first CO₂ through a C—C fission producing a free radical, HOOCCH(OH)CH(OH)·, and V(IV) in the rate determining step, k_3 and k'_3 , respectively, for the oxidation with no control and with constant ionic strength.

$$(X^{*2+}) \xrightarrow{k_3} \text{HOOCCH(OH)C} + CO_2 \\ OH \\ + \cdot V(OH)_2 \text{HSO}_4^+ + \text{H}^+ + \text{H}_2 \text{O} \quad (3)$$

and

$$(Y^{*2+}) \xrightarrow{k_{3^{*}}} HOOCCH(OH)C \cdot + CO_{2}$$

OH
$$+ \cdot V(OH)(HSO_{4})_{2}^{+} + H^{+} + H_{2}O \quad (3')$$

This free radical is rapidly oxidized through another mol of V(V) and produces one more carbon dioxide, two moles of formaldehyde and V(IV), according to the following scheme in the absence of ionic strength control,

and, in a similar way at constant ionic strength. As-

suming the slow step as the rate-determining one, k_3 , and $k_{3'}$, respectively, these mechanisms lead to the rate law (5) for the oxidation of tartaric acid by V(V) in sulfuric acid medium with no control of ionic strength,

$$-\frac{d[V(V)]_{t}}{dt} = \frac{k_{3}K_{2}[H^{+}][HTA][V(V)]_{t}}{1 + K_{2}[H^{+}][HTA]}$$
(5)

and

$$-\frac{d[V(V)]_{t}}{dt} = \frac{k_{3'}K_{2'}[H^+][HTA][V(V)]_{t}}{1 + K_{2'}[H^+][HTA]}$$
(5')

at constant ionic strength, where the total or analytical concentrations of V(V) are given by

$$[V(V)]_{t} = [(X^{*2+})] + [V(OH)_{3}HSO_{4}^{+}]$$

or

$$[V(V)]_t = [(Y^{*2+})] + [V(OH)_2(HSO_4^+)_2]$$

The rate laws, (5) and (5'), are in agreement with the experimental results in sulfuric acid medium, with no control or under fixed ionic strength, because the investigated reactions are of first-order with respect to the vanadium(V) concentration, and of fractional-orders to both tartaric acid and hydrogen ion concentrations. From the slopes and intercepts of the double reciprocal plots at constant vanadium(V) and sulfuric acid concentrations (Fig. 2, $r \ge 0.9736$ and $s \le$



Figure 2 A double reciprocal plot of the pseudo-first-order rate constant, k_{obs} , and tartaric acid concentration, [HTA] for $[V(V)] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ and $[H_2SO_4] = 0.15 \text{ mol dm}^{-3}$ at 303 K. (**II**) No control of the ionic strength and (**O**) constant ionic strength (I = 1.10 mol dm}^{-3}).

18.8089) the equilibrium constant, K_2 was determined as ca. 6.0 mol⁻² dm⁶ at 303 K, while the rate constant for rate-determining constant, k_3 , was obtained as 3.38×10^{-3} mol⁻¹ dm³ s⁻¹ with no control of ionic strength control. When this was adjusted to 1.10 mol dm⁻³, these values become 25.1 mol⁻² dm⁶ and 4.51×10^{-3} mol⁻¹ dm³ s⁻¹, respectively. In conclusion, these results and the experimental rate laws show that the oxidation mechanism of tartaric acid involves different active species of vanadium(V) in sulfuric acid medium and depend on the ionic strength conditions of the experiments.

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