

Oxidation of tartaric acid by carboxylato bound chromium(V)

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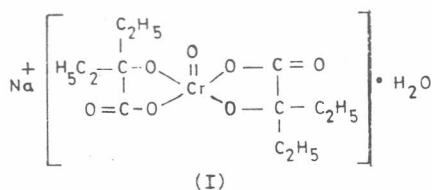
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The reaction between sodium bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) monohydrate, [Cr(V)HEBA], and *dl*-tartaric acid exhibits total second order kinetics—first order in each reactant. The reaction is H⁺-dependent and the rate is unaffected by added unbound ligand. The reaction mixture initiates acrylonitrile polymerisation, suggesting the formation of radical intermediate. The product of the reaction has been identified as glyoxal. The above results are accounted for by a mechanism involving the intermediacy of Cr(IV) and tartrate radical. The intermediacy of Cr(IV) is evidenced by the formation of cobalt(II) by an induced electron transfer reaction when Cr(V) reaction is carried out in the presence of mandelatopentaamminecobalt(III) perchlorate.

Air-stable carboxylato bound chromium(V) complex, sodium bis(2-hydroxy-2-ethylbutyrato)oxochromate(V) monohydrate(I) has been used as an oxidant in several redox reactions and a review of these reactions by Gould¹ has revealed the diversified behaviour of this oxidant. Surprisingly complex (I) behaves as a less selective oxidant towards organic substrates like 2-propanol, lactic and mandelic acids². As the oxidant is a bis-chelate of tertiary acid (2-hydroxy-2-ethylbutyric acid), its reaction with a secondary α -hydroxy acid may throw light on the stability of chromium(V) complex in solution. The title investigation is an attempt in this direction.



Materials and Methods

Complex (I) was prepared following the procedure of Rocék and Krumpolc³ and purified by precipitating it from acetone solution periodically by the addition of hexane. *dl*-Tartaric acid of extra pure variety (Aldrich) was recrystallised before use. Acetic acid (AR), acetone, sodium acetate trihydrate and sodium dichromate were of reagent

grade (BDH). Lithium perchlorate was prepared following the literature procedure⁴.

Rate measurements

The reactions were carried out in acetate-acetic acid buffer at pH 4.05 and constant ionic strength of 0.20 mol dm⁻³ NaClO₄. From the decrease in absorbance measured periodically at 510 nm [one of the absorption maxima of chromium(V) complex ($\epsilon_{510}^3 = 160 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)] using a Carl-Zeiss VSU 2-P spectrophotometer at 32 ± 0.2°C, the specific rates were calculated using integrated first order equation as well as from linear plots of log (A_t - A_∞) versus time. All the experiments were carried out in duplicate and the rate constants obtained were reproducible within ± 7%.

Product analysis and stoichiometric studies

Reaction mixtures containing complex(I), in the concentration range of 1.0 × 10⁻³ mol dm⁻³ to 5.0 × 10⁻³ mol dm⁻³ and *dl*-tartaric acid of 4.0 × 10⁻⁴ to 8.0 × 10⁻⁴ mol dm⁻³ after nine half-lives were scanned spectrophotometrically from 350 nm to 650 nm. The absorption maxima were found to occur at 420 nm ($\epsilon = 39 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 565 nm ($\epsilon = 34 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), corresponding to chromium(III) complex. Further the molar extinction coefficients were suggestive of the formation of monocarboxylatochromium(III).

After nine half-lives, the organic product in the reaction mixture was extracted with ether. The

Table 1—Kinetic data for chromium(V) oxidation of tartaric acid^{a,c,d}

10^2 [tartaric acid] mol dm ⁻³	10^3 [Cr(V)] mol dm ⁻³	10^5 [H ⁺] mol dm ⁻³	10^3 [HEBA] mol dm ⁻³	$10^3 k_1$ s ⁻¹
2.0	1.0	8.9	1.0	1.66
2.0	2.0	8.9	1.0	1.64
2.0	4.0	8.9	1.0	1.63
0.50	1.0	8.9	1.0	0.43
1.0	1.0	8.9	1.0	0.86
1.50	1.0	8.9	1.0	1.28
4.0 ^b	1.0	8.9	1.0	3.5
0.75	1.0	20	1.0	14.1
0.75	1.0	5.0	1.0	3.5
0.75	1.0	3.2	1.0	2.2
2.0	2.0	8.9	2.0	1.64
2.0	2.0	8.9	4.0	1.65
2.0	2.0	8.9	8.0	1.70
2.0	2.0	8.9	12.0	1.68

^aReactions were carried out in acetate-acetic acid buffer at pH 4.05 and $32 \pm 0.2^\circ\text{C}$ at constant ionic strength 0.20 mol dm^{-3}

^bAt this concentration of tartaric acid, there is slight change in pH of the buffer solution to the extent of 0.10 unit. Hence higher concentrations of tartaric acid were not tried.

^cUnder the same reaction conditions, the specific rate for Cr(VI) oxidation of tartaric acid is $8.4 \times 10^{-6} \text{ s}^{-1}$ when $[\text{Cr(VI)}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{tartaric acid}] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$.

^dWhen both acetic acid and acetate concentrations are either doubled or halved, specific rate for the Cr(V)-tartaric acid obtained is $1.69 \times 10^{-3} \text{ s}^{-1}$, as there is no buffer catalysis.

ether extract was dried (anhydrous Na_2SO_4) and concentrated to leave a liquid residue which on IR analysis ($\nu\text{C-H}$ and a deformation mode at 2900 cm^{-1} and 1975 cm^{-1} respectively and $\nu\text{C=O}$ in the range $1730\text{--}1740 \text{ cm}^{-1}$) showed the product to be glyoxal.

The stoichiometry of Cr(V)-*dl*-tartaric acid reaction was determined by taking the oxidant in excess at different concentrations, in acetate-acetic buffer of pH 4.05 at $32 \pm 0.2^\circ\text{C}$. After nine half-lives, the unreacted Cr(V) was estimated spectrophotometrically at 510 nm. Due blank corrections for the decomposition/disproportionation of Cr(V) were applied. Stoichiometric results indicate that 1 mol of tartaric acid requires 2 mol of Cr(V) to give glyoxal.

Polymerisation test

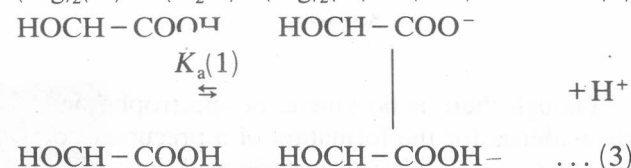
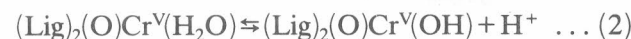
The reaction mixture containing Cr(V) and tartaric acid initiated polymerisation of acrylonitrile indicating that the reaction proceeds by a radical pathway. It was ascertained before hand that neither chromium(V) nor the medium initiated polymerisation of acrylonitrile.

Results and Discussion

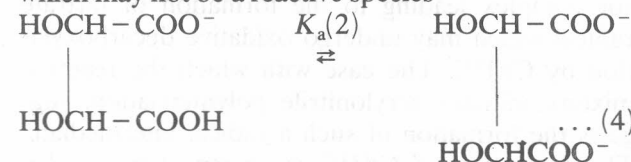
Table 1 summarises the kinetic data for the Cr(V) oxidation of *dl*-tartaric acid. The rate of disappearance of Cr(V) depends on first power of [Cr(V)]. The order in tartaric acid is also found to be one, from the unit slope of linear log-log plot of k_1 versus [tartaric acid]. Hence the rate-law for the Cr(V) oxidation of *dl*-tartaric acid can be given by Eq. (1)

$$-\frac{d[\text{Cr(V)}]}{dt} = k_2[\text{Cr(V)}][\text{tartaric acid}] \quad \dots (1)$$

With decrease in $[\text{H}^+]$ the rate decreases (Table 1). A plot of $\log [\text{H}^+]$ versus $\log k_1$ has a unit slope and this can be explained by more than one way. Possibly the equilibrium (2) is shifted to the forward direction with decrease in $[\text{H}^+]$ lowering the concentration of reactive species, viz. $(\text{O})\text{Cr}^{\text{V}}(\text{Lig})_2(\text{H}_2\text{O})$. Alternatively, as the pK_a (1) and pK_a (2) of *dl*-tartaric acid are 3.03 and 4.37 (ref. 5) respectively and as the reaction is carried out at pH 4.05, in this medium, possibly the monoanion of *dl*-tartaric acid may be the reactive species.



With decrease in $[\text{H}^+]$, the forward reaction is favoured, thereby increasing the [dianion] (Eq. 4) which may not be a reactive species



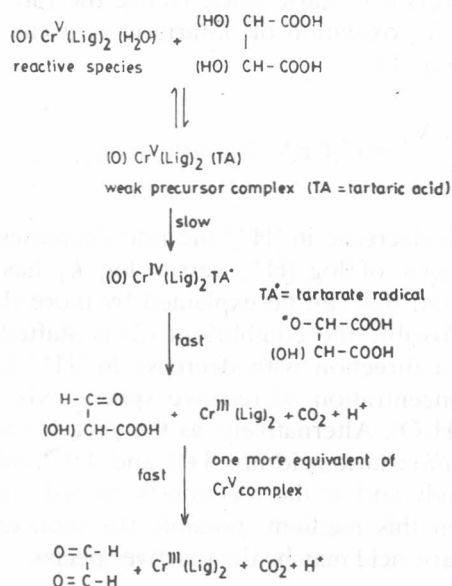
As similar $[\text{H}^+]$ dependence has been observed in the Cr(V) oxidation of NO_2^- also⁶, the above observation can be attributed to the change in [Cr(V) species]. The rate expression for such a H^+ -dependent reaction can be given by Eq. (5).

$$-\frac{d[\text{Cr(V)}]}{dt} = k_{\text{obs}}[\text{Cr(V)}][\text{tartaric acid}][\text{H}^+] \quad \dots (5)$$

The addition of unbound carboxylate does not alter the rate of Cr(V) oxidation of tartaric acid (Table 1), unlike the results observed in the Cr(V) oxidation of N_2H_4 (ref. 7) and NH_2OH (ref. 8) but similar to that observed in the Cr(V) oxidation of

NO_2^- (ref. 6). This possibly suggests that there is no reversible loss of carboxylato ligand from the Cr(V) complex before electron transfer in the rate-determining step.

The foregoing results lead to a mechanism shown in Scheme 1.



Scheme 1

Though there is no kinetic or spectrophotometric evidence for the formation of a precursor complex between Cr(V) and tartaric acid, it is still assumed so that the electron transfer to Cr(V) by an inner-sphere path can be envisaged. In a slow step, there is an internal electron transfer in the precursor complex leading to the formation of tartrate radical which may undergo oxidative decarboxylation by Cr(IV). The ease with which the reaction mixture initiates acrylonitrile polymerisation, suggests the formation of such a radical intermediate. The formation of Cr(IV) as intermediate is also evidenced by the reduction at Co(III) centre in mandelatopentaammine cobalt(III) perchlorate by an induced electron transfer when the reaction was carried out in the presence of added mandelatopentammine cobalt(III) perchlorate. Chromium(IV) is known to induce such an electron transfer in Co(III) complexes of α -hydroxy acids⁹. The amount of Co(II) formed corresponds to nearly 60% of $[\text{Co(III)}]_{\text{initial}}$. Possibly Cr(IV) is in-

involved in more than one competing reaction. By a similar route another equivalent of Cr(V) may be consumed by the initial product to yield glyoxal as the ultimate product. Although diligated Cr(III) product is expected according to the reaction sequence, the spectral studies on Cr(III) product favour only a monoligated product. Probably one of the bound ligands is lost in a fast step involving Cr(IV) species. As Cr(VI) oxidises *dl*-tartaric acid at a slower rate (see footnote c in Table 1), possibly, it may not be involved in the reaction sequence involving Cr(V) and tartaric acid.

Under the conditions $[\text{substrate}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Cr(V)}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HEBA}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ and $\text{pH} = 4.05$, $10^4 k_1$ values for Cr(V) oxidation *dl*-tartaric acid, *dl*-lactic acid and *dl*-mandelic acid are 16.9, 1.6 and 0.59 s^{-1} respectively while thiolactic acid reaction is over in 10 s. But for the greater reactivity of thiolactic acid, among the oxo compounds, *dl*-tartaric acid gets oxidised faster than other compounds. Also tartaric acid-Cr(V) mixture is unique in inducing acrylonitrile polymerisation as well as effecting reduction at Co(III) centre. As the reaction mixture containing Cr(V)-lactic acid/Cr(V)-thiolactic acid/Cr(V)-mandelic acid/Cr(V)-malonic acid/does not exhibit any of these characteristics, possibly these reactions proceed by a single two-electron transfer to Cr(V) without the intervention of organic radicals. The preference for two one-electron transfer steps by Cr(V) in the presence of tartaric acid may be due to the presence of two -OH groups in tartaric acid as Cr(V) oxidation of malonic acid proceeds very slowly under the same reaction conditions. Possibly Cr(IV) formed is stabilised by the radical intermediate with one more -OH group.

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