Monatshefte für Chemie 134, 1321–1331 (2003)
DOI 10.1007/s00706-003-0069-2

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Oxidation of Two α-Hydroxy Acids by Vanadium(V)

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Received April 8, 2003; accepted May 10, 2003

Summary. The pathways for the oxidation of tartaric acid and citric acid by vanadium(V) in perchloric acid medium have been studied at 303 K by following the formation of vanadium(IV) spectrophotometrically at 760 nm. The oxidation reaction displays fractional order dependence with respect to both the α-hydroxy acids concentrations as well as fractional (tartaric acid) and first order (citric acid) dependencies with respect to the perchloric acid concentration. It does not matter at all whether the ionic strength was varied or was maintained constant. The reaction rate remains essentially constant with increasing ionic strength in the tartaric acid oxidation, but decreases slightly in the citric acid case. A decrease of the dielectric constant of the reaction medium results in a rate decrease in the tartaric acid oxidation and in a rate enhancement in the citric acid reaction. The activation parameters were obtained from studies of the reactions at different temperatures (293 to 313 K). Based on the experimentally determined rate laws oxidation mechanisms and theoretical rate laws were proposed.

Keywords. Reaction kinetics; Aqueous solutions; Tartaric acid; Citric acid; Vanadium(V).

Introduction

The oxidation chemistry of aqueous acidic solutions of vanadium(V) is often complicated because different species may be involved in equilibrium steps prior to oxidation. For example, it has been established that vanadium(V) in acidic solution exists as pervanadyl ion (VO_2^+) [1]. This ion is produced by the interaction of vanadate ion (VO_3^-) with water and yields more or less reactive species depending on the nature of the acidic medium. Vanadium(V) species such as $VO(OH)^{2+}$ and $V(OH)_3^{2+}$ are frequently involved in aqueous perchloric acid medium [2] whereas reactive species in sulfuric acid are attributed to $V(OH)_3HSO_4^+$ and $V(OH)_2(HSO_4^+)_2$ [3]. In general, oxidation of α-hydroxy acids by vanadium(V) has been shown to be faster in sulfuric acid under constant ionic strength

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conditions. As a part of our mechanistic studies [4–8], in this paper we report the kinetic and mechanistic behavior of tartaric acid and citric acid oxidation by vanadium(V) in aqueous perchloric acid medium. In these cases rates are faster under conditions in which the ionic strength is varied.

Results

Effect of Reactants Concentration

The kinetic behavior at 303 K was studied at different substrate concentrations, [S], maintaining constant the initial concentrations of V(V), $[V(V)]_o$, and of perchloric acid, $[HClO_4]_o$, as shown in Table 1 ($r \geq 0.9990$; $s \leq 4.26 \times 10^{-5}$). For both substrates, H*Ta* and H*Ci*, the oxidation rate was observed to be faster in experiments carried out at variable ionic strength. Thus, the rates are about 9% for H*Ta* and about 25% for H*Ci* higher than those observed under conditions of constant ionic strength. Fractional orders with respect to [H*Ta*] ($r \geq 0.9985$; $s \leq 1.43 \times 10^{-2}$) and [H*Ci*] ($r \geq 0.9863$; $s \leq 3.79 \times 10^{-2}$) were found, if the ionic strength was varied or was maintained constant. The first order dependence on the V(V) concentration,

Table 1. Pseudo-first order rate constants for the oxidation of tartaric acid and citric acid by V(V) at 303 K for variable and constant ionic strength (*I*)

$[S]/\text{mol dm}^{-3}$	$[V(V)]/10^{-2}\,\text{mol dm}^{-3}$	$I/\text{mol dm}^{-3}$	$k_{obs}/10^{-3}\,\text{s}^{-1}$	
			H*Ta*	H*Ci*
0.50	1.00	[a]	1.06	3.09
0.75	1.00	[a]	1.29	3.56
1.00	1.00	[a]	1.49	4.10
1.25	1.00	[a]	1.67	4.70
1.50	1.00	[a]	1.87	5.15
0.50	1.00	[b]	0.97	2.51
0.75	1.00	[b]	1.17	2.85
1.00	1.00	[b]	1.36	3.21
1.25	1.00	[b]	1.56	3.67
1.50	1.00	[b]	1.72	4.15
1.00	0.50	[a]	1.30	4.57
1.00	1.50	[a]	1.63	3.28
1.00	2.00	[a]	1.78	2.79
1.00	2.50	[a]	1.82	–
1.00	0.50	[b]	1.28	4.10
1.00	1.50	[b]	1.44	2.42
1.00	2.00	[b]	1.53	1.90
1.00	2.50	[b]	1.61	–

[a] Initial ionic strength is $0.16\,\text{mol dm}^{-3}$ and $[HClO_4] = [H^+] = 0.15\,\text{mol dm}^{-3}$ for H*Ta* and $0.21\,\text{mol dm}^{-3}$ and $[H^+] = 0.20\,\text{mol dm}^{-3}$ for H*Ci*, but changes in the course of the reaction; [b] The ionic strength for H*Ta* is $1.10\,\text{mol dm}^{-3}$ and $1.00\,\text{mol dm}^{-3}$ for H*Ci* achieved by using $NaClO_4$ as added electrolyte

[V(V)], in perchloric acid can be inferred from the satisfactory linearity observed ($r \geq 0.9988$; $s \leq 3.58 \times 10^{-4}$) for the individual plots of ln [V(V)] as a function of time at 303 K. For H*Ta* oxidation, variation of $[V(V)]_o$ from 0.50×10^{-2} to 2.50×10^{-2} mol dm^{-3} increased the rate constant by approximately 40% ($r = 0.9815$; $s = 4.56 \times 10^{-5}$) in solutions at variable ionic strength, and by approximately 24% ($r = 0.9998$; $s = 3.16 \times 10^{-6}$) at constant ionic strength. By comparison, the H*Ci* oxidation decreases by about 63% ($r = -0.9939$; $s = 1.08 \times 10^{-4}$) in media with variable ionic strength, and by more than 100% ($r = -0.9935$; $s = 1.34 \times 10^{-4}$) at constant ionic strength, when [V(V)] is varied in the range from 0.50×10^{-2} to 2.00×10^{-2} mol dm^{-3} as presented in Table 1.

Effect of Hydrogen Ion Concentration

The H*Ta* oxidation rate was measured at different hydrogen ion concentrations while maintaining the same initial reactant concentrations, $[V(V)]_o$ and $[S]_o$ at 303 K. Results are shown in Table 2 for $[H^+]$ (perchloric acid) ranging from 0.05 to 1.00 mol dm^{-3}. The reaction order with respect to $[H^+]$ is fractional whether the ionic strength was varied or was equal to 1.10 mol dm^{-3} ($r \geq 0.9978$; $s \leq 2.81 \times 10^{-2}$). For the H*Ci* oxidation, $[H^+]$ was varied from 0.10 to 0.90 mol dm^{-3} and a first order dependence for variable and constant ionic strength medium of 1.00 mol dm^{-3} ($r \geq 0.9978$; $s \leq 5.06 \times 10^{-2}$) was obtained.

Effect of Ionic Strength

The ionic strength effect on the reaction rate was investigated by adding the proper amount of sodium perchlorate to cover the range from 0.16 to 2.00 mol dm^{-3} in the H*Ta* oxidation, and from 0.30 to 1.25 mol dm^{-3} in the H*Ci* case (Table 3). Applying the *Debye-Hückel* equation by a plot of log k_{obs} as a function of the square root of ionic strength at 303 K [9, 10] yields practically zero ($r = 0.9888$; $s = 2.85 \times 10^{-3}$) for z_+z_-, the product of ionic charges for H*Ta*, and -0.2 ($r = 0.9940$; $s = 3.71 \times 10^{-3}$) for H*Ci*. A good linear relationship is observed in both cases even though the activity coefficients of many electrolytes are known to be fairly dependent on ionic strength. Moreover, the range of ionic strength covered in the oxidation by V(V) is somewhat outside the usual range where an extended *Debye-Hückel* law is valid.

Effect of Solvent

The reaction was studied in methanol/water mixtures of different composition (Table 4). For H*Ta* oxidation, reducing the dielectric constant (ε) of the medium by varying the methanol content (0–40% v/v) decreased the rate constant by approximately 7% for variable ionic strength and by approximately 46% at constant ionic strength. On the other hand, an increase by around 50% at variable ionic strength and by around 30% at fixed ionic strength was observed for the H*Ci* oxidation rate constant by varying the methanol content (0–35% v/v). Plots of ln k_{obs} *vs.* the reciprocal of the medium dielectric constant, $1/\varepsilon$, [11] of both substrates resulted in straight lines with negative ($r \geq -0.9920$; $s \leq 2.00 \times 10^{-2}$)

Table 2. Perchloric acid concentration effect on the pseudo-first order rate constants for the oxidation of tartaric acid and citric acid by V(V) at 303 K for variable and constant ionic strength (*I*); $[\mathrm{V(V)}] = 1.00 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$; $[\mathrm{H}Ta] = [\mathrm{H}Ci] = 1.00\ \mathrm{mol\,dm^{-3}}$

$[\mathrm{HClO_4}]/\mathrm{mol\,dm^{-3}}$	$I/\mathrm{mol\,dm^{-3}}$	$k_{\mathrm{obs}}/10^{-3}\ \mathrm{s^{-1}}$	
		H*Ta*	H*Ci*
0.05	[a]	1.07	–
0.10	[a]	1.35	1.97
0.15	[a]	1.49	–
0.20	[a]	–	4.10
0.25	[a]	1.92	–
0.30	[a]	–	5.64
0.40	[a]	–	8.05
0.50	[a]	2.22	10.96
0.55	[a]	2.60	–
0.60	[a]	–	12.22
0.70	[a]	2.87	13.69
0.80	[a]	–	15.97
0.85	[a]	3.04	–
0.90	[a]	–	16.87
1.00	[a]	3.30	–
0.10	[b]	1.16	1.41
0.15	[b]	1.36	–
0.20	[b]	–	3.21
0.25	[b]	1.82	–
0.30	[b]	–	5.58
0.40	[b]	2.37	7.37
0.50	[b]	–	10.29
0.55	[b]	2.73	–
0.60	[b]	–	10.81
0.70	[b]	3.17	14.85
0.80	[b]	–	15.84
0.85	[b]	3.44	–
0.90	[b]	–	18.56
1.00	[b]	3.73	–

[a] For H*Ta*, initial ionic strength is $0.16\ \mathrm{mol\,dm^{-3}}$ and $[\mathrm{HClO_4}] = [\mathrm{H^+}] = 0.15\ \mathrm{mol\,dm^{-3}}$; for H*Ci*, $0.21\ \mathrm{mol\,dm^{-3}}$ and $[\mathrm{H^+}] = 0.20\ \mathrm{mol\,dm^{-3}}$, but changes in the course of the reaction; [b] The ionic strength for H*Ta* is $1.10\ \mathrm{mol\,dm^{-3}}$ and $1.00\ \mathrm{mol\,dm^{-3}}$ for H*Ci* achieved by using $\mathrm{NaClO_4}$ as added electrolyte

and positive ($r \geq 0.9892$; $s \leq 9.79 \times 10^{-3}$) slopes, respectively. Control experiments showed negligible oxidation of methanol by V(V).

Effect of Temperature

The oxidation rates were measured at five different temperatures (293 to 313 K) by varying the substrate concentration (0.50 to $1.50\ \mathrm{mol\,dm^{-3}}$) while maintaining

Table 3. Ionic strength (I) effect on the pseudo-first order rate constants for tartaric acid and citric acid oxidation by V(V) at 303 K; $[V(V)] = 1.00 \times 10^{-2}$ mol dm^{-3}; [H*Ta*] = [H*Ci*] = 1.00 mol dm^{-3}

I/mol dm^{-3}	$k_{obs}/10^{-3}$ s^{-1}	
	H*Ta*[a]	H*Ci*[b]
0.16	1.26	–
0.20	1.29	–
0.30	–	3.90
0.40	–	3.72
0.50	1.31	3.61
0.60	–	3.57
0.70	–	3.40
0.80	1.33	3.37
0.90	–	3.31
1.00	–	3.21
1.10	1.36	–
1.25	–	3.10
1.40	1.38	–
1.70	1.39	–
2.00	1.42	–

[a] Initial ionic strength is 0.16 mol dm^{-3} and $[H^+] = 0.15$ mol dm^{-3}; [b] Initial ionic strength is 0.21 mol dm^{-3} and $[H^+] = 0.20$ mol dm^{-3}

Table 4. Pseudo-first order rate constants for H*Ta* and H*Ci* oxidation by V(V) in aqueous methanol solutions at 303 K for variable and constant ionic strength (I); $[V(V)] = 1.00 \times 10^{-2}$ mol dm^{-3}; [H*Ta*] = [H*Ci*] = 1.00 mol dm^{-3}

[*Me*OH]/%	I/mol dm^{-3}	$k_{obs}/10^{-3}$ s^{-1}	
		H*Ta*	H*Ci*
0	[a]	1.49	4.10
15	[a]	–	4.62
20	[a]	1.45	4.91
25	[a]	1.43	5.08
30	[a]	1.42	5.46
35	[a]	1.41	5.83
40	[a]	1.39	–
0	[b]	1.36	3.21
15	[b]	–	3.40
20	[b]	1.19	3.55
25	[b]	1.10	3.63
30	[b]	1.03	3.70
35	[b]	0.96	3.77
40	[b]	0.93	–

[a] For H*Ta* initial ionic strength is 0.16 mol dm^{-3} and $[H^+] = 0.15$ mol dm^{-3}; for H*Ci*, 0.21 mol dm^{-3} and $[H^+] = 0.20$ mol dm^{-3}, but changes in the course of the reaction; [b] The ionic strength for H*Ta* is 1.10 mol dm^{-3} and 1.00 mol dm^{-3} for H*Ci* achieved by using $NaClO_4$ as added electrolyte

Table 5. Temperature effect on the tartaric acid (H*Ta*) and citric acid (H*Ci*) oxidation by V(V) for variable and constant ionic strength (*I*)[a]; $[\mathrm{V(V)}] = 1.00\times10^{-2}\,\mathrm{mol\,dm^{-3}}$; $[\mathrm{S}] = 0.50-1.50\,\mathrm{mol\,dm^{-3}}$

T/K	I/mol dm^{-3}		$k_{\mathrm{obs}}/10^{-3}\,\mathrm{s^{-1}}$				
		[H*Ta*]/mol dm^{-3}	0.50	0.75	1.00	1.25	1.50
293	[b]		0.36	0.43	0.50	0.56	0.60
298	[b]		0.66	0.77	0.88	0.97	1.08
303	[b]		1.06	1.29	1.49	1.67	1.87
308	[b]		1.79	2.25	2.40	2.93	3.09
313	[b]		3.30	4.06	4.58	5.14	5.87
293	1.10		0.31	0.39	0.46	0.55	0.63
298	1.10		0.54	0.69	0.81	0.90	1.03
303	1.10		0.97	1.17	1.36	1.56	1.72
308	1.10		1.72	2.11	2.54	2.88	3.12
313	1.10		3.16	3.90	4.63	5.16	5.69
T/K	I/mol dm^{-3}		$k_{\mathrm{obs}}/10^{-3}\,\mathrm{s^{-1}}$				
		[H*Ci*]/mol dm^{-3}	0.50	0.75	1.00	1.25	1.50
293	[c]		1.00	1.20	1.35	1.54	1.75
298	[c]		1.92	2.23	2.47	2.68	2.99
303	[c]		3.09	3.56	4.10	4.70	5.15
308	[c]		4.65	5.80	6.72	7.31	8.17
313	[c]		7.54	8.95	10.33	11.01	12.55
293	1.00		0.75	0.87	0.99	1.10	1.28
298	1.00		1.57	1.69	1.96	2.17	2.44
303	1.00		2.51	2.85	3.21	3.67	4.15
308	1.00		3.90	4.29	5.19	5.81	6.38
313	1.00		5.49	6.83	7.35	8.24	8.97

[a] Constant ionic strength by using $\mathrm{NaClO_4}$ as added electrolyte; [b] Initial ionic strength is $0.16\,\mathrm{mol\,dm^{-3}}$ and $[\mathrm{H^+}] = 0.15\,\mathrm{mol\,dm^{-3}}$, but changes in the course of the reaction; [c] Initial ionic strength is $0.21\,\mathrm{mol\,dm^{-3}}$ and $[\mathrm{H^+}] = 0.20\,\mathrm{mol\,dm^{-3}}$, but changes in the course of the reaction

constant the other experimental conditions. The results for H*Ta* ($r \geq 0.9962$; $s \leq 3.89\times10^{-5}$) and for H*Ci* ($r \geq 0.9930$; $s \leq 4.65\times10^{-5}$) are shown in Table 5. The reaction order for both α-hydroxy acids remained around 0.5 in this temperature range. The apparent second order rate constants, k', were calculated from the slopes of the linear plots of k_{obs} against substrate concentration at different temperatures ($r \geq 0.9903$; $s \leq 2.14\times10^{-4}$). Activation parameters were calculated from the *Eyring* equation. For H*Ta* oxidation, the enthalpies of activation, $\Delta H^{\ddagger}$, 86.4 and $77.3\,\mathrm{kJ\,mol^{-1}}$, and the activation entropies, $\Delta S^{\ddagger}$, –19 and $-49\,\mathrm{J\,mol^{-1}\,K^{-1}}$ ($r \geq 0.9990$; $s \leq 7.52\times10^{-2}$) were calculated for variable and constant ionic strength, respectively. For H*Ci*, the enthalpies of activation are, 73.2 and $71.1\,\mathrm{kJ\,mol^{-1}}$, and the activation entropies, -56 and $-65\,\mathrm{J\,mol^{-1}\,K^{-1}}$ ($r \geq 0.9926$; $s \leq 4.02\times10^{-2}$) for variable and constant ionic strength, respectively.

Discussion

The empirical rate law found for H*Ta* oxidation, whether the ionic strength was varied or was kept constant, obeys fractional order dependence with respect to the H*Ta* (Table 1) and to the hydrogen ion concentration (perchloric acid) from 0.05 to 1.00 mol dm^{-3} (Table 2). The H*Ci* oxidation displays fractional order dependence with respect to the substrate and first order dependence on the hydrogen ion concentration. This is observed in the range of 0.10 to 0.90 mol dm^{-3} regardless of the ionic strength being variable or constant. The reaction is of first order with respect to the individual V(V) concentration, but the rate constants increase for H*Ta* oxidation between 0.50×10^{-2} and 2.50×10^{-2} mol dm^{-3} V(V) and decrease for H*Ci* oxidation from 0.50×10^{-2} until 2.00×10^{-2} mol dm^{-3} V(V) (Table 1).

Unlike the H*Ta* and H*Ci* oxidation by V(V) in sulfuric acid medium [4, 5], these two substrates are oxidized faster in perchloric acid when the ionic strength is varied. In order to understand this behavior, it is relevant to know the reactivity of V(V) species in perchloric acid medium under both conditions. With this in mind, geometrical optimization of V(V) hydrated species, namely $V(OH)_4^+$ and $V(OH)_3^{2+}$ [1, 3], was performed through density functional theory (DFT) at the SVWN/DN* [12] level. These calculations yield a tetrahedral structure for $V(OH)_4^+$ with no dipole moment, whereas $V(OH)_3^{2+}$ is predicted to be a planar symmetric species with a dipole moment. Based on these results, the higher reactivity can be attributed to $V(OH)_3^{2+}$ which is presumably the reactive species in perchloric acid medium at variable ionic strength. Whereas the less reactive species, $V(OH)_4^+$, would be found in a medium of constant ionic strength.

A positive dielectric effect (Table 4) and the absence of a primary salt effect (Table 3) in the H*Ta* oxidation suggest the production of a charged H*Ta*-V(V) complex, X^{*2+}, in the fast pre-equilibrium step. Furthermore, the activation entropies found for H*Ta* of –19 and $-49\,\text{J mol}^{-1}\,\text{K}^{-1}$ at variable and constant ionic strength, respectively, indicate that the activated complexes formed are more compact than the reagents. The interaction of the activated species with a water molecule yields the first CO_2 through a C–C fission and a free radical, $HOOCCH_2(OH)C\bullet CH_2COOH$ in the slow step. The formation of a polymeric product by addition of acrylamide indicates that V(V) behaves as an one-equivalent oxidant [13]. Subsequently, this radical could react with another V(V) to produce formaldehyde according to the scheme presented for constant ionic strength:

$$V(OH)_4^+ + H^+ + HOOCCH(OH)CH(OH)COOH \overset{K_1}{\rightleftharpoons} X^{*2+} \tag{1}$$

$$X^{*2+} \xrightarrow{k_2} HOOCCH(OH)\bullet CH(OH) + V(OH)_3^+ + CO_2 + H_3O^+ \tag{2}$$

$$HOOCCH(OH)\bullet CH(OH) + V(OH)_4^+ \xrightarrow{k_3} 2\,HCOH + CO_2 + V(OH)_3^+ + H_2O \tag{3}$$

The mechanism under conditions of variable ionic strength is similar to the one mentioned above, but $V(OH)_3^{2+}$ has to be taken into account as the oxidant. The rate law, assuming k_2 to represent the slow step, leads to

$$v = \frac{k_2 K_1 [\mathrm{H}Ta][\mathrm{H}^+][\mathrm{V(V)}]_t}{1 + K_1[\mathrm{H}Ta][\mathrm{H}^+]} \quad v = k_{\mathrm{obs}}[\mathrm{V(V)}]_t \quad k_{\mathrm{obs}} = \frac{k_2 K_1 [\mathrm{H}Ta][\mathrm{H}^+]}{1 + K_1[\mathrm{H}Ta][\mathrm{H}^+]} \tag{4}$$

where the total V(V) concentration at constant ionic strength is given by $[\mathrm{V(V)}]_t = [(X^*)] + [\mathrm{V(OH)_4}^+]$. The rate law (4) is in agreement with the experimental results since linearity is observed for the plot of $k_{\mathrm{obs}}{}^{-1}$ *vs.* $[\mathrm{H}Ta]^{-1}$ ($r \geq 0.9913$; $s \leq 27.3741$). K_1 is calculated to be 7.94 and k_2, $2.82\times10^{-3}\,\mathrm{s}^{-1}$ for variable ionic strength, while $K_1{}' = 7.53$ and $k_2{}' = 2.64\times10^{-3}\,\mathrm{s}^{-1}$ for fixed ionic strength.

On the other hand, increasing the methanol content in the reaction mixture, leads to an increase in the rate constant for the H*Ci* oxidation (Table 4). This may be attributed to a larger stabilization of the activated complex at low relative permittivity, which is less solvated than V(V) at higher dielectric constant because of its larger size. In addition, the activated complex is less polar than the reagents, *i.e.*, there is a negative charge delocalization of the carboxylate group through the bonds involved in the reaction. The entropies of activation found for H*Ci* are –56 and $-65\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for variable and constant ionic strength, respectively. These values indicate that the activated complexes with H*Ci* are more compact than those with H*Ta*. Except for the nature of the V(V) species, the mechanism is similar for media of variable and constant ionic strength. Taking into account that one of the reasons for the rate decrease is due to the lower solubility of H*Ci* in perchloric acid medium than in sulfuric acid, the oxidation rate as a function of the ionic strength may be considered practically constant, although the ionic charges product is −0.2 (Table 3). Hence, H*Ci* should undergo two deprotonation steps prior to reaction with $\mathrm{V(OH)_3}^{2+}$ to provide a neutral species, Y^*, in the transition state in a medium with variable ionic strength. Subsequently, the activated species Y^* interacts with H^+ to produce the first $\mathrm{CO_2}$ and the radical $\mathrm{HOOCCH_2(OH)C\bullet CH_2COOH}$ in the rate limiting step, as described in the following scheme:

$$\mathrm{V(OH)_3}^{2+} + \mathrm{HOOCCH_2(OH)C(COO^-)CH_2COO^-} \overset{K_4}{\rightleftharpoons} Y^* \tag{5}$$

$$Y^* + \mathrm{H}^+ \xrightarrow{k_5} \mathrm{HOOCCH_2(OH)C\bullet CH_2COOH} + \mathrm{CO_2} + \mathrm{V(OH)_3}^+ \tag{6}$$

By comparison, H*Ci* should undergo only one deprotonation before interacting with $\mathrm{V(OH)_4}^+$ to produce a neutral activated species Z^* in a medium of constant ionic strength:

$$\mathrm{V(OH)_4}^+ + \mathrm{HOOCCH_2(OH)C(COO^-)CH_2COOH} \overset{K_4'}{\rightleftharpoons} Z^* \tag{5'}$$

$$Z^* + \mathrm{H}^+ \xrightarrow{k_5} \mathrm{HOOCCH_2(OH)C\bullet CH_2COOH} + \mathrm{CO_2} + \mathrm{V(OH)_3}^+ \tag{6'}$$

In both cases, the subsequent rapid step would be the production of one more $\mathrm{CO_2}$, the $\mathrm{HOOCCH_2(OH)C\bullet CH_3}$ radical, and V(IV). In the final step, acetone is produced along with the release of a third $\mathrm{CO_2}$ molecule. Assuming the slow step as the rate-determining one, k_5 and $k_5{}'$, these mechanisms lead to the rate laws (7) for the oxidation of H*Ci* by V(V) in perchloric acid medium for variable and constant ionic strength, respectively.

$$v=\frac{k_5K_4[\mathrm{H}Ci][\mathrm{H}^+][\mathrm{V(V)}]_t}{1+K_3[\mathrm{H}Ci]} \qquad v=k_{\mathrm{obs}}[\mathrm{V(V)}]_t \quad k_{\mathrm{obs}}=\frac{k_5K_4[\mathrm{H}Ci][\mathrm{H}^+]}{1+K_4[\mathrm{H}Ci]} \tag{7}$$

Here the total concentrations of V(V) are given by $[\mathrm{V(V)}]_t=[(Y^*)]+[\mathrm{V(OH)_3}^{2+}]$ at variable ionic strength, and by $[\mathrm{V(V)}]_t=[(Z^*)]+[\mathrm{V(OH)_4}^{+}]$ at constant ionic strength. The rate law (7) is consistent with the experimental data, verified by the excellent linear plots of ${k_{\mathrm{obs}}}^{-1}$ *vs.* $[\mathrm{H}^+]^{-1}$ ($r\geq 0.9977$; $s\leq 15.3616$) rather than ${k_{\mathrm{obs}}}^{-1}$ *vs.* $[\mathrm{H}Ci]^{-1}$ ($r\geq 0.9698$; $s\leq 17.7849$). However, the numerical values of K_4 and k_5 (or K_4' and k_5') cannot be calculated from the expression above because of the dependence between $[\mathrm{H}^+]$ and $[\mathrm{H}Ci]$.

So far our approach has been based entirely on the experimental results. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ have been obtained from the *Eyring* equation and interpreted at a molecular level. The lower $\Delta H^\ddagger$ and the more negative $\Delta S^\ddagger$ account for the reaction being faster in sulfuric acid medium [4–7]. However, the oxidation takes place faster when the ionic strength is variable in perchloric acid medium and surprisingly the activation parameters follow the same trend as that observed in sulfuric acid medium. These values are presented in the section about the temperature effect and obtained from Table 5. This inversion suggests that occasionally it is adequate to link the equilibrium properties to the kinetic process. Furthermore, it is relevant to mention that there is a correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values [14] obtained from the oxidation of all the α-hydroxy acids by V(V) in both acidic media already investigated [4–8] with tartaric acid and citric acid in this work. Fig. 1 ($r=0.9984$; $s=0.9111$) shows the excellent linearity obtained for all these substrates. This means that the mechanism is independent of the structure of these α-hydroxy acids and that, the reactivity order may be reversed at a lower temperature than the isokinetic [14] one calculated to be 323 K.

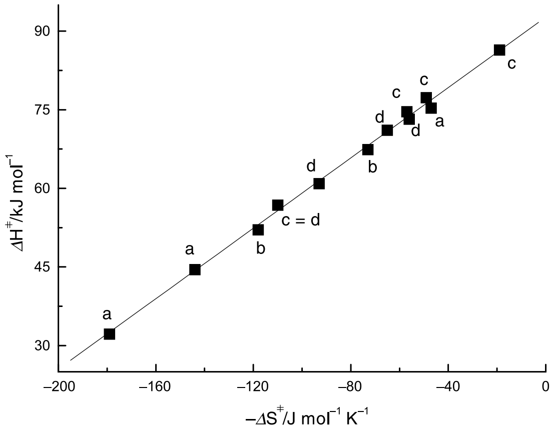

Fig. 1. Relationship between enthalpy ($\Delta H^\ddagger$) and entropy of activation ($\Delta S^\ddagger$) obtained from some α-hydroxy acids oxidation by V(V) in acidic medium; (a) malic acid; (b) lactic acid; (c) citric acid; (d) tartaric acid

In conclusion, the smaller V(V) reactivity in perchloric acid towards the H*Ci* and H*Ta* has brought out one characteristic not found previously in sulfuric acid medium, *i.e.*, the reactions are more favorable at variable ionic strength. Besides, the rate constant decrease with increasing V(V) concentration is more perceptible for the H*Ci* oxidation than for the H*Ta* one. This is due to the fact that H*Ci* oxidations suffer more from steric hindrances than H*Ta* oxidations do. In addition, H*Ci* deprotonates once and twice in media of constant and variable ionic strength, respectively. Sulfuric acid behaves differently, it reacts in the molecular form prior to the equilibrium step to yield the activated complex.

Experimental

Reagent grade chemicals and deionized water were employed in this work. Stock solutions of vanadium(V), V(V), were prepared as described previously [6]. $NaClO_4$ was used to maintain the ionic strength.

The kinetic measurements were carried out under pseudo-first order conditions with the substrate and perchloric acid in excess over V(V). The appearance of vanadium(IV), V(IV), was monitored spectrophotometrically (Hitachi U3000) at 760 nm (molar absorption coefficient, $18.91 \pm 0.83\,\mathrm{mol\,dm^{-3}\,cm^{-1}}$). The bath water was recirculated and maintained at a temperature of 303.0 ± 0.1 K (Microquímica MQBTC99-20). The oxidation progress was followed in a thermostated 1 cm quartz cell for periods of up to four half-lives. First-order rate constants, k_{obs}, were determined from the slopes of linear plots of ln [V(V)] against time, and were reproducible within $\pm 5\%$. The measurements were carried out in duplicate and, when necessary, in triplicate. The mediation of free radicals in the oxidation, the production of CO_2, the characterization of formaldehyde produced from tartaric acid, H*Ta*, and acetone from citric acid, H*Ci*, as well as the reaction stoichiometry have been previously described [4, 5]. The overall reaction for H*Ta* and H*Ci* oxidation by vanadium(V) may be represented by the following equations:

$$\mathrm{HOOCCH(OH)CH(OH)COOH + 2\ V(V) \rightarrow 2\ HCOH + 2\ CO_2 + 2\ V(IV) + H_2O}$$

$$\mathrm{HOOCCH_2(OH)C(COOH)CH_2COOH + 3\ V(V) \rightarrow CH_3COCH_3 + 3\ CO_2 + 3\ V(IV) + H_2O}$$

Here, V(V) stands for $\mathrm{V(OH)_3}^{2+}$ and $\mathrm{V(OH)_4}^{+}$ species in perchloric acid solutions for variable and constant ionic strength, respectively, while V(IV) represents the $\mathrm{V(OH)_3}^{+}$ species under both conditions.

Acknowledgments

This work was possible through the financial support of PADCT/CAPES, CNPq/PIBIC (*R.A.A.*), and CPG/UEL. We thank Prof. *J. M. Riveros* (University of São Paulo) for valuable suggestions concerning this study.

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