Formation of chromium(V)-lactic acid complex in the chromic acid oxidation of lactic acid

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Oxidation of lactic acid proceeds in two steps; the first step leads to the formation of chromium(III) and an unusually stable chromium(V) intermediate complex whereas the second step pertains to reduction of the latter to chromium(III) as the final product. Kinetics of formation of the stable chromium(V) lactic acid complex has been studied by spectrophotometry. The reaction has been found to be second order in lactic acid. Chromium(V) complex reacts with lactic acid in a slower manner than does chromium(VI). Under specific acid concentrations the two steps can be separated and investigated individually.

The formation of chromium(V) as an intermediate in the redox reactions of chromium(VI) with a variety of organic substrates in perchloric acid medium has generated a lot of debate. Roczek and his coworkers prepared the first stable water soluble chromium(V) compound from 2-hydroxy-2-methylbutyric acid and chromium trioxide. The implication of chromium(V) in the mechanism of chromium-induced cancers has generated a considerable amount of interest in its chemistry and biochemistry. We have been studying the possible fate of chromium(VI) in biological reductants. Previous investigations of chromium(VI) oxidations of secondary 2-hydroxy acids failed to reveal the formation of stable chromium(V) intermediates. The meagre information available concerning the mechanism of oxidation of 2-hydroxypropionic acid (lactic acid) by chromium(VI) makes the system worthwhile to be reinvestigated.

Here we wish to report our results of the chromic acid oxidation of lactic acid with spectrophotometric evidence indicating stabilization of chromium(V)-lactic acid complex as an intermediate.

Experimental
Lactic acid (Aldrich) and potassium dichromate (s.d. fine, AR) were used without further purification. Stock solutions of the oxidant and reductant were prepared in potassium phthalate-hydrochloric acid buffer solutions at desired pH (the pH was verified with a digital dynamic control pH meter). HClO₄ solutions were prepared from 70% E. Merck (India) product. H₂SO₄ and CH₃COOH were of A.R. grade. Aqueous solutions were prepared in doubly distilled water. The reaction was followed spectrophotometrically at 25°C by monitoring formation of chromium(V) at 750 nm (where chromium(V) is the only absorbing species) on a Spectronic 21-D spectrophotometer under pseudo-first order conditions of [lactic acid]₀=16 [Cr(VI)]. The pseudo-first order rate constants (kₗ) were obtained from the plots of log (A₀−A₁) versus time for the formation of chromium(V)-lactic acid complex. The addition of acrylonitrile to reaction mixture (8.4x10⁻³ mol dm⁻³ lactic acid) showed polymer formation (white precipitate) indicating free radical intervention in the reaction.

Results and discussion
For determining the nature of the reaction product, the ultraviolet and visible spectra of the reaction mixture containing [K₂Cr₂O₇]=2.8x10⁻³ mol dm⁻³ and [lactic acid]₀=0.4 mol dm⁻³ were recorded after completion of the reaction. Two sharp bands in the 350-700 nm region with two d-d transitions at 410 (ε=113 mol⁻¹ dm³) and 575 nm (ε=97.6 mol⁻¹ dm³) were observed (as can be seen in Fig. 1 for a typical example); it is to be recalled that these transitions are the most characteristic part of the aquachromium(III) spectrum. Two d-d bands, ascribed to chromium(III), were observed at λₘₐₓ=408 and 570 nm. In case of complexation of chromium(III) with organic acids shift in chromium(III) bands to shorter wavelengths have been observed. Therefore, we can safely conclude that the complex of lactic acid-aquachromium(III) ion is one of the products. Secondly, the reaction mixture was used to charge a Dowex 50 W-x8, 100-200 mesh cation-exchange resin. The column was rinsed first with water and then with a solution of HClO₄-NaClO₄ having [H⁺]=2.0 mol dm⁻³. The result of a fraction (lactic acid-chromium(III) complex) was blue in colour with λₘₐₓ=410 and 575 nm.
The redox reaction between chromium(VI) (8.3×10⁻³ mol dm⁻³) and lactic acid (≥0.14 mol dm⁻³) in potassium phthalate-hydrochloric acid buffer at 25°C resulted in the formation of a relatively long-lived chromium(V) species (λᵥₐₓ_max=750 nm). At constant [chromium(VI)], as the concentration of lactic acid was increased, the absorbance due to chromium(V) species (at 750 nm) increased. At a ratio of 0.57:8.3×10⁻³ (lactic acid:chromium(VI)), the total amount of chromium(V) reached a maximum within 30 min and then slowly decayed. On the other hand, at [lactic acid]≤0.21 mol dm⁻³, no decomposition of chromium(V) species was observed even up to 100 min (Fig. 2). The values of k₀obs are given in Table 1. At all acidities the slope of plots of log (k₀obs) versus log [lactic acid] were ca. 2 corresponding to second order dependence on [lactic acid]. The chromium(VI) oxidation of α-hydroxycarboxylic acids involves the formation of a cyclic ester intermediate. Therefore, the presence of anionic species of lactic acid is essential. In order to test whether the presence of –COOH group in lactic acid is an equally important requirement in the oxidation, we monitored the oxidation at different [H⁺] (adjusted with NaOH). The reaction was studied as a function of [H⁺] between 1.0×10⁻⁶-1.0×10⁻⁴ mol dm⁻³ at fixed [lactic acid] and [chromium(VI)] at 25°C. The oxidation was not observable at all, even after prolonged incubation at 25°C. These results confirm that the reaction can proceed with significant rate only when the lactic acid supplies a proton to chromium(VI). Since the Kₛ of lactic acid is 6.4×10⁻⁵ and the reaction occurs at pH<3.0, the conclusion of unionised form of lactic acid being the active species seems justified.

Evidently, the mechanism of chromium(VI) reduction depends strongly both on the nature of the substrate and the reaction medium. Hasan and Rocek proposed two different mechanisms: at high [chromium(VI)] in strongly acidic medium, one-step two-electron mechanism operates while at lower [chromium(VI)] and in less acidic medium one-step three-electron mechanism is preferred. The most common examples of one-step three-electron oxidations proceed through a 1:2 chromium(VI)-
substrate complex. On the basis of the above discussion and experimental evidence (e.g., second order with respect to [lactic acid]), the following one-step three-electron oxidation mechanism is proposed:

As regards the nature of chromium(V)-lactic acid complex, it is pertinent to recall earlier relevant work. Rocek et al.\(^3\) were the first to report a synthetic method for water-soluble stable chromium(V) compound. A bicyclic anionic structure was proposed on the basis of elemental composition and spectral data, also confirmed by X-ray diffraction. On the other hand, Sala et al.\(^2\) proposed a cationic complex (Cr(V)-glucose\(^+\)) and stated that the sixth position in the hexa-coordinate oxochromate(V) species is occupied by a molecule of the solvent yielding [CrO\(\text{L}_2\)(OH)\(_2\)]. In analogy with the \(\alpha\)-hydroxy acid reactions, lactic acid forms an anionic complex(E) with chromium(V).

In the light of observed results and the mechanism outlined in Scheme 1, the following rate equation has been derived.

\[
k_{\text{obs}} = k_1 K_1 K_2 [\text{lactic acid}]^2 / (1 + K'[\text{H}^+]) \quad \text{... (1)}
\]

Accordingly, plot of \(k_{\text{obs}}\) versus [lactic acid]\(^2\) should be linear with zero intercept. This has indeed been found to be the case.
During the course of oxidation, it was also observed that the rate of formation of chromium(V)-lactic acid complex depends on the acidity of the medium and identity of the acid (Table 1). In a typical experiment (0.35 mol dm$^{-3}$ lactic acid and 8.3$\times$10$^{-3}$ mol dm$^{-3}$ potassium dichromate), the formation of the complex was completed within 40-45 min and absorbance of the reaction mixture at 750 nm became 0.12. Decomposition of chromium(V) started after 10 min. Under the same conditions as above but in presence of 0.13 mol dm$^{-3}$ H$_2$SO$_4$, the absorbance at 750 nm reached only up to 0.09 within 10 min and then fell down rapidly showing that decomposition is occurring simultaneously. The behaviour in HClO$_4$ was similar. These observations confirm that the formation and decomposition of chromium(V) complex takes place side by side and the two steps can be separated with or without added CH$_3$COOH and only at lower concentrations of strong acids (H$_2$SO$_4$ or HClO$_4$).

Effects of [CH$_3$COOH], [H$_2$SO$_4$] and [HClO$_4$] were studied at fixed [lactic acid] and constant [chromium(VI)]. The reaction rate increased with these acids (Table 1). The absorption spectra of mixtures containing the same chromium(VI) and CH$_3$COOH in different molar ratios exhibited...
different absorptions at the same $\lambda_{\text{max}}$ (0.450 nm),
indicating that HCrO$_4^-$ is converted into acetyl chromate$^3$. The same results were obtained in
the presence of H$_2$SO$_4$ and HClO$_4$. Formation of
chromate esters has been reported in the presence
of CH$_3$COOH, H$_2$SO$_4$ and HClO$_4$ according to reaction
(2)$^{14}$.

$$\text{HCrO}_4^- + \text{H}^+ + \text{HX} \rightarrow \text{HOOCR}_2\text{X} + \text{H}_2\text{O} \quad \ldots \quad (2)$$

where X=-Oac, -ClO$_4$ or -HSO$_4$

The ester (HOOCR$_2$X) seems to react with lactic acid
and forms the following species (chromate-lactic acid
ester). A partial explanation of the enhanced rates of
the oxidation observed in

$$\text{HOOCR}_2\text{X} + \text{CH}_3\text{-CH-CH-COOH} \rightleftharpoons \text{HOOC-CH} \quad \ldots \quad (3)$$

CH$_3$COOH, H$_2$SO$_4$ or HClO$_4$ solutions may be found
in this suggestion since the X group would increase
the electron-accepting power of chromium. -HSO$_4$
and -ClO$_4$ groups which are electron withdrawing
will decrease the ease of protonation of the chromate-
ester but increase the tendency of the chromium
species to accept electrons from reducing agent (lactic
acid).

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