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KINETICS AND MECHANISM OF CHROMIC ACID OXIDATION OF LACTIC ACID†

P. C. SAMAL,‡ B. B. PATTNAIK,† S. CH. DHARMA RAO and S. N. MAHAPATRO*
Department of Chemistry, Berhampur University, Berhampur-760007, Orissa, India

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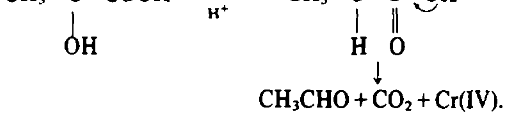
Abstract—The chromic acid oxidation of lactic acid (LA) has the rate expression $-dCr(VI)/dt = [Cr(VI)][LA](k_1 + k_2[H^+] + k_3[LA])$. Both the first order and second order reactions are two electron oxidations giving pyruvic acid. There is insignificant C–C cleavage.

All known chromic acid oxidations involve Cr(IV) and/or Cr(V) as reactive transients.[1] Cr(IV) is known to have a selectivity for C–C cleavage in the oxidation of cyclobutanol.[2] An unequivocal demonstration of this preference is given by the V(IV)–Cr(VI)–cyclobutanol system.[2] Cr(V) closely resembles Cr(VI) in affecting C–H cleavage in cyclobutanol oxidation. The oxidation of α-hydroxy acids has been particularly interesting because both C–H and C–C cleavage products have been reported. The Cr(V) intermediate oxidizes glycolic acid to glyoxalic acid by C–H cleavage.[3] In the oxidation of mandelic acid,[4] the growth and decay of a Cr(V) intermediate at 750 nm has been demonstrated and this reacts by C–C cleavage giving benzaldehyde. We searched for another closely related system, where there is a possibility of C–H and C–C bond breaking. The oxidation of lactic acid (LA) presents such a situation. Previous work on the oxidation of lactic acid has been fragmentary[5,6] and the kinetics were studied in narrow concentration ranges and no product analysis has been reported under kinetic conditions. In two of the authoritative reviews on chromic acid oxidation by Westheimer[7] and Wiberg,[1] lactic acid was shown to give the C–C cleavage product *viz* acetaldehyde.

$$3CH_3CHOH{\cdot}COOH + 2Cr(VI) \rightarrow$$

$$3CH_3CHO + 3CO_2 + 2Cr(III). \qquad (1)$$

The decarboxylation was thought to occur as a part of the oxidation without initial oxidation to pyruvic acid.



$$CH_3\text{—}\underset{OH}{\overset{H}{C}}\text{—}COOH \xrightarrow[H^+]{HCrO_4^-} CH_3\text{—}\underset{H}{\overset{O\text{—}CrO_3H}{C}}\text{—}\underset{O}{\overset{}{\underset{\|}{C}}}\text{—}OH$$

$$\downarrow$$

$$CH_3CHO + CO_2 + Cr(IV).$$

A reexamination of the kinetics of Cr(VI) oxidation of lactic acid in an extended concentration range, and product analysis under conditions when the LA:Cr(VI) ratio is high, revealed several new features. We wish to report in this paper that a two electron oxidation to pyruvic acid by C–H cleavage is the dominant reaction in the Cr(VI) oxidation of lactic acid.

EXPERIMENTAL

Sodium dichromate dihydrate (Baker Reagent) was used as received. Perchloric acid solns were prepared from 70% perchloric acid (BDH 70% analytical reagent). Stock solns of sodium dichromate in distilled water were standardized iodometrically. Low acidity measurements were carried out in potassium hydrogen phthalate–hydrochloric acid buffers and the pH was checked on a systronics digital pH meter. Merck 80% lactic acid was standardized by titrating with NaOH soln. Lactic acid is known to undergo self condensation to lactyl lactic acid ($CH_3CHOHCOOCHCH_3COOH$) at higher temps. The presence of this impurity was confirmed by C^{13} NMR. Distillation under reduced pressure did not remove this impurity. C^{13} NMR of an acidic soln of lactic acid under conditions used for kinetic and product studies showed only three peaks (180.9, 69.5 and 22.1 ppm) indicating that the lactyl lactate has been hydrolysed.

Kinetic measurements. The kinetics of oxidation were followed by a standard iodometric method. Pseudo-first-order rate constants (k_{obs}, s^{-1}) have been computed with respect to the disappearance of total Cr(VI). Plots of log titre vs time showed excellent linearity for well over two half lives. A large excess of lactic acid was used for all the kinetic runs. Rate constants are reproducible within ±7%. Least-squares analysis of the rate data were done by DCM mini computer microsystem 1121.

Chromium(*V*). Very recently the growth and decay of a Cr(V) intermediate at 750 nm (where Cr(VI) and Cr(III) have zero absorbance) has been reported in the Cr(VI) oxidation of mandelic acid.[4] A couple of experiments were performed at 750 nm in a Pye Unicom 700, UV visible double beam spectrophotometer at I.I.Sc. Bangalore. Under conditions of low H^+ (5×10^{-3} M), LA (1–2 M) and Cr(VI) (5×10^{-3} M), an intermediate grows and rapidly decays to zero absorbance. The absorbance was too small for quantitative estimation of Cr(V). Iodometic estimation at pH 3 under conditions when the Cr(VI) oxidation of I^- is extremely slow indicated that a reactive Cr(V) has accumulated which is about 10% of the total Cr(VI).

Product analysis. CO_2 was determined manometrically in a Warburg apparatus. The instrument was calibrated by CO_2 generated by the chromic acid oxidation of oxalic acid.

$$3H_2C_2O_4 + 2Cr(VI) \rightarrow 6CO_2 + 2Cr(III). \qquad (2)$$

Pyruvic acid and acetaldehyde were estimated gravimetrically as their 2,4-dinitrophenylhydrazones. 2,4-DNPH of pyruvic acid has considerable solubility in water because of the carboxyl group. The yield was calculated from a calibration graph.

In a typical experiment 10 ml of (5M) LA, 5 ml of (10M) $HClO_4$ was made to a total volume of 90 ml and was taken in a 250 ml 3-necked flask fitted with a N_2 entry tube, a separatory funnel, a gas outlet tube with polythene tubing connecting to a gas inlet tube which dipped into a sat. soln of 2,4-dinitrophenylhydrazine in 2NHCl (50 ml). 10 ml of 0.1M $Na_2Cr_2O_7$ soln was added while

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*Author to whom correspondence should be addressed.

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‡Department of Chemistry, S.K.C.G. College, Parlakhemundi, 761200, Orissa, India.

a slow stream of O_2 free N_2 was bubbling. The mixture was warmed (60°) to sweep any acetaldehyde into the 2,4-dinitrophenylhydrazine soln. Negligibly small amounts of acetaldehyde 2,4-dinitrophenylhydrazone formed, m.p. 165° (lit. 168). The main mixture was then treated with 100 ml sat. soln of 2,4-dinitrophenylhydrazine in 2NHCl and kept overnight. The precipitated 2,4 DNPH was filtered, dried and was characterised as pyruvic acid 2,4-DNPH, n.p. 218° (lit. 218). The IR and ^1H NMR spectra were identical with those of an authentic sample indicating that it was essentially free from acetaldehyde 2,4-DNPH impurity.

RESULTS AND DISCUSSION

Good first-order plots were obtained in all the experiments in which an excess of lactic acid over Cr(VI) was used. Table 1 records the pseudo first order rate constants ($k_{obs}\, s^{-1}$) for various initial concentrations of Cr(VI) and this clearly shows the first order dependence on total Cr(VI).

Lactic acid (LA) dependence. The reaction is first order in lactic acid at low substrate concentrations and high [H^+], it changes to second order in LA at high substrate concentration and low [H^+] (Table 2).

Acidity dependence. Table 2 shows that the oxidation reaction is first order in hydrogen ion at high acidities and low LA and approaches a zero order dependence at low H^+ and high LA. At any given acidity the substrate dependence can be expressed as

$$k_{obs} = k'(LA) + k_3(LA)^2. \quad (3)$$

A plot of $k_{obs/LA}$ vs LA should give a straight line whose slope is k_3 and intercept is k'. Reasonably good linear plots were obtained at $[H^+] = 0.01$ and 5×10^{-4} M (Fig. 1). At higher acidities, the first order term in LA is only significant as seen from the constancy of the $k_{obs/LA}$ values (Table 2) and we could see an incursion of the second order term in LA (k_3) only at high lactic acid concentrations.

A least square analysis of the observed rate data for equation (5) was done and the values of $k'\, M^{-1}\, s^{-1}$ and $k_3\, M^{-2}\, s^{-1}$ are recorded in Table 3. The near constancy of the k_3 values in the entire range of acidity of this study clearly shows that it is practically acid-independent. The k' term clearly shows an acidity dependence. A plot of k' vs H^+ (Fig. 2) gives a linear plot with a small positive intercept indicating that the acidity dependence of k' could be expressed as

$$k' = k_1[LA] + k_2[LA][H^+]. \quad (4)$$

Thus the rate expression for the chromic acid oxidation of lactic acid in the concentration range of this study has the form

$$k_{obs} = k_1[LA] + k_2[LA][H^+] + k_3[LA]^2. \quad (5)$$

Table 1. Dependence of oxidation rate on initial concentration of total Chromium (VI)[a]

$10^4[Cr(VI)]_0$	$10^4\, k_{obs}\, s^{-1}$
4.95	3.37
9.70	3.30
19.30	3.47
100.00	3.30

a, 35°, LA = 0.08 M, $HClO_4$ = 0.1 M.

Table 2. Observed and calculated pseudo-first-order rate constants for the chromic acid oxidation of lactic acid (LA)[a]

H^+	LA, M	$10^4\, k_{obs}\, s^{-1}$	$10^4\, k_{obs/LA}$	$10^4\, k_{cal}\, s^{-1}$
0.5	0.08	17.0	212.0	18.10
	0.04	7.71	192.0	8.96
	0.016	3.23	201.0	3.56
	0.0096	1.90	197.0	2.14
	0.004	0.660	165.0	0.88
0.1	1.6	185.0	115.0	210.0
	1.2	111.0	92.5	132.0
	0.656	38.3	58.4	53.1
	0.328	13.5	41.1	20.82
	0.144	5.5	38.2	7.73
	0.08	3.37	42.1	4.02
	0.0352	1.44	40.9	1.68
0.05	1.6	169.0	105.0	174.8
	1.28	99.0	77.3	118.0
	0.4	13.2	33.0	18.12
	0.08	1.87	23.3	2.26
	0.04	0.978	24.4	1.04
	0.008	0.188	23.5	0.195
	0.004	0.091	22.75	0.097
0.01	0.816	44.3	54.3	40.71
	0.41	11.9	29.0	11.58
	0.163	2.69	16.5	2.46
	0.081	0.934	11.5	0.868
	0.041	0.401	9.78	0.352
	0.016	0.129	8.06	0.116
	0.008	0.067	8.37	0.055
5×10^{-4}	0.8	34.0	42.5	35.38
	0.4	7.1	17.7	9.41
	0.16	1.59	9.93	1.72
	0.08	0.54	6.75	0.52
	0.016	0.034	2.12	0.052

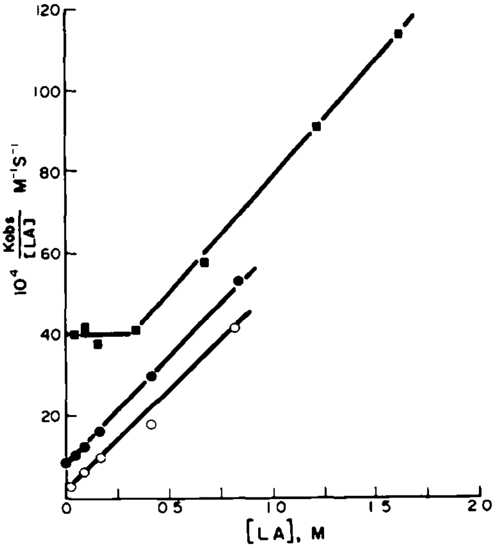


Fig. 1. Determination of rate constants k' and k_3. Data of Table 2, conditions 35°, $[Cr(VI)]_0 = 1 \times 10^{-3}$ M, (■) H^+ = 0.1 M, (●) H^+ = 0.01 M, (⊙) $H^+ = 5 \times 10^{-4}$ M.

Table 3. Acidity dependence of k' M^{-1} s^{-1} and k_3 M^{-2} s^{-1}

H^+, M	$10^3 k'$ M^{-1} s^{-1}	$10^3 k_3$ M^{-2} s^{-1}
5×10^{-4}	0.250	5.0
0.01	0.800	5.4
0.05	2.35	5.23
0.1	4.10	5.7
0.5*	19.30	—

*At 0.5 M $HClO_4$, a value of k_3 could not be computed, as the $k_{obs/LA}$ values are nearly constant.

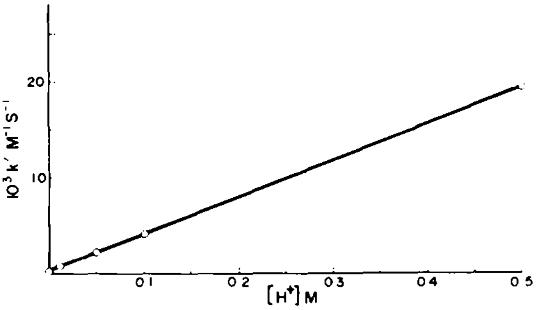


Fig. 2. Plot of k' vs H^+. Data from Table 3.

Least squares values of k_1, k_2 and k_3 are

$$k_1 = 2.0 \times 10^{-4} M^{-1} s^{-1}$$
$$k_2 = 4.44 \times 10^{-2} M^{-2} s^{-1}$$
$$k_3 = 5.33 \times 10^{-3} M^{-2} s^{-1}.$$

Rate constants calculated from eqn (5) when compared with the experimental k_{obs} give a fair agreement over a wide range of concentration except for the values at high H^+.

Reaction products. Table 4 shows the product yields/mole of Cr(VI). CO_2, a product of C–C cleavage could arise in the oxidation of lactic acid by either Cr(VI), Cr(V) and/or Cr(IV) or by the oxidative decarboxylation of pyruvic acid by any one of the Cr species. Acetaldehyde is a product of C–C cleavage. It could also arise by the decarboxylation of pyruvic acid. In independent experiments, the thermal decarboxylation was found to be nil. In view of the insignificant yields of CH_3CHO, we have used the CO_2 values as rough estimates of the CH_3COOH yields. The product yields account for about 85% of the total Cr(VI) introduced. The chromic acid oxidation rates for lactic acid, pyruvic acid and acetaldehyde under comparable conditions are given in Table 5.

Pyruvic acid is nearly as reactive as lactic acid and thus it should be possible to identify it in the presence of a large excess of lactic acid over Cr(VI). Acetaldehyde reacts about 1.4 times faster than lactic acid at high H^+ (0.5 M) and is much less reactive at lower acidities (1 ×

Table 4. Product yields in the chromic acid oxidation of lactic acid[a,b]

			Yield mole/mole of Cr(VI)				
H^+, M	LA, M	Kinetic term	$CH_3COCOOH$[b]	CH_3CHO[b]	CH_3COOH[c]	CO_2[d]	total[e]
0.5	0.5	First order 85%	0.7	0.05	0.3	0.3	1.35
0.1	2.0	Second order 95%	0.8	0.05	0.2	0.2	1.25

[a] 35°, $[Cr(VI)]_0 = 0.02$ M/100 ml; [b] gravimetric yields of 2,4 dinitrophenyl hydrazone; [c] based on CO_2 values; [d] CO_2 was measured in a Warburg apparatus which was calibrated with oxalic acid. $3H_2C_2O_4 + 2Cr(VI) \rightarrow 6CO_2 + 2Cr(III)$; [e] Total yield = $CH_3COCOOH + CH_3CHO + 2CH_3COOH$; theoretical = 1.5 mole/mole of Cr(VI).

Table 5. Cr(VI) oxidation rates of lactic acid and related compounds[a]

Compound	H^+, M	S, M	$10^4 k_{obs}$ s^{-1}	$10^4 k_{obs/S}$ M^{-1} s^{-1}
$CH_3CHOHCOOH$	0.5	0.016	3.23	201.0
		0.08	17.0	212.0
	0.01	0.016	0.129	8.1
$CH_3COCOOH$	0.5	0.00064	0.815	130.0
		0.011	1.71	150.0
CH_3CHO	0.5	0.036	10.1	280.0
	0.01	0.036	0.0268	0.74
		0.161	0.100	0.621
		0.246	0.173	0.703

[a] 35°, $[Cr(VI)]_0 = 1 \times 10^{-3}$ M.

$10^{-2}-5\times10^{-4}$ M) and it should have accumulated in considerable amounts had it been formed in one of the primary steps of oxidation. We are now convinced that acetaldehyde is not a primary product, and it seems unlikely that it is oxidized to acetic acid from a consideration of relative rates of oxidation of lactic acid and acetaldehyde. The small amounts of acetaldehyde detected must be due to a side reaction due to one of the intermediate chromium species like Cr(IV) and/or Cr(V).

Mechanism

Any mechanism for the chromic acid oxidation of lactic acid must take into account the following facts:

(1) The only carbonyl product which was isolated in significant amounts is the two electron oxidation product pyruvic acid.

(2) Acetaldehyde is formed in negligibly small amounts. The following two electron oxidation of lactic acid to pyruvic acid is consistent with our rate and product studies.

C_1 most probably involves both the -OH and -COOH groups as ethyl lactate is oxidized about six times slower than lactic acid. The complex C_2 (second order region in LA) is formed from C_1 and is in keeping with the zero order dependence on acidity.

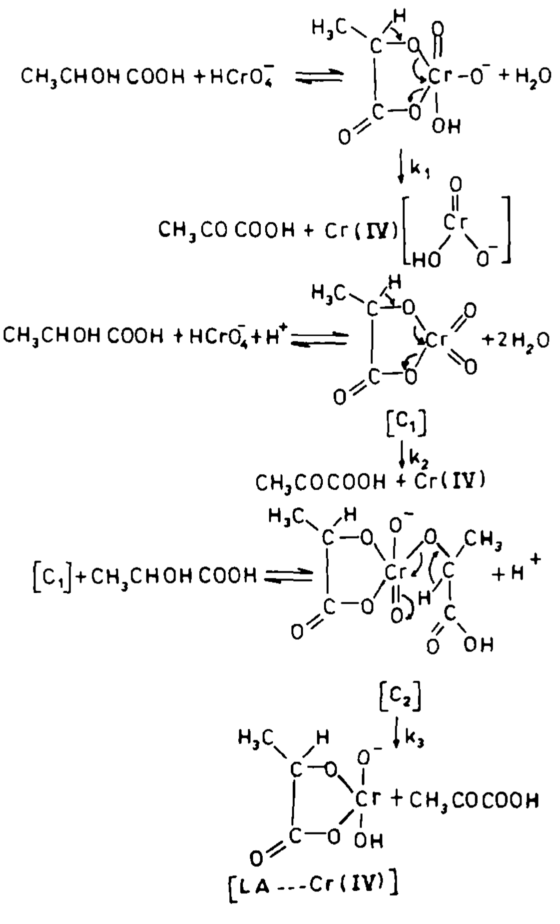
The next important aspect of the mechanism is the fate of Cr(IV). Cr(IV) is known for its selectivity for C-C cleavage in cyclobutanol oxidation. The absence of acetaldehyde under conditions of this product study in stoichiometric amounts:

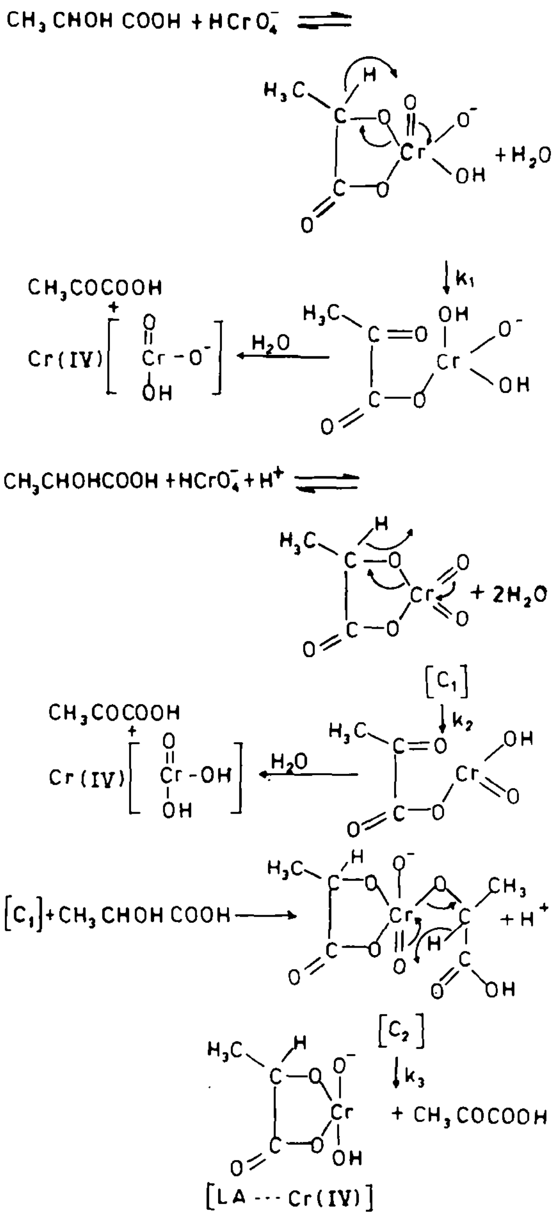
$$\mathrm{Cr(IV)+Cr(VI)} \rightleftharpoons \mathrm{2Cr(V)} \tag{6}$$

$$\mathrm{CH_3CHOHCOOH+Cr(IV)} \rightarrow \mathrm{CH_3CHO+.COOH+Cr(III)} \tag{7}$$

$$\mathrm{CH_3CHOHCOOH+Cr(V)} \rightarrow \mathrm{CH_3COCOOH+Cr(III)} \tag{8}$$

clearly points to the fact that it is most probably oxidized to Cr(V) (reaction 6) before it could cleave the C-C bond (reaction 7). Reaction 6 has been questioned on theromodynamic grounds in the oxidation of 2-propanol.[8] This is understandable, as 2-propanol like other alcohols is a poor ligand to stabilize Cr(V). The intermediacy of Cr(V) has been observed in the oxidation of oxalic acid,[9] 2-hydroxy 2-methylbutyric acid,[10] citric acid[11] and mandelic acid.[4] The presence of two carboxyls or one hydroxyl and one carboxyl seems to be necessary for the





stability of Cr(V). It seems to us, that in the presence of a bifunctional molecule like lactic acid, the Cr(IV) may well be oxidized to Cr(V). At low H^+ (5×10^{-3} M), high LA (1-2 M) and high Cr(VI) (5×10^{-3} M), the mixture reacted extremely rapidly under conditions where the Cr(VI) – I^- reaction is negligibly slow. Iodometric estimation showed that Cr(V) is formed in about 10% of the theoretical amounts. This suggests that the Cr(V)-lactic acid reaction is extremely fast when compared to the mandelic acid –Cr(V) reaction, where the Cr(V) intermediate accumulated in near stoichiometric amounts. The absence of acetaldehyde points to the fact that the Cr(V) is reacting by C–H cleavage in this oxidation though it is intriguing how the Cr(V) cleaves the C–C bond of mandelic acid. In the oxidation of 2-propanol, cyclobutanol and glycollic acid, Cr(V) bears a close resemblance with Cr(VI) in affecting C–H cleavage.[12,13]

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