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Kinetics of the Effect of Some Bidentate Amino Acid Ligands in the Oxidation of Lactic Acid by Chromium(VI)[1]

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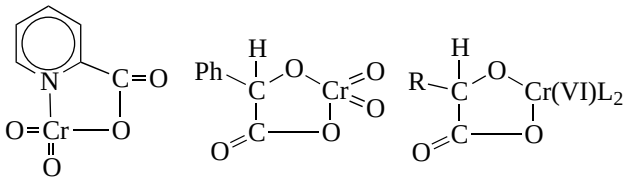
Abstract—The oxidation of lactic acid by Cr(VI) under acidic conditions is catalyzed by bidentate amino acid ligands such as glycine, alanine, aspartic acid and hydroxyproline. Catalysis is a function of [L]/[Cr(VI)] ratio and acidity. Pyruvic acid and acetaldehyde in a ratio of 2 : 1 are obtained as oxidation products in both uncatalyzed and catalyzed oxidation. This supports the previous understanding of the oxidation of α-substituted carboxylic acids. Cromium(V) and chromium(VI) behave similarly in a C–H bond rupture (Rocek, J. and Radkowsky, A.E., *J. Am. Chem. Soc.*, 1973, vol. 95, p. 7123), whereas Cr(IV) is responsible for C–C bond cleavage products (Wiberg, K.B. and Schafer, H., *J. Am. Chem. Soc.*, 1969, vol. 91, p. 927).

INTRODUCTION

Peng and Rocek [1] reported specific catalysis by picolinic acid in the oxidation of isopropyl alcohol by chromic acid under acid conditions. The catalytic effect was attributed to the stabilization of intermediate chromium valance states produced through precursor complex formation. These authors ascribe the catalytic activity to the proximity of a nitrogen atom and a carboxylic group. The bidentate complex **1** seems to be analogous to the cyclic anhydride **2** postulated by Bakore and Narain [2] in the oxidation of mandelic acid by Cr(VI). Bakore and Narain [2] suggested that cyclic ester and anhydride complex **2** can explain the faster reaction of Cr(VI) with hydroxy acid and would imply that complexation with Cr(VI) may lead to the enhanced rate of oxidation under appropriate conditions. It is likely that complex **1** may be a better electron abstractor than $HCrO_4^-$. Complex **1** may incorporate the substrate in its coordination sphere to form **3**, which then disproportionates (as such or solvolytically) in a rate-limiting step. The substrate can compete with the ligand to enter the coordination sphere or can enter the coordination sphere by ligand substitution. In either case, an increase in ligand concentration would ultimately cause a decrease after reaching a limiting condition. Therefore, it was considered fruitful to examine if the catalysis reported by Peng and Rocek [1] depends on the experimental conditions such as the [Cr(VI)] : [**L**] ratio and other factors. The present report deals with the oxidation of lactic acid by chromic acid in the presence of ligands such as glycine, alanine, hydroxyproline and aspartic acid.



1 **2** **3**

EXPERIMENTAL

All the chemicals used were either Analar grade or were purified and the purity was checked by m.p or b.p. The reactions were carried out in a thermostat (±0.05°C). A decrease in the concentration of Cr(VI) was monitored iodometrically taking all the usual precautions. The first-order rate constants k_1 were calculated graphically using a plot of $\log(a - x)$ vs. t and checked using the linear least-squares method. The k_1 values had a standard deviation of ±0.2. The reaction stoichiometry (catalyzed and uncatalyzed) corresponds to the equation

$$2HCrO_4^- + 8H^+ + 3CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCOOH \longrightarrow 2CH_3COCOOH + CH_3CHO + CO_2 + 8H_2O + 2Cr(III).$$

No free radical formation could be detected using the polymerization test.

PRODUCT STUDY

Products were studied under kinetic conditions in the presence or absence of ligands. The oxidized reaction mixture was completely neutralized by sodium bicarbonate and then extracted with ether. An ethereal

[1] This article was submitted by the authors in English.

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Table 1. Variation of the rate with the concentration of lactic acid in the presence of glycine (LA), $[HClO_4^-] = 0.5$ mol/l, $[Cr(VI)] = 4.0 \times 10^{-3}$ mol/l, [Glycine] = 5.0×10^{-2} M, $T = 304$ K

$[LA] \times 10^2$, M	$k_1 \times 10^5$, s^{-1}	$k_1/[LA]$, l mol^{-1} s^{-1}
1.0	5.15	5.15
1.5	7.33	4.89
2.0	10.00	5.00
3.0	14.83	4.94
		Average 4.99

layer was used for the detection and determination of acetaldehyde, while an aqueous layer was used to detect and estimate pyruvic acid. In both cases, an aqueous HCl solution of 2,4-dinitrophenylhydrazine was used to precipitate hydrazones. Parallel blanks were run and parallel determination (three only) using known amounts of pyruvic acid and acetaldehyde were used. Corrections were made in the estimation accordingly. The ratio of acetaldehyde to pyruvic acid was always found to be 1 : 2 whether the reaction was catalyzed (by all the ligands) or uncatalyzed. The products were qualitatively checked by m.p. of the hydrazones of pyruvic acid (m.p., 218°C) and that of acetaldehyde (m.p., 168°C).

RESULTS AND DISCUSSION

1. The Effect of Cr (VI)

No effect of Cr(VI) on the rate was observed in the Cr(VI) concentration range 1×10^{-3} to 6×10^{-3} mol/l. The rate is first-order with respect to Cr(VI) in both presence and absence of the ligands.

2. The Effect of Lactic Acid

The rate constant increases with an increase in the lactic acid concentration in both the absence and presence of the ligands. Typical data were provided for glycine ligand showing an effect of the lactic acid concentration at a constant concentration of glycine (Table 1).

3. The Effect of the Ligand Concentration

The effect of ligand concentration on the rate of oxidation of lactic acid was carried out at 0.5, 0.7, and 1.0 mol/l $[H^+]$ for ligands in Table 2: hydroxyproline, alanine, glycine, and aspartic acid. The figure shows the effect of [glycine]/[Cr(VI)] on the rate of oxidation of lactic acid by Cr(VI) at different $[H^+]$.

Table 2. Variation of rate with concentration of perchloric acid in the presence of glycine ligand $T = 303$ K

	$[H^+]$, mol/l	$\Delta k_1^* \times 10^5$, s^{-1}				
Hydroxyproline	[L]/[Cr(VI)]	0.67	1.87	6.25	12.50	18.75
	0.5	0.62	0.15	–0.92	–2.33	–2.56
	0.7	3.90	3.02	1.80	–0.15	–0.51
	1.0	2.71	0.50	0.06	–0.15	–0.54
Alanine	[L]/[Cr(VI)]	0.50	1.00	1.50	2.00	2.50
	0.5	1.58	–0.48	–1.90	–2.93	–3.65
	0.7	2.23	1.10	0.35	–0.18	–0.59
	1.0	0.73	0.31	0.07	0.15	–0.33
Asparitc acid	[L]/[Cr(VI)]	0.62	1.25	6.25	8.75	12.50
	0.5	0.05	–0.56	–1.83	–2.60	–3.35
	0.7	3.00	2.33	0.48	–0.43	–1.52
	1.0	2.22	1.05	0.45	0.13	–0.12
Glycine	[L]/[Cr(VI)]	0.25	1.25	1.75	2.25	2.50
	0.5	7.92	3.33	1.17	0.00	–1.66
	0.7	6.85	4.00	2.22	0.76	–0.16
	1.0	5.66	2.71	1.20	–0.47	–1.40

* $\Delta k_1 = k_1$ (overall) – k_1 (uncatalysed).

The results obtained (typical runs of variations are provided) are as follows.

(1) In the case of amino acids, the effect is dependent on the [L]/[Cr(VI)] ratio and on the concentration of H^+ used in the reaction. Thus, in case of glycine, there is rate acceleration as long as the ratio of [L]/[Cr(VI)] is ~2 at $[H^+] = 0.5$, 0.7, and 1.0 mol/l. At a higher [L]/[Cr(VI)] ratio, the rate decreases. In the case of alanine, an increase in the rate is observed up to a [L]/[Cr(VI)] ratio of 0.9 at $[H^+] = 0.5$ mol/l, 1.8 at $[H^+] = 0.7$ mol/l, and 2.2 at $[H^+] = 1.0$ mol/l. A further increase in the ratio of [L]/[Cr(VI)] causes a decrease in the rate. Then, in all cases, the effect of glycine is much more pronounced than that of alanine (Table 3). In case of aspartic acid, an increase in the rate is observed up to a ratio of

$[L]/[Cr(VI)] = 10$ at $[H^+] = 1.0$ mol/l,

$[L]/[Cr(VI)] = 7.5$ at $[H^+] = 0.7$ mol/l, and

$[L]/[Cr(VI)] = 1$ at $[H^+] = 0.5$ mol.

(2) In the case of hydroxyproline, the rate acceleration ratio is

$[L]/[Cr(VI)] \le 7$ at $[H^+] = 1.0$ mol/l,

$[L]/[Cr(VI)] \le 11$ at $[H^+] = 0.7$ mol/l, and

$[L]/[Cr(VI)] \le 3$ at $[H^+] = 0.5$ mol/l.

(3) In the case of aspartic acid, for a given ratio of [L]/[Cr(VI)] = 0.62, the rate acceleration is higher at $[H^+] = 0.7$ mol/l and the lowest at $[H^+] = 0.5$ mol/l; beyond this ratio of [L]/[Cr(VI)], the rates decrease. Thus, it appears that each amino acid has its own dependence of rate, which is a function of the ratio [L]/[Cr(VI)] and $[H^+]$.

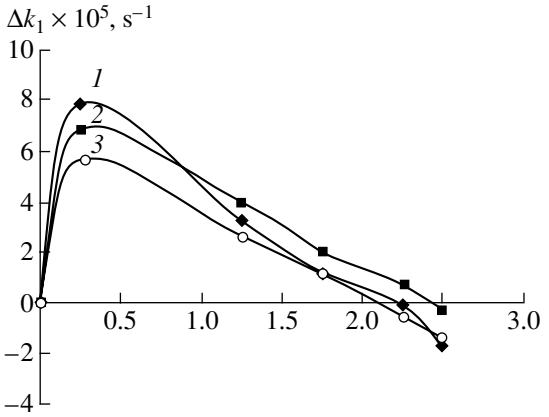
4. The Effect of H^+

At a constant ligand concentration, the rate increases with the concentration of H^+ ion (see Table 3 for a typical run). It was observed that the rate is first-order with respect to H^+ in both the absence and presence of the ligands.

5. The Effect of Temperature

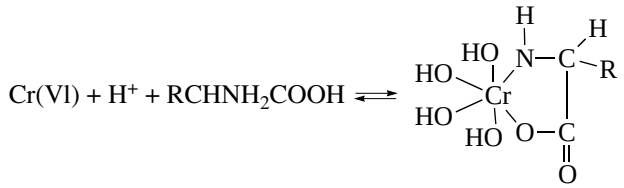
The reaction rate was studied at different temperatures (Table 4) at one ligand concentration and one H^+ concentration. The activation energy was calculated from the plot $\log k_1$ vs. $1/T$. The temperature effect (Table 4) indicates a very low value of $\Delta E_a^{\neq}$ for the catalyzed reaction. This may be due to the overall value of $\Delta E_a^{\neq}$ for various substitution equilibria involved in the system.

Ligands like amino acids, i.e., glycine, alanine, aspartic acid, and hydroxyproline cause an increase in the reaction rate under certain conditions. In the case of glycine and alanine, the catalysis is observed provided the ratio [L]/[Cr(VI)] is lower than 2.0. For a higher ratio of [L]/[Cr(VI)], the presence of a ligand causes a decrease in the rate. For hydroxyproline, catalysis is observed if [L]/[Cr(VI)] is lower than 3.0. For a higher ratio, there is reaction retardation. For aspartic acid, catalysis is observed if [L]/[Cr(VI)] is lower than 1.0. For a higher ratio, there is again reaction retardation. The behavior of the ligands and the extent of catalysis depend on the H^+ concentration.



Variation of rate with [ligand (Glycine)]/[Cr(VI)] T = 303 K, [Lactic Acid] = 2×10^{-2}: (*1*) 0.5, (*2*) 0.7, and (*3*) 1.0 mol/l.

The complex formation may be represented by choosing α-amino acid as an example:



The complex with Cr(VI) is octahedral. Chromium(VI) is known to exist in the octahedral form. Naturally, with this type of complex formation three ligand

Table 3. Variation of the catalyzed rate ($R = k_1$) with the ligand concentration [Lactic acid] = 2.0×10^{-2} mol/l, $[Cr(VI)] = 4.0 \times 10^{-3}$ mol/l, $[Glycine] = 5.0 \times 10^{-2}$ mol/l, T = 304 K

$[HClO_4]$, M	$k_1 \times 10^5$, s^{-1}	$\frac{k_1 \times 10^5}{[HClO_4]}$, l mol^{-1} s^{-1}
0.2	3.83	19.15
0.3	5.67	18.90
0.4	8.13	20.43
0.5	10.00	20.00
0.7	13.83	19.81
1.0	18.90	18.90
		Average 19.53

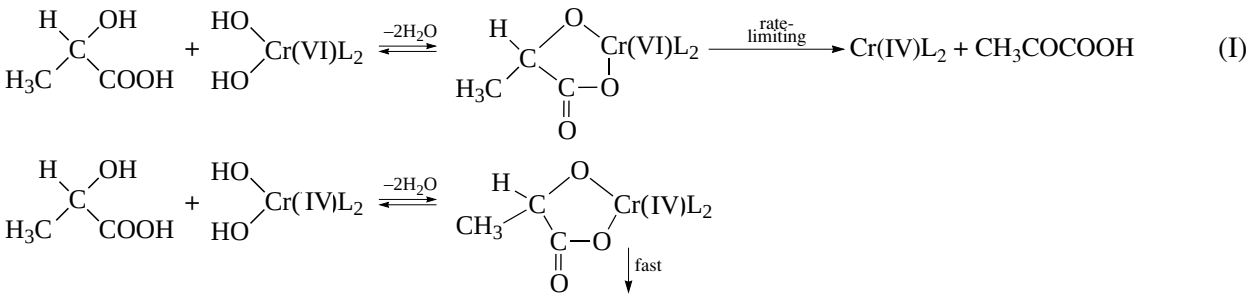
Table 4. The effect of temperature on the reaction rate in the presence of the ligand $[HClO_4^-]$ = 0.5 mol/l, [Lactic acid] = 2.0×10^{-2} mol/l, [Cr(VI)] = 4.0×10^{-2} mol/l, [Ligand] = 5×10^{-2} mol/l

Ligand	$k_1 \times 10^5$, s^{-1}				$\Delta E_a^{\neq}$, kJ mol^{-1}
	299 K	304 K	309 K	314 K	
Hydroxyproline	4.88	5.50	5.83	6.16	11.29 ± 0.46
Alanine	3.00	3.17	3.35	3.52	7.89 ± 0.06
Asparitic Acid	3.73	4.00	4.28	4.55	10.20 ± 0.06
Glycine	4.23	4.50	4.75	5.00	8.52 ± 0.08

Table 5. Product study [Cr(VI)] = 4.0×10^{-2} mol/l, [Lactic acid] = 2×10^{-1} mol/l, $[H^+]$ = 0.5 mol/l

Ligand	$\frac{\text{Moles of Acetaldehyde}}{\text{Moles of Lactic acid}}$	$\frac{\text{Moles of Pyruvic acid}}{\text{Moles of Lactic acid}}$
Hydroxyproline	0.27	0.67
Alanine	0.30	0.66
Asparitic Acid	0.26	0.70
Glycine	0.31	0.65

molecules can occupy six coordination sites. Sundari and Vasuki [6] also suggested a termolecular complex of picolinic acid and Cr(VI) in the oxidation of mandelic acid by Cr(VI) catalyzed by picolinic acid. The fact is that the catalysis is observed for [L]/[Cr(VI)] = 2.0. In the case of glycine, the remaining two coordination sites are occupied by lactic acid under a condition where catalysis is observed (Scheme 1). For higher ratios of [L] to [Cr(VI)], lactic acid can only enter the coordination sphere of Cr(VI) by displacing the ligand molecules from the coordination sphere.



Scheme 1

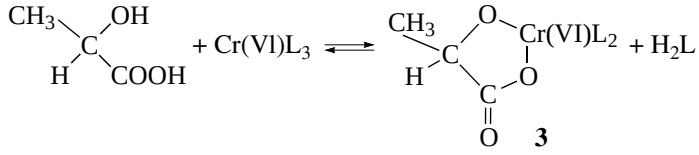
where L is the bidentate ligand.

The Cr(VI) ligand complex is a better oxidant than Cr(VI) alone. The $Cr(VI)L_2(OH)_2$ ligand complex and lactic acid may react with a precursor complex formation, which decomposes with a rate-limiting step as suggested in Scheme 1. The free radical produced in the initial step reacts with Cr(V) to give aldehyde and Cr(V). Chromium(V) will react with lactic acid to form $CH_3COCOOH$ by a two-electron step (IV). Thus, the activation of Cr(VI) by complex formation leads to an increase in the reaction rate and the ratio of pyruvic acid to acetaldehyde is 2 : 1 (Table 5). The fact that there is no induced polymerization indicates that radicals rapidly react with Cr(VI).

Inhibition

The reaction retardation with an increase in the ligand concentration (after optimum [L]/[Cr(VI)]) can be explained by Scheme 2.

When the coordination sphere of Cr(VI) is fully occupied, the lactic acid can only enter the coordination sphere by displacing L as shown in equilibrium.



Scheme 2

The addition of ligand H_2L decreases the rate by decreasing the concentration of **3**.

The fact that catalysis is observed in the case of glycine and alanine for [L]/[Cr(VI)] < 2.0 indicates that the complex of Cr(VI) with glycine and alanine has a large formation constant. In the case of aspartic acid and hydroxyproline, the catalysis is observed up to the ratio [L]/[Cr(VI)] = 10.0, indicating that the complex is labile.

Since the order with respect to lactic acid is first and since the lowest [L]/[Cr(VI)] ratio under which the acceleration effect is observed is 2.0, it is unlikely that this reaction involves a single-step three-electron oxidation as proposed by Rocek and Hasan [4]. The fact that two thirds of the product is pyruvic acid indicates that Cr(VI) changes to Cr(IV) in the oxidation of lactic acid and Cr(IV) causes further oxidation of lactic acid by a one-electron change. This supports the concept that Cr(VI) and Cr(V) cause C–H bond rupture [7] and Cr(IV) is responsible for the C–C cleavage [8] products in case of oxidation of α-substituted acids.

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