Citric Acid Oxidation by Vanadium(V) in Sulfuric Acid Medium: Kinetic and Mechanistic Study

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ABSTRACT: The citric acid oxidation by vanadium(V) in sulfuric acid medium at 303 K is reported. The reaction rate was determined spectrophotometrically by monitoring the formation of vanadium(IV) at 760 nm. The oxidation showed a first-order dependence with respect to vanadium(V) concentration and fractional order with respect to citric acid concentrations, with no control and with constant ionic strength. The reaction is also first order with respect to sulfuric acid concentration with no control and of fractional order at constant ionic strength. The reaction rate is enhanced by an increase of ionic strength and increased by a decrease of the dielectric constant. 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. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 566–572, 2000

INTRODUCTION

The kinetics and mechanism of the oxidation of organic ligands by aquavanadium(V) ions has been previously reviewed [1]. However, relatively few studies have addressed the question of the nature of the oxidizing species in these systems [2,3] because, apparently, the kinetic behavior of hydroxyacids oxidations are considered well established.

We have observed in our investigations [4–7] that the mechanism route depends on several factors, such as the structure of the substrates, the nature and the oxidizing capacity of the oxidant, the reaction conditions, and the actual products isolated. The participation of some active species of vanadium(V) in these oxidations [4–7] showed that different mechanisms are operative in sulfuric acid and/or perchloric acid media. For example, the oxidation of malic acid was carried out in both media [5,7] and displays a faster rate in sulfuric acid with ionic strength control. The reaction rate in this medium showed first-order behavior with respect to oxidant, substrate, and hydrogen ion concentrations with or without control of the ionic strength [5]. However, when this oxidation was performed in perchloric acid, the rate law was the same regardless of the ionic strength variation displaying first-order behavior with respect to the oxidant and malic acid concentrations and fractional order with respect to the hydrogen ion concentration. Therefore, a similar mechanism appears to be in effect with or without control of ionic strength [7]. Meanwhile, the tartaric acid oxidation in sulfuric acid medium presented a first-order dependence with respect to vanadium(V) and fractional orders with respect to tartaric acid and sulfuric acid concentrations, with no control and with constant ionic strength. In this case, a faster rate is

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Correspondence to: K. Takashima (keiko@uel.br) observed at a fixed ionic strength [4]. When lactic acid was oxidized in sulfuric acid medium, a faster rate was also observed with ionic strength control, and the plot of ln k_{obs} vs. ln$[H^+]$ displayed an inflection under both conditions, indicating two different orders in the investigated hydrogen ion concentration range. 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 [8]. In continuation with our studies, we report herein the results of the oxidation of citric acid by vanadium(V) in sulfuric acid medium under variable and constant ionic strength conditions.

EXPERIMENTAL SECTION

Solutions of vanadium(V), V(V), (Merck) and citric acid, HCi (Reagen), were prepared by dissolving appropriate amounts in deionized water, with or without control of the ionic strength, as described previously [4–7]. $NaHSO_4$ was used to maintain the ionic strength. All the reagents were of analytical grade.

All kinetic measurements were performed under pseudo-first-order rate conditions with citric acid in at least 50-fold excess over vanadium(V), V(V), by 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). Spectra of different vanadium(IV) solutions in the range from 5.0×10^{-3} to 3.0×10^{-2} mol dm^{-3} were recorded from 500 to 800 nm using a cell of 1-cm path length. At 760 nm, the molar absorption coefficient has been found to be (18.91 ± 0.83) mol dm^{-3} cm^{-1}. The first-order rate constants, k_{obs}, were evaluated from the slopes of the linear plots of ln[V(V)] against time and were reproducible within ±5%. The measurements were carried out in duplicate and, when necessary, in triplicate.

The reaction mixture was allowed to stand for several hours with recrystallized acrylamide (25% v/v) under kinetic conditions. The formation of gel indicates free-radical intervention in the oxidation. Control experiments in which either V(V) or HCi were excluded demonstrated the absence of polymerization.

The other oxidation product was identified as acetone after some reactions, such as with 2,4-dinitrophenylhydrazine, displayed positive result; the Tollens reagent and chromotropic acid test both yielded negative [8]. The stoichiometry was determined as described earlier [6]. A reaction mixture containing an excess of V(V) of 0.15 M over HCi (2.0×10^{-3} mol dm^{-3}) in acidic medium (2.50 mol dm^{-3}) was thermostated at 313 K. A yield of 3.0 (±0.3) moles of CO_2 for each mole of HCi was obtained in a Warburg

Table I Pseudo-First-Order Rate Constants for the Oxidation of Citric Acid by V(V) with No Control of Ionic Strength (I) and at Constant Ionic Strength;* $[H_2SO_4] = 0.20$ mol dm^{-3} and T = 303 K

I/mol dm^{-3}	[V(V)]/10^{-2} mol dm^{-3}	[HCi]/mol dm^{-3}	$k_{obs}/10^{-3}$ s^{-1}
[a]	1.00	0.50	4.11
[a]	1.00	0.75	4.84
[a]	1.00	1.00	5.71
[a]	1.00	1.25	6.19
[a]	1.00	1.50	6.97
1.00	1.00	0.50	6.35
1.00	1.00	0.75	7.91
1.00	1.00	1.00	9.40
1.00	1.00	1.25	10.57
1.00	1.00	1.50	12.13
[a]	0.50	1.00	6.10
[a]	1.50	1.00	5.38
[a]	2.00	1.00	5.08
[a]	2.50	1.00	4.87
1.00	0.50	1.00	10.37
1.00	1.50	1.00	7.65
1.00	2.00	1.00	6.93
1.00	2.50	1.00	6.23

[a] Initial ionic strength is 0.21 mol dm^{-3} but changes in the course of the reaction.

* Ionic strength was achieved by using $NaHSO_4$ as added electrolyte.

respirometer (B. Braun, model V-85) at 313 K. The overall reaction for citric acid oxidation may be represented by the following equation:

$$HOOCCH_2(OH)C(COOH)CH_2COOH + 3V(V) \longrightarrow CH_3COCH_3 + 3CO_2 + 3V(IV) + 2H_2O$$

where V(V) and V(IV) represent the charged vanadium species in sulfuric acid medium with no control of ionic strength—$V(OH)_3HSO_4^+$ and $V(OH)_2HSO_4^+$, respectively.

RESULTS

Effect of Reactants Concentration

The citric acid concentration, [HCi], was varied in the range from 0.50 to 1.50 mol dm^{-3} when the initial concentrations of V(V), $[V(V)]_0$, and sulfuric acid, $[H_2SO_4]_0$, were maintained constant at 303 K. The oxidation rate was more rapid when the ionic strength was controlled and the rate constants, k_{obs}, varied by about 65% with no control of ionic strength and ~90% at constant ionic strength as shown in Table I ($r \geq 0.9963$ and $s \leq 1.087 \times 10^{-4}$). Individual plots of ln[V(V)] as a function of time for different initial concentrations of citric acid, $[HCi]_0$, display satisfactory linearity ($r \geq 0.9988$ and $s \leq 3.580 \times 10^{-4}$) at 303 K, and the order with respect to [HCi] is around 0.5 ($r \geq 0.9978$ and $s \leq 1.567 \times 10^{-2}$) in both media with no control of ionic strength and at constant ionic strength. The variation of $[V(V)]_0$ from 0.50×10^{-2} to 2.50×10^{-2} mol dm^{-3} decreased the rate constant by about 20% ($r = -0.9943$ and $s = 6.074 \times 10^{-5}$) in solutions with no control of ionic strength, and by about 40% ($r = -0.9850$ and $s = 3.435 \times 10^{-4}$) at constant ionic strength as indicated also in Table I.

Effect of Hydrogen Ion Concentration

The oxidation rate increased with increasing hydrogen ion concentration, [H$^+$], from 0.10 to 0.90 mol dm^{-3} through the addition of sulfuric acid by about an eightfold with no control and approximately threefold with control, maintaining the same initial reactant concentrations, $[V(V)]_0$ and $[HTA]_0$. The pseudo-first-order rate constants at 303 K are presented in Table II. The reaction order for the reaction without ionic strength control was first order ($r = 0.9977$ and $s = 4.792 \times 10^{-2}$); and with control, around 0.50 ($r = 0.9937$ and $s = 4.712 \times 10^{-2}$).

Table II Effect of the H_2SO_4 Concentration on the Pseudo-First-Order Rate Constants at 303 K with No Control of Ionic Strength (I) and at Constant Ionic Strength;* $[V(V)] = 1.00 \times 10^{-2}$ mol dm^{-3} and [HCi] = 1.00 mol dm^{-3}

$[H_2SO_4]$/mol dm^{-3}	I/mol dm^{-3}	$k_{obs}/10^{-3}$ s^{-1}
0.10	0.11	2.78
0.20	0.21	5.71
0.30	0.31	8.40
0.40	0.41	11.21
0.50	0.51	12.89
0.60	0.61	16.80
0.70	0.71	17.14
0.80	0.81	18.44
0.90	0.91	21.49
0.10	1.00	6.88
0.20	1.00	9.40
0.30	1.00	11.54
0.40	1.00	13.52
0.50	1.00	15.72
0.60	1.00	17.61
0.70	1.00	18.86
0.80	1.00	22.52
0.90	1.00	23.14
0.20	0.30	4.94
0.20	0.40	5.38
0.20	0.50	5.85
0.20	0.60	6.76
0.20	0.70	7.34
0.20	0.80	7.84
0.20	0.90	8.22
0.20	1.25	10.59

[a] Constant ionic strength was achieved by using $NaHSO_4$ as added electrolyte.

Effect of Ionic Strength

The pseudo-first-order rate constant doubled when the ionic strength was changed in the range of 0.30 to 1.25 mol dm^{-3} by the addition of a concentrated solution of sodium bisulfate (5.0 mol dm^{-3}) in the reactant solution (Table II). The plot of log k_{obs} as a function of the square root of the ionic strength at 303 K [9, 10] gives a product of the ionic charges, z_+z_-, of 0.60 ($r = 0.9959$ and $s = 1.07 \times 10^{-2}$).

Effect of Solvent

The oxidation rate enhanced with the increase of methanol content for ~50% with no control of ionic strength and ~30% with control (Table III), changing the solvent composition by the addition of methanol to aqueous medium (0–35% v/v). Plots of ln k_{obs} vs. the reciprocal of dielectric constant of the medium,

Table III Pseudo-First-Order Rate Constants for the Oxidation of Citric Acid by V(V) in Binary Aqueous Mixtures of Methanol with No Control of Ionic Strength (I) and at Constant Ionic Strength;* [V(V)] = 1.00×10^{-2} mol dm^{-3}, [HCi] = 1.00 mol dm^{-3}, [H_2SO_4] = 0.20 mol dm^{-3} and T = 303 K

[MeOH]/%	I/mol dm^{-3}	$k_{obs}/10^{-3}$ s^{-1}
0	[a]	5.71
15	[a]	7.05
20	[a]	7.47
25	[a]	8.04
30	[a]	8.25
35	[a]	8.55
0	1.00	9.40
15	1.00	9.86
20	1.00	10.51
25	1.00	10.95
30	1.00	11.56
35	1.00	12.15

* Ionic strength was achieved by using $NaHSO_4$ as added electrolyte

[a] Initial ionic strength is 0.21 mol dm^{-3} but changes in the course of the reaction.

1/**ε** [11] resulted in straight lines ($r \geq 0.9753$, $s \leq 3.65 \times 10^{-2}$). Control experiments showed a negligible oxidation of methanol by V(V).

Effect of Temperature

The oxidation rate was measured by varying the temperature from 293 to 313 K, keeping the other experimental conditions constant. These results are given in Table IV ($r \geq 0.9963$ and $s \leq 1.087 \times 10^{-4}$), and the reaction order with respect to [HCi] remains around 0.5. Arrhenius plots were constructed from ln k' (the apparent second-order rate constants, obtained from Table IV) vs. the reciprocal absolute temperature. The activation parameters were calculated from the slopes and intercepts of Arrhenius plots ($r \geq 0.9937$ and $s \leq 8.018 \times 10^{-2}$) and Eyring equation. The activation energies are 63.4 and 59.3 kJ mol^{-1}; the enthalpies of activation, 60.9 and 56.8 kJ mol^{-1}; and the activation entropies, -93 and -101 J mol^{-1} K^{-1}, with no control and at constant ionic strength, respectively.

DISCUSSION

The first-order dependence of the rate on the vanadium(V) concentration, [V(V)], in sulfuric acid medium, is evident from the linearity of the ln[V(V)] as a function of time plots. Contrary to the oxidations investigated earlier [4–7], a decrease was observed in the rate constants when the concentrations were varied from 0.50×10^{-2} to 2.50×10^{-2} mol dm^{-3} without or with control of ionic strength and maintaining all the other experimental conditions (Table I). The increase in the oxidation rate was attributed as a consequence of the interaction between the hydrated form $V(OH)_4^+$ and one or two bisulfate ions to produce the species $V(OH)_3HSO_4^+$ and $V(OH)_2(HSO_4)_2^+$ with no control and constant ionic strength, respectively:

$$V(OH)_3^{2+} + HSO_4^- = V(OH)_3HSO_4^+$$

and

$$V(OH)_3^{2+} + H^+ + 2\ HSO_4^- = V(OH)_2(OH)_2(HSO_4)_2^+$$

Table IV Effect of Temperature on the Citric Acid Oxidation with No Control of Ionic Strength (I) and at Constant Ionic Strength;* [V(V)] = 1.00×10^{-2} mol dm^{-3}, [HCi] = 0.50–1.50 mol dm^{-3}, [H_2SO_4] = 0.20 mol dm^{-3}

			$k_{obs}/10^{-3}$s^{-1}				
I/mol dm^{-3}	[HCi]/mol dm^{-3}	T/K	293	298	303	308	313
[a]	0.50		1.30	2.32	4.11	5.47	8.72
[a]	0.75		1.60	2.68	4.48	6.54	9.85
[a]	1.00		1.83	3.17	5.71	7.50	11.90
[a]	1.25		2.22	3.70	6.19	8.84	13.75
[a]	1.50		2.56	4.11	6.87	9.98	14.77
1.00	0.50		2.13	4.20	6.16	9.10	13.61
1.00	0.75		2.60	5.23	8.07	10.45	16.10
1.00	1.00		3.34	6.29	9.40	12.65	19.06
1.00	1.25		3.89	7.04	10.57	14.51	22.91
1.00	1.50		4.54	8.38	12.13	16.39	25.89

* Ionic strength was achieved by using $NaHSO_4$ as added electrolyte.

[a] Initial ionic strength is 0.21 mol dm^{-3} but changes in the course of the reaction.

On the other hand, the decrease in the rate-varying [V(V)] in this interval of concentrations was around 25% with no control and about 66% at constant ionic strength. This behavior indicates that the vanadium(V) reacts in the coordinated form, and thus the three carboxyl groups of the citric acid are responsible for the steric hindrance and a decrease in the rate. The more concentrated the vanadium(V), the less the citric acid solubility and consequently less reactivity. In all the other substrate oxidations, such as tartaric, malic, and lactic acids [4–6], the opened structures favored the approximation of vanadium(V) enhancing gradually the rate constants. As related previously, we assumed that sulfuric acid behaves as a strong monobasic acid for the purpose of hydrogen and/or bisulfate ions.

The oxidation of citric acid, HCi, by vanadium(V) takes place more rapidly in comparison with lactic acid [6], malic acid [5, 7], and tartaric acid [4], indicating that electron-withdrawing substituents at the α-position increase the oxidation rate. This was experimentally verified through the use of a smaller concentration of sulfuric acid in the kinetic measurements. The variation of $[H^+]$ from 0.10 to 0.90 mol dm^{-3} (Table II) resulted in rate constants, with no control of ionic strength, larger than those at constant ionic strength; and both showed the trend to a limiting value and that at higher concentrations of sulfuric acid the oxidation capacity decreases. The experimental rate laws that represent the kinetic data are given as

$$\nu = -\frac{d[\mathrm{V(V)}]}{dt} = k_{\mathrm{obs}}[\mathrm{HCi}]^{0.5}[\mathrm{H^+}][\mathrm{V(V)}]$$

with no control of ionic strength

and

$$\nu = -\frac{d[\mathrm{V(V)}]}{dt} = k_{\mathrm{obs}}[\mathrm{HCi}]^{0.5}[\mathrm{H^+}]^{0.5}[\mathrm{V(V)}]$$

with control of ionic strength

The fractional dependence on the citric acid concentration with no control of ionic strength may be due to the participation in two steps of the mechanism and protonation of citric acid prior to equilibrium according to

$$\mathrm{V(OH)_3HSO_4^+ + H + [HOOCCH_2(OH)C(COOH)CH_2COOH]} \xrightleftharpoons{K_1} X^{*2+} \qquad (1)$$

The fractional orders with respect to [HCi] and $[H^+]$ provide a concerted equilibrium among vanadium(V), HCi, and H^+ when the ionic strength is controlled:

$$\mathrm{V(OH)_2(HSO_4)_2^+ + H^+ + HOOCCH_2(OH)C(COOH)CH_2COOH} \xrightleftharpoons{K_1'} Y^{*2+} \qquad (1')$$

It has been shown earlier that most reactions involving V(V) proceed via a free-radical mechanism [12]. 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 a one-equivalent oxidant. Thus, the activated species, X^{*2+}, interacts with H^+ in a bimolecular way, while Y^{*2+} species decomposes unimolecularly in the rate-determining step to give the first CO_2 through a C—C fission producing free radicals, $(HO)_2C^+CH_2C\bullet(OH)CH_2C^+(OH)_2$ and $HOOCCH_2C\bullet(OH)CH_2C^+(OH)_2$, without and with control of ionic strength respectively, in the rate-determining step:

$$X^{*2+} + \mathrm{H^+} \xrightarrow{k_2} \mathrm{(HO)_2C^+CH_2C\bullet(OH)CH_2C^+(OH)_2 + CO_2 + V(OH)_2HSO_4^+ + H_2O} \qquad (2)$$

and

$$Y^{*2+} \xrightarrow{k_{2'}} \mathrm{HOOCCH_2C\bullet(OH)CH_2C^+(OH)_2 + CO_2 + V(OH)(HSO_4)_2^+ + H_2O} \qquad (2')$$

In the absence of ionic strength control, the free radical produced is rapidly oxidized through another mole of V(V), yielding one more carbon dioxide; a charged intermediate, V(IV); and H_2O according to the following scheme:

$$\mathrm{(HO)_2C^+CH_2C\bullet(OH)CH_2C^+(OH)_2 + V(OH)_3HSO_4^+} \xrightarrow{k_3} \mathrm{(HO)_2C^+CH_2COCH_3 + CO_2 + V(OH)_2HSO_4^+ + H^+ + H_2O} \qquad (3)$$

and, in a similar way, between the cation radical $HOOCCH_2C\bullet(OH)CH_2C^+(OH)_2$ and a mole of $V(OH)_2(HSO_4)_2^+$ at constant ionic strength.

In the last step, the formation of acetone takes place with the liberation of the third mole of carbon dioxide with no control of ionic strength, according to the following reaction:

$$\mathrm{(HO)_2C^+CH_2COCH_3 + V(OH)_3HSO_4^+} \xrightarrow{k_4} \mathrm{CH_3COCH_3 + CO_2 + V(OH)_2HSO_4^+ + H_2O} \qquad (4)$$

and, in a similar manner, at fixed ionic strength.

The increase of the ionic strength from 0.30 to 1.25 mol dm^{-3} doubled the rate constants (Table II) and presented a linear dependence on the plot of log k_{obs} against the square root of the ionic strength, giving an ionic charge product of 0.60. From this value alone it is difficult to suggest that the vanadium(V) reacts with citric acid either as the protonated form or in the molecular form. The application of the primary salt effect [9] in ionic strengths up to 0.05 mol dm^{-3} also works in this oxidation. This may indicate that some other factors, such as size and structure of the substrate and oxidant, compensate the ionic charge and concentration of the species in the solution and lead to the application of the expression for a primary salt effect.

The effect of solvent on the reaction rate was studied varying the methanol-water composition (Table III). Plots of ln k_{obs} against the reciprocal of the dielectric constant of the binary mixtures [11], with no control or constant ionic strength, resulted in straight lines with positive slopes. This is similar to malic and lactic acids oxidations and unlike that of tartaric acid, that is, an increase in the oxidation rate with the decrease in the solvent polarity. Thus, the transition state is either less polar than the reactants [13] 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 mechanism.

The negative values of the entropy of activation, -93 and -101 J mol^{-1} K^{-1}, calculated from the values of the apparent second-order rate constant, are expected because there is a charge increase of reactive vanadium(V) species in the rate-determining species, which undergo electrostriction with the solvent molecules [14]. However, when compared with the other α-hydroxyacids investigated [4–6], it is clear that the complex stability is practically the same when the ionic strength is fixed (-101 J mol^{-1} K^{-1}) compared with no control (-93 J mol^{-1} K^{-1}). This means that in the activated complex formation the presence of three carboxyl groups of the citric acid is predominant with respect to the coordinated forms of vanadium(V). While the oxidation rates are systematically greater in the fixed ionic strength, the difference between the activation energy with fixed control and without control of ionic strength is slightly lower than that previously observed [4–6]. The same trend occurs with the enthalpy of activation, and this may be justified by the steric hindrance, which is caused by the carboxyl groups of the citric acid in this oxidation.

Assuming the slow step as the rate-determining one (k_2, and k_2', respectively), these mechanisms lead to the rate laws (5) and (5′) for the oxidation of citric acid by V(V) in sulfuric acid medium with no control and with fixed ionic strength, respectively:

$$\nu = \frac{k_2 K_1\,[\mathrm{HCi}][\mathrm{H}^+][\mathrm{V(V)}]_t}{1 + K_1\,[\mathrm{HCi}]} \tag{5}$$

and

$$\nu' = \frac{k_{2'} K_{1'}\,[\mathrm{HCi}][\mathrm{H}^+][\mathrm{V(V)}]_t}{1 + K_{1'}\,[\mathrm{HCi}][\mathrm{H}^+]} \tag{5'}$$

where the total or analytical concentrations of V(V) are given by

$$[\mathrm{V(V)}]_t = [(X^{*2+})] + [\mathrm{V(OH)_3HSO_4^+}]$$

or

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

The rate laws, (5) and (5′), are in agreement with the experimental data in sulfuric acid medium. The investigated reactions are of first order with respect to the vanadium(V) and hydrogen ion concentrations, and of

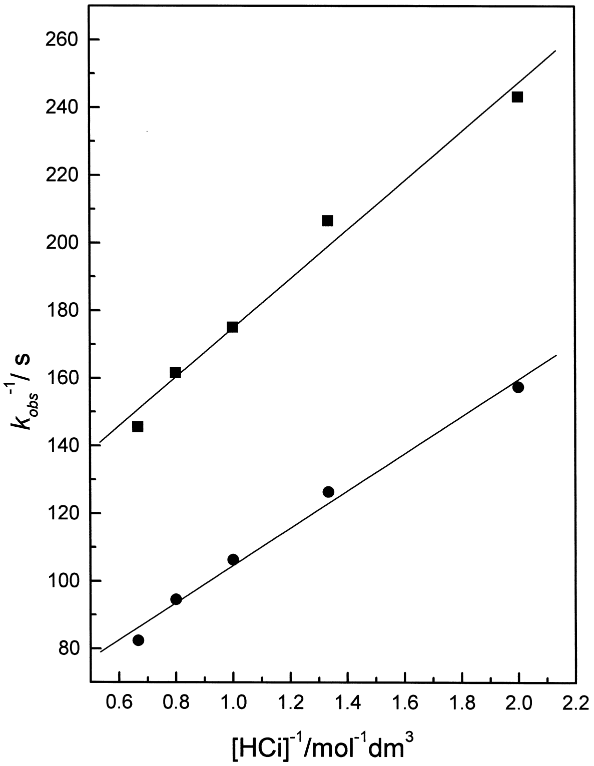

Figure 1 A double reciprocal plot of the pseudo-first-order rate constant, $k_{obs,}$ and citric acid concentration; [HCi] for V(V)] = 1.00×10^{-2} mol dm^{-3}, $[H_2SO_4] = 0.20$ mol dm^{-3} at 303 K. (■) No control of the ionic strength and (●) constant ionic strength (I = 1.00 mol dm^{-3}).

fractional order with the respect to the citric acid without ionic strength control. When it was controlled, the rate was of first order only for vanadium(V) concentration since for citric acid and hydrogen ion concentrations the order was fractional. From the slopes and intercepts of the double reciprocal plots at constant vanadium(V) and citric acid concentrations (Figure 1, $r \geq 0.97548$ and $s \leq 7.8210$) the equilibrium constant, K_1, was determined as 0.178 $\text{mol}^{-2}\ \text{dm}^6$ at 303 K, while the rate constant for rate-determining constant k_2 was obtained as $1.60 \times 10^{-1}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$ with no control of ionic strength control. When this was adjusted to 1.00 mol dm^{-3}, these values become equal to 5.03 $\text{mol}^{-2}\ \text{dm}^6$ and $2.54 \times 10^{-2}\ \text{s}^{-1}$, respectively.

In conclusion, the decrease of the oxidation rate as a function of the vanadium(V) concentration as well as the equilibrium constants, K_1 and K'_1, when compared with other hydroxyacids [4–6] is due to the steric hindrance caused by three carboxyl groups of the citric acid. On the other hand, the small rigidity in the activated species, X^{*2+} and Y^{*2+}, leading to the faster oxidation rates with respect to the other investigated substrates, is apparently due to the small difference in the activation energies.

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