

## OXIDATION OF LACTIC ACID BY VANADIUM(V) IN SULPHURIC ACID MEDIUM: A KINETIC AND MECHANISTIC STUDY

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The rate of lactic acid, HL, oxidation by vanadium(V), V(V), in sulphuric acid solution has been measured by monitoring, spectrophotometrically, the absorbance change of vanadium(IV), V(IV) in 760 nm at 30°C. This oxidation is acid-catalysed, its dependence on acidity being complex. The rate showed a change in the reaction order with respect to the sulphuric acid concentration keeping constant or not the ionic strength. This reaction exhibited first order dependence on the V(V) and HL concentrations respectively and minimal dependence on sulphuric acid at lower concentrations (0.25 - 1.00 M) and fractionary ( $n = 0.40$ ) at higher range (1.25 - 1.75 M) in constant ionic strength. Without this control, the sulphuric acid dependence was greater and the order ( $n = 1.71$ ) was practically doubled in the higher concentration range (1.00 - 1.75 M) when compared with the lower one (0.25 - 0.75 M) and equal to 0.87. Dielectric constant decrease of the medium increased the rate constant. Energy of activation and parameters of activation were calculated studying the reaction at different temperatures. Oxidation mechanisms are proposed.

**Keywords:** lactic acid; oxidation kinetics; vanadium(V) oxidation.

## INTRODUCTION

Numerous reports are available on kinetics of oxidation of  $\alpha$ -hydroxycarboxylic acids by a variety of oxidants.<sup>1-8</sup> It has been established that the oxidation of some glycols<sup>9</sup> and hydroxy acids such as lactic, malic and mandelic acids<sup>10</sup> by vanadium(V) takes place through the C-C bond fission. In this paper we present the kinetic behaviour of the lactic acid (2-hydroxy propionic acid) oxidation by vanadium(V) in the sulphuric acid medium. Controlling or not the ionic strength, it was shown an inflexion on the slope, obtained from the plots between the observed rate constant and medium concentration, contrary to the malic acid<sup>11</sup> which exhibited a linear behaviour in the investigated concentration range.

## MATERIALS AND METHODS

The stock solution of vanadium(V), V(V), was prepared dissolving ammonium metavanadate,  $\text{NH}_4\text{VO}_3$  (Merck, p.a.) in an appropriate amount of sulphuric acid, yielding very stable pervanadyl ion,  $\text{VO}_2^+$ . This solution was diluted to the desired concentration by adding  $\text{NaHSO}_4$  solution to control ionic strength. The lactic acid, HL (Sigma, 98%), was used without previous purification. These solutions were prepared just before the experiments and the used reagents were of analytical grade.

The oxidation rate was measured spectrophotometrically (Varian spectrophotometer, mod. DMS-80) through vanadium(IV), V(IV) absorbance in the vanadyl form,  $\text{VO}^{2+}$ , at 760 nm using 1 cm pathlength cell at 30°C (variation  $\pm 0.1^\circ\text{C}$ ). These reactions were studied under pseudo-first order conditions and followed for four or five half-lives. The first order rate constants,  $k_{\text{obs}}$ , were estimated from the logarithm of V(V) absorbance in function of time and were reproducible to within 5%. The linearity of the plots (correlation coefficient,  $r > 0.9997$ , standard deviation,  $s \leq 4.0 \cdot 10^{-5}$ ) indicates that any

product formed during the reaction does not interfere in the rate. The rate constant,  $k_{\text{obs}}$ , calculation was carried out using a personal computer. The measurements were carried out in duplicates and, when necessary, in triplicates.

## RESULTS

## Stoichiometry of the reaction and product analysis

A reaction mixture of 3.0 ml containing HL ( $2 \times 10^{-3}$  moles) and V(V) (0.2 moles) in acidic medium (2.5 M) was thermostated at 40°C. The amount of yielded  $\text{CO}_2$  was determined by using a Warburg respirometer (B. Braun, mod. V-85). The ratio between HL and  $\text{CO}_2$  is equal one, and it was determined through the amount of liberated  $\text{CO}_2$  after more or less 6 hours of reaction.

In the kinetic measurement condition the reaction was allowed to stand at room temperature by several hours to determine the other products. The presence of aldehyde and/or ketone was characterized through the reaction with 2,4-dinitrophenylhydrazine. The differentiation was carried out by using the Tollens' reagent<sup>12</sup>. The reaction was positive to aldehyde. The characterization of formaldehyde was carried out through the chromotropic acid test<sup>13</sup>. The test was negative. The acetaldehyde was characterized through the formation of 1 mol of carbon dioxide.

## Free radical test

The reaction between V(V) and HL was carried out under kinetic conditions in the presence of recrystallized acrilamide solution (25%). After some hours, it was obtained a viscous solution indicating the presence of free radical species, capable to initiate the acrylamide polymerization. Control experiments were carried out excluding V(V) and/or hydroxy acid and the polymerization was not observed.

### Effect of reagents concentration

The oxidation rate increased, controlling or not the ionic strength, with the increase of lactic acid concentration, [HL] in excess keeping constant the initial concentrations of V(V), [V(V)]<sub>0</sub> and sulphuric acid, [H<sub>2</sub>SO<sub>4</sub>]<sub>0</sub>, as it is showed in Table I ( $r > 0.9992$ ,  $s \leq 6.2 \times 10^{-5}$ ). Plots of  $\log [V(V)]$  in function of time in different initial concentrations of lactic acid, [HL]<sub>0</sub>, are linear ( $r > 0.9988$ ,  $s \leq 0.026$ ). The order with respect to HL is approximately one and it was determined from the slope of the linear plot obtained between the logarithms of  $k_{obs}$  and [HL]<sub>0</sub>. The variation of [V(V)]<sub>0</sub> from 0.005 to 0.025 M increased the rate constant for around 20% without ionic strength control, and about 30% with control, as it can be observed in the Table II.

**Table I.** Effect of concentration of lactic acid on the reaction rate at 30°C in sulphuric acid medium.

[H <sub>2</sub> SO <sub>4</sub> ] M	I/M [S]/M	$k_{obs}/10^{-3}s^{-1}$					$k' \cdot 10^3$ M <sup>-1</sup> · s <sup>-1</sup>
		0.50	0.75	1.00	1.24	1.50	
0.75	—	1.22	1.74	2.43	3.05	3.70	2.51
1.25	—	2.17	3.08	4.15	5.18	6.05	3.95
0.75	2.0	2.97	4.18	5.54	6.69	7.92	4.96

[S] = [HL], [V(V)] = 0.010 M.

**Table II.** Effect of the concentration of V(V) on the reaction rate at 30°C.

[H <sub>2</sub> SO <sub>4</sub> ] M	I M	[HL] M	[V]/10 <sup>-2</sup> M	$k_{obs}/10^{-3}s^{-1}$				
				0.50	1.00	1.50	2.00	2.50
0.75	—	1.0		2.21	2.43	2.49	2.56	2.65
0.75	2.0	1.0		5.33	5.54	6.15	6.45	7.03

### Effect of medium concentration

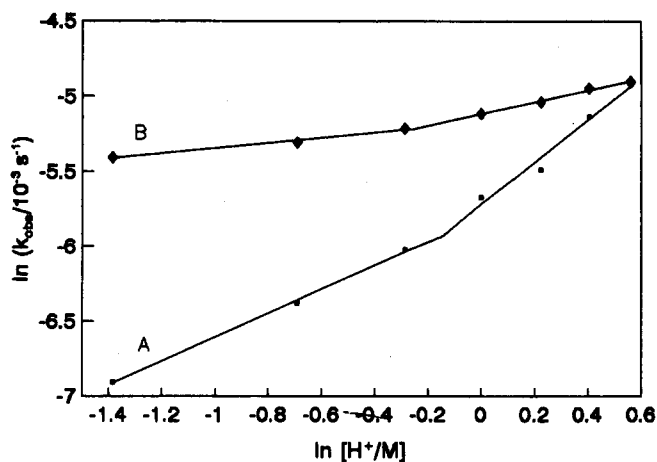
An increase in the oxidation rate was observed with the increase of acid sulphuric concentration, [H<sub>2</sub>SO<sub>4</sub>] ( $r = 0.9984$ ,  $s \leq 6.9 \times 10^{-5}$ ), as it is shown in the Table III, maintaining fixed the ionic strength and initial reagent concentrations at 30°C. The reaction order with respect sulphuric acid concentration was estimated through the plot between the logarithm of  $k_{obs}$  and [H<sup>+</sup>], given by [H<sub>2</sub>SO<sub>4</sub>]<sub>0</sub> (Figure 1). It was found to be 0.17 ( $r = 0.9916$ ,  $s \leq 0.017$ ) in the concentration range of 0.25 to 0.75 M and 0.40 ( $r = 0.9946$ ,  $s \leq 0.012$ ) from 1.00 to 1.75 M. When the ionic strength was not controlled, it was observed a more accentuated trend change around 1.0 M [H<sub>2</sub>SO<sub>4</sub>], whose orders were found to be respectively,

**Table III.** Effect of the medium concentration on the reaction rate at 30°C.

I/M [HL] M	[H <sup>+</sup> ] M	$k_{obs}/10^{-3}s^{-1}$							<i>n</i>
		0.25	0.50	0.75	1.00	1.25	1.50	1.75	
—	1.0	1.00	1.70	2.43	3.44				0.87 <sup>a</sup>
—	1.0					4.15	5.90	7.36	1.71 <sup>a</sup>
2.0	1.0	4.49	4.96	5.44					0.17 <sup>b</sup>
2.0	1.0				6.01	6.49	7.13	7.44	0.40 <sup>b</sup>

[V(V)] = 0.010 M, [H<sup>+</sup>] = [H<sub>2</sub>SO<sub>4</sub>]

<sup>a</sup> and <sup>b</sup>: values of two experimental series.



**Figure 1.** Plots of  $\ln k_{obs}$  vs  $\ln [H^+]$  at 30°C. [V(V)] = 0.010 M, [HL] = 1.0 M, [H<sub>2</sub>SO<sub>4</sub>] = 0.25 - 1.75 M, (A) without ionic strength control, (B) I = 2.0 M.

0.87 ( $r = 0.9954$ ,  $s \leq 0.062$ ) and 1.71 ( $r = 0.9966$ ,  $s \leq 0.034$ ). These behaviours indicate that the mechanism of oxidation changes in the investigated concentration range.

### Effect of ionic strength

The ionic strength was varied through the addition of the concentrated solution of sodium bisulphate (5 M). The rate was doubled in the range from 1.0 to 2.5 M (Table IV).

**Table IV.** Effect of the ionic strength on the reaction rate at 30°C.

[H <sub>2</sub> SO <sub>4</sub> ] M	[HL] M	I/M	$k_{obs}/10^{-3}s^{-1}$				<i>z+z.</i>
			1.00	1.50	2.00	2.50	
0.75	1.0		3.05	4.36	5.68	7.40	0.66

[V(V)] = 0.010 M.

### Effect of solvent

The oxidation was performed in water-methanol mixtures varying the compositions. The decrease of dielectric constant of the medium by the addition of methanol exhibited an increase in the oxidation rate (Table V). The control experiment was carried out oxidizing methanol by V(V) in kinetic measurement condition, being verified a negligible oxidation.

**Table V.** Effect of the dielectric constant on the rate of reaction at 30°C.

[H <sub>2</sub> SO <sub>4</sub> ] M	[HL] M	MeOH/%	$k_{obs}/10^{-3}s^{-1}$				
			20	25	30	35	40
0.75	1.0		3.22	4.12	4.42	5.93	6.00

[V(V)] = 0.010 M.

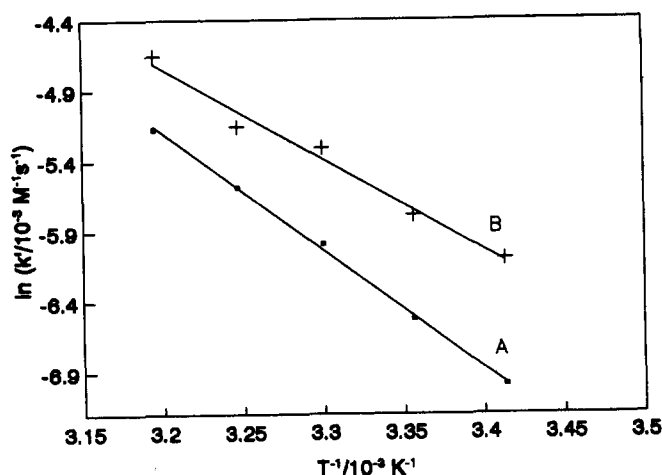
### Effect of temperature

The oxidation rate was measured varying the temperatures from 20 to 40°C and maintaining constant all the other experimental conditions. These results are given in Table VI ( $r > 0.9980$ ,  $s \leq 1.1 \times 10^{-4}$ ). From Arrhenius plots (Figure 2,  $r > 0.9902$ ,  $s \leq 0.090$ ) between second order rate constant,  $k'$  and reciprocal of absolute temperature,  $1/T$ , the activation energy and other activation parameters were estimated (Table VII).

**Table VI.** Effect of the temperature on the rate of reaction in sulphuric acid medium.

I/M	t/°C	$k_{obs}/10^{-3}s^{-1}$					$k'$ $10^{-3}M^{-1}s^{-1}$
		[S]/M	0.50	0.75	1.00	1.25	
—	20	0.49	0.68	0.93	1.13	1.41	0.92
—	25	0.77	1.09	1.51	1.85	2.23	1.47
—	30	1.22	1.74	2.43	3.05	3.70	2.51
—	35	1.98	2.73	3.80	4.84	5.61	3.75
—	40	3.07	4.31	5.81	7.36	8.65	5.68
2.0	20	1.13	1.65	2.15	2.74	3.40	2.25
2.0	25	1.98	2.75	3.40	4.18	5.10	3.07
2.0	30	2.97	4.18	5.54	6.69	7.92	4.96
2.0	35	5.55	6.89	8.31	9.83	11.29	5.77
2.0	40	6.88	9.33	11.76	14.40	16.24	9.52

[S] = [HL], [V(V)] = 0.010 M, [H<sub>2</sub>SO<sub>4</sub>] = 0.75 M.



**Figure 2.** Plots between  $\ln k'$  and  $1/T$  for  $[V(V)] = 0.010 M$ ,  $[H_2SO_4] = 0.75 M$ ,  $[HL] = 0.50 - 1.50 M$ , (A) without ionic strength control, (B)  $I = 2.0 M$ .

**Table VII.** Thermodynamic parameters for the oxidation of lactic acid by V(V) calculated from the values of  $k'$  (Table VI).

medium	I/M	$E^\ddagger$	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta S^\ddagger$
		$kJ/mol$	$kJ/mol$	$kJ/mol$	$kJ/mol.K$
H <sub>2</sub> SO <sub>4</sub>	—	69.9	67.4	89.2	-73
H <sub>2</sub> SO <sub>4</sub>	2.0	54.5	52.1	87.2	-118

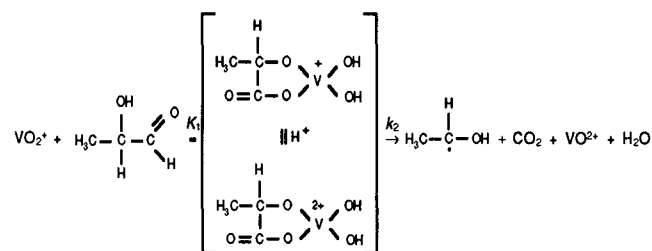
## DISCUSSION

The HL oxidation rate law, in sulphuric acid medium, is given by  $r = k[V(V)][HL][H^+]^x$  where  $x = 0.87$  in the range of 0.25 to 1.00 M and  $x = 1.71$  from 1.25 to 1.75 M without ionic strength control. When it is maintained constant and equal to 2 M,  $x = 0.17$  from 0.25 to 0.75 M and 0.40 from 1.00 to 1.75 M. We assumed that sulphuric acid behaves like a strong monobasic acid, that is, in terms of the concentration of hydrogen and/or bisulphate ions.

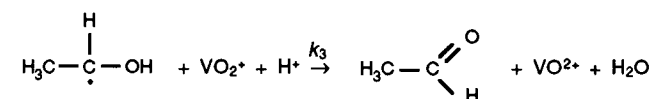
Although vanadium (V) is amphoteric, the oxidation by it in acidic solution ( $>0.005 M$ ) involves cationic species. In the acidity region of 0.1 M vanadium(V) exists as pervanadyl ion,  $VO_2^+$ , which is also believed to exist in the hydrated form  $V(OH)_4^+$ <sup>14</sup>. It has been established that, in more concentrated

solution, the protonated form of the oxidant  $V(OH)_3^{2+}$  is more reactive<sup>15</sup>. The rate increase with the ionic strength is especially due to the greater interactions of the system with NaHSO<sub>4</sub>, and on the other hand, a small rate dependence with the increase of sulphuric acid concentration in the constant ionic strength was observed (Table III). In the lower concentration range, we presume that the active oxidant is in the form of pervanadyl ion,  $VO_2^+$ , rather than  $V(OH)_3^{2+}$ , as takes place in the higher concentration range. As the ionic charge product,  $z_1z_2$ , is 0.66 ( $r = 0.9995$ ,  $s \leq 0.0051$ ) (Table IV), the reaction takes place between ions of same charge and/or ion-dipole<sup>17</sup> in the rate-determining step. The increase of oxidation rate with the decrease of dielectric constant of the solution (Table V) indicates that a decrease in the solvent polarity favours the reaction.<sup>18,19</sup> Thus, the transition state is less polar than the reagents or solvents providing more hydrogen bonding that can stabilize the activated complex, and in this manner to decrease the next step of the reaction.

Taking into account all mentioned aspects in constant ionic strength, the cyclic activated complex is formed in a rapid equilibrium ( $K_1 = k_1/k_{-1}$ ) between V(V) and HL in a mechanism practically independent on hydrogen ions, since those would do an intramolecular exchange in these cyclic complexes in the concentration range varying from 0.25 to 0.75 M.



The rupture of the C-C bond might occur from the activated complex in the slow step,  $k_2$  producing the carbon dioxide and consequently the formation of a free radical and vanadium (IV). It has been exhibited earlier<sup>9</sup> that the most reactions involving V(V) proceed via free radical mechanism, wherein V(V) undergoes an one-electron reduction. In the present investigation as in the malic acid oxidation<sup>11</sup> the addition of acrylamide to the reaction mixture gave a polymeric product indicating that, V(V) behaves as an one-equivalent oxidant, and that free radicals are formed in the rate-determining step. This free radical is, then, attacked by another mole of V(V) to produce immediately acetaldehyde and V(IV)



Through this mechanism and considering the slow step as the rate-determining one,  $k_2$ , it obtains

$$R = -\frac{d[V(V)]_t}{dt} = \frac{k_1 k_2 [V(V)][HL]}{k_2 + k_{-1}} \quad (1)$$

where  $[V(V)]$  is equal to  $[VO_2^+]$  and  $[HL]$ , the lactic acid concentration, and assuming that  $k_2 \ll k_{-1}$  the equation (1) can be simplified to

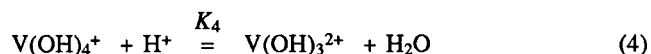
$$R = -\frac{d[V(V)]}{dt} = k_2 K_1 [V(V)] [HL] = k_{obs} [V(V)] \quad (2)$$

where

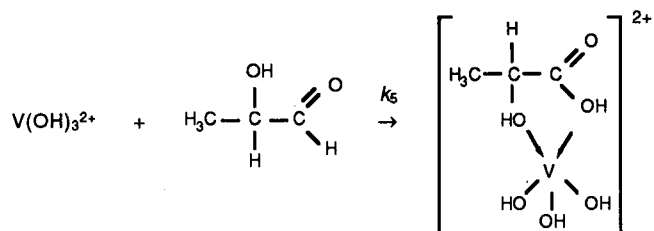
$$k_{obs} = k_2 K_1 [HL] \quad (3)$$

This rate law is in agreement with the experimental rate law mentioned above, that is, first order dependence on  $[V(V)]$  and  $[HL]$  and independent on  $[H^+]$ . Substituting the results of the Table I in the equation (3) the product  $k_2K_1$  becomes equal to  $4.96 \cdot 10^{-3} M^{-1} s^{-1}$ .

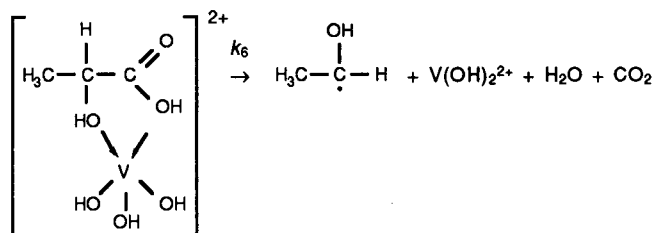
On the other hand, it was observed a fractionary dependence on hydrogen ions in the higher concentration range, that is, from 1.25 to 1.75 M in constant ionic strength. In this case the mechanism is similar to malic acid oxidation<sup>11</sup> through the hydrated species of the pervanadyl ion,  $V(OH)_4^+$ , in equilibrium with  $V(OH)_3^{2+}$  according to the equation (4)



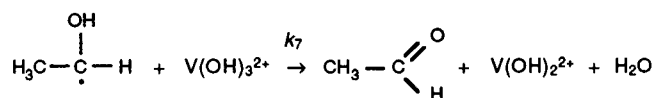
This species reacts, in the slow step, with the HL in the unionized form and produces an activated complex with a positive charge of 2+



In a rapid subsequent reaction the rupture of the C-C bond takes place to give  $\text{CO}_2$ , and consequently the formation of a free radical and  $V(IV)$ .



This free radical is, then, attacked by another  $V(V)$  to produce immediately acetaldehyde and  $V(IV)$  likewise the rapid step,  $k_3$ , of acid-independent mechanism



When this mechanism is taken into account the acid-dependent reaction rate becomes

$$R = -\frac{d[V(V)]_t}{dt} = \frac{K_4 k_5 [V(V)]_t [H^+][HL]}{(k_5/k_{-4})[HL] + 1 + K_4 [H^+]} \quad (5)$$

where the total or analytical concentration of vanadium(V) is given by

$$[V(V)]_t = [V(OH)_4^+] + [V(OH)_3^{2+}] \quad (6)$$

Assuming that  $k_5[HL]$ ,  $k_{-4}$  the equation (5) becomes

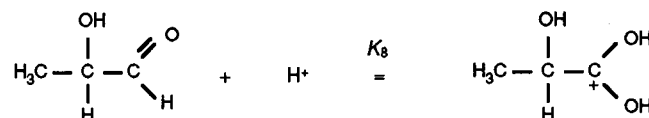
$$R = \frac{K_4 k_5 [V(V)]_t [H^+][HL]}{1 + K_4 [H^+]} = k_{\text{obs}} [V(V)]_t \quad (7)$$

where

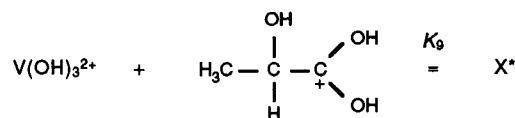
$$k_{\text{obs}} = \frac{K_4 k_5 [H^+][HL]}{1 + K_4 [H^+]} \quad (8)$$

From the slope and intercept of the double reciprocal plots of the equation (8),  $1/k_{\text{obs}}$  vs  $1/[H^+]$  ( $r = 0.9939$ ,  $s \leq 1.94$ ) at constant  $[HL]$  were obtained the equilibrium constant,  $K_4$ , equal to 1.18 at  $30^\circ\text{C}$  and the value of the rate constant in the rate-determining step,  $k_2$ , equal to  $11.05 \cdot 10^{-3} M^{-1} s^{-1}$  at constant ionic strength equal to 2.0 M.

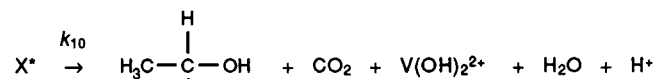
In order to account for the effect of the hydrogen ion concentration in this oxidation, without ionic strength control (Table III), it is necessary to postulate that for  $[H^+] < 1.0 M$  the active species is  $V(OH)_3^{2+}$ , as the rate is approximately proportional to first order. For  $[H^+] > 1.0 M$  besides the species  $V(OH)_3^{2+}$ , it may occur the protonation of HL, and the kinetic behaviour is approximately of second order. Therefore, in these conditions the oxidations are acid-catalysed, and the pervanadyl ion,  $\text{VO}_2^+$ , could be found in the hydrated species, such as  $V(OH)_4^+$  in equilibrium with  $V(OH)_3^{2+}$  according to the equation (4), and in higher acidity of the medium HL could be in the protonated form



These species react rapidly to yield an activated complex,  $X^*$



which produces the free radical,  $\text{CO}_2$  and  $V(IV)$  in the slow step,  $k_{10}$



Finally, this radical with another mol of  $V(V)$  yields a mol of acetaldehyde and  $V(IV)$  by the same way of the rapid step,  $k_3$ . When this mechanism is taken into account the acid-dependent reaction rate becomes

$$R = -\frac{d[V(V)]_t}{dt} = \frac{K_4 k_9 k_{10} [V(V)]_t [H^+][HL]}{K_{-9} + k_{10}} \quad (9)$$

where the total or analytical concentration of  $V(V)$  is given by (6) and assuming that  $k_9 \gg k_{10}$  the equation (9) can be written in terms of the product formed by the equilibrium and rate constants,  $K_4 K_9 k_{10}$

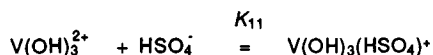
$$R = -\frac{d[V(V)]_t}{dt} = K_4 K_9 k_{10} [H^+][HL][V(V)]_t \quad (10)$$

where

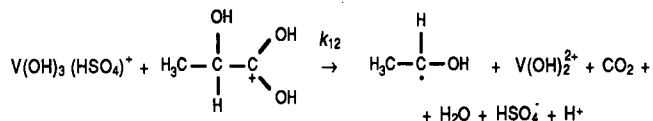
$$k_{\text{obs}} = K_4 K_9 k_{10} [H^+][HL] \quad (11)$$

This rate law is in agreement with the experimental one, considering  $x \cong 1$  for oxidation in low concentration range of sulphuric acid. Substituting the values of the Table III in the equation (11) at constant  $[HL]$ , the slope given by the product  $K_4 K_9 k_{10}$  is equal to  $3.22 \times 10^{-3} M^{-1} s^{-1}$  ( $r = 0.9958$ ,  $s \leq 1.17 \times 10^{-4}$ ).

When  $[H_2SO_4]$  is more than 1.0 M, without ionic strength control, the reaction order is 1.7, and in this case the mechanism involves another reactive species besides  $V(OH)_3^{2+}$ , formed through the interaction between  $V(OH)_3^{2+}$  and  $HSO_4^-$ ,  $V(OH)_3(HSO_4)^+$ <sup>15</sup>



and HL could be in the protonated form,  $K_8$ . Both the species would produce, in the rate determining step, a mol of carbon dioxide through the C-C bond rupture, the free radical and V(IV)



and in a rapid subsequent and final step,  $k_3$ , the formation of acetaldehyde and V(IV). From this mechanism, we may obtain the following rate equation:

$$R = \frac{d[V(V)]_t}{dt} = \frac{K_8 k_{11} k_{12} [V(V)]_t [H^+] [HSO_4^-] [HL]}{K_{11} [HSO_4^-] + k_{11} + K_8 k_{12} [HL] [H^+]} \quad (12)$$

Taking into account  $[HSO_4^-] = [H^+]$  and as  $k_{11} \gg k_{12}$  the equation (12) can be simplified, and in terms of equilibrium constants,  $K_8$  and  $K_{11}$ , it obtains

$$R = - \frac{d[V(V)]_t}{dt} = \frac{K_8 k_{11} k_{12} [V(V)]_t [H^+]^2 [HL]}{1 + K_{11} [H^+]} = k_{obs} [V(V)]_t \quad (13)$$

where

$$k_{obs} = \frac{K_8 k_{11} k_{12} [H^+]^2 [HL]}{1 + K_{11} [H^+]} \quad (14)$$

The rate law (14) is consistent with experimental rate law, as it supports the fractional order dependence higher than one with respect to  $[H^+]$  and first order dependence on  $[HL]$  and  $[V(V)]$ , respectively. Substituting the values of the Table III in the equation (14), the product  $K_8 k_{12}$  is equal to  $5.73 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$  and  $K_{11}$ , equal to 0.82. These values were determined using a non-linear regression program.<sup>20</sup>

The negative values of entropy of activation (Table VII) indicate that the activated complexes are more rigid than the reagents. In the case of fixed ionic strength the value is more negative (-118 J/mol.K), because these species are little affected by the medium acidity, as it occurs when the ionic strength is not constant (-73 J/mol.K). The small values of  $\Delta H^\ddagger$  suggest that the oxidation is controlled by entropy. Therefore, these results and experimental rate laws suggest that the

oxidation mechanism of the HL by V(V) in sulphuric acid medium depends on the control or not of the ionic strength of the solution.

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