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KINETICS AND MECHANISM OF CHROMIC ACID OXIDATION OF LACTIC ACID

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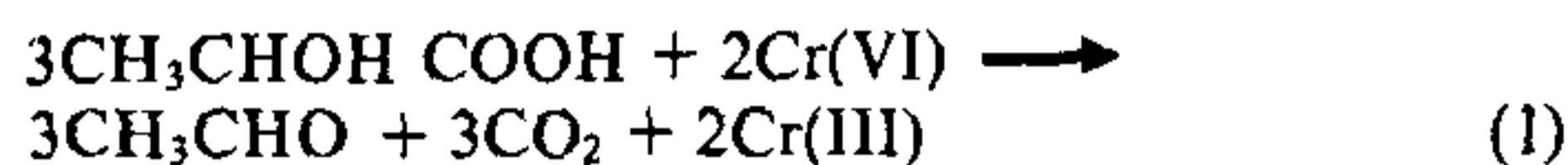
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ALL known chromic acid oxidations involve either Cr(IV) and/or Cr(V) as transient species¹. Cr(V) closely parallels in the reactivity with Cr(VI) in affecting C-H cleavage in the oxidation of alcohols^{2,3}. Cr(IV) is responsible for the C-C cleavage product in the oxidation of cyclobutanol⁴. Both C-H and C-C cleavage products have been reported in the Cr(VI) oxidation of glycolic⁵ and mandelic⁶ acids.

In our search for other closely related systems where there is a possibility of C-H and C-C bond breaking,

we found that previous work on the oxidation of lactic acid has been fragmentary⁷⁻⁸. In two of the authentic reviews on chromic acid oxidation by Westheimer⁹ and Wiberg¹, lactic acid oxidation was shown to give quantitative yields of the C-C cleavage product viz. acetaldehyde.



We have reexamined the oxidation of lactic acid by Cr(VI). The following new features emerged from our study.

1. In the concentration range LA (5×10^{-3} – 2.0M), H^+ (5×10^{-4} – $5 \times 10^{-1}\text{M}$) and Cr(VI) (5×10^{-4} – $2 \times 10^{-2}\text{M}$), the rate expression has the form.

$$-\frac{[\text{Cr(VI)}]}{dt} = [\text{HCrO}_4^-] [\text{LA}] (k_1 + k_2 (\text{H}^+) + k_3 (\text{LA})) \quad (2)$$

At 35° the least square values of the rate constants are:

$$k_1 = 2.17 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

$$k_2 = 4.44 \times 10^{-2} \text{ s}^{-1} \text{ and } k_3 = 5.33 \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$$

The second order term in lactic acid (LA) is dominant at low $[\text{H}^+]$ and is being reported for the first time.

2. Oxidation of lactic acid under conditions when the LA: Cr(VI) ratio is high yielded the C-H cleavage product, pyruvic acid.

Table I presents the product yields in the Cr(VI) oxidation of lactic acid.

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 flash fitted with a nitrogen entry tube, a separatory funnel, a gas outlet tube with polythene tubing connecting to a gas inlet tube which dipped into a saturated solution of 2,4-dinitrophenylhydrazine in 2N HCl (50 ml). 10 ml of 0.1M $\text{Na}_2\text{Cr}_2\text{O}_7$ solution was added while a slow stream of oxygen free nitrogen was bubbling. The reaction mixture was warmed (60°C) to sweep off any acetaldehyde by nitrogen into the 2,4-dinitrophenyl hydrazine solution. Negligibly small amounts of acetaldehyde-2,4-dinitrophenyl hydrazone formed mp 165° (lit. 168). The main reaction mixture was then treated with 100 ml of saturated solution of 2,4-dinitrophenyl hydrazine in 2N HCl and kept overnight. The precipitated 2,4 DNPH was filtered, dried and was characterised as pyruvic acid, 2,4 DNPH mp 218°C (lit. 218). The IR and ¹HNMR spectra was identical with that of an authentic sample indicating that it is essentially free from acetaldehyde-2,4 DNPH impurity.

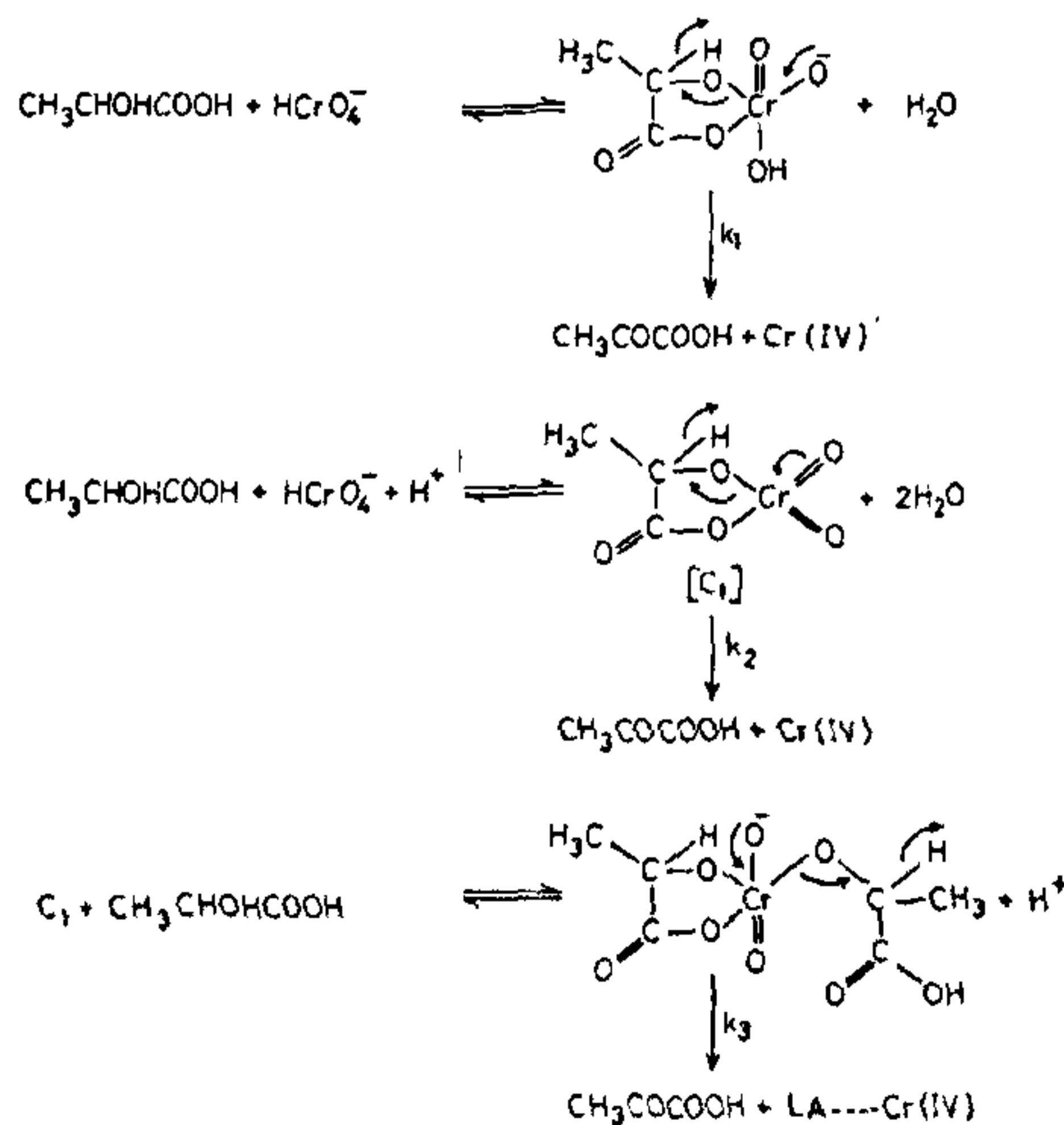


TABLE I

Product yields in the chromic acid oxidation of lactic acid^{a,b}

[H ⁺]M	[LA]M	Kinetic term	Yield mole/mole of Cr(VI)				
			CH ₃ COCOOH ^c	CH ₃ CHO ^c	CH ₃ COOH ^d	CO ₂ ^e	Total ^f
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, Lactic acid is known to undergo self condensation to give lactyl lactic acid, CH₃CHOHCOOCHCH₃COOH at higher temperatures. The presence of this impurity was confirmed by C¹³ NMR. Acidic solutions 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.

^c, gravimetric yields of 2,4-dinitrophenyl hydrazone. The 2,4-dinitrophenyl hydrazone of pyruvic acid has considerable solubility in water because of the carboxyl group. The yield was calculated from a calibration graph.

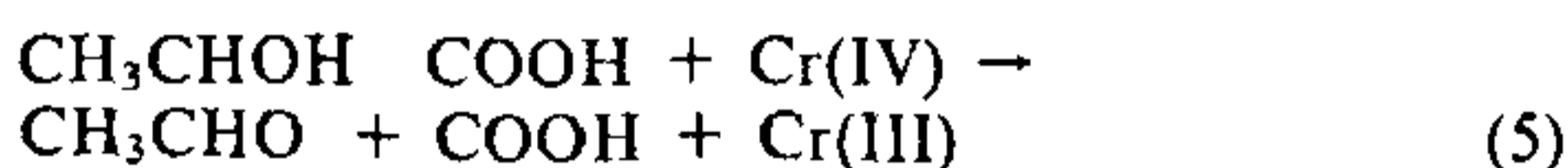
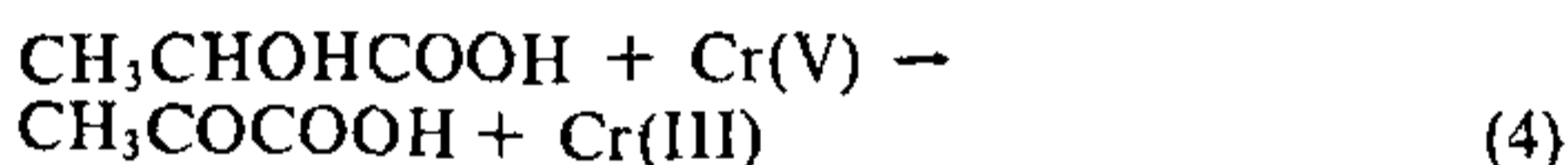
^d, based on CO₂ values.

^e, CO₂ was measured in a Warburg apparatus which was calibrated with oxalic acid.

^f, 3H₂C₂O₄ + 2Cr(VI) → 6CO₂ + 2Cr(III).

^f, total yield: CH₃COCOOH + CH₃CHO + 2CH₃COOH, theoretical = 1.5 mole/mole of Cr(VI).

The formation of pyruvic acid as the major reaction product points to a two electron oxidation involving C-H cleavage. The following reaction scheme is consistent with our rate and product studies.



Acetaldehyde reacts about two times faster than lactic acid at high H⁺ (0.5 M) and is much less reactive at low H⁺ (5 × 10⁻³ M) and it should have accumulated in considerable amounts under conditions when the lactic acid: Cr(VI) ratio is high. The absence of acetaldehyde in stoichiometric amounts under conditions of this product study clearly points to the fact that the Cr(IV) is most probably oxidized to Cr(V) [reaction (3)] before it could cleave the C-C bond [reaction (5)]. Chromium(V) oxidizes lactic acid by C-H cleavage as given in equation (4). Reaction (3) has been questioned on thermodynamic grounds in the oxidation of 2-propanol which is a poor ligand to stabilize Cr(V). We believe that in the presence of a bifunctional molecule like lactic acid the Cr(V) may well be stabilized. At low H⁺ (5 × 10⁻³ M), high LA (1–2 M) and Cr(VI) (5 × 10⁻³ M) the reaction mixture reacted extremely rapidly with iodide indicating a highly reactive intermediate species of chromium (V) has

accumulated.

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