Micellar effect on the reaction of chromium(VI) oxidation of some representative α–hydroxy acids in the presence and absence of 2,2´-bipyridyl in aqueous acid media: A kinetic study

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The kinetics and mechanism of chromic acid oxidation of α-hydroxy acids in the presence and absence of 2,2´-bipyridyl in aqueous acid media have been studied at different temperatures by quenching technique under the conditions of [α-hydroxy acid] >> [Cr(VI)] and [bpy] >> [Cr(VI)]. Under the kinetic conditions, the monomeric species of Cr(VI) has been found to be kinetically active in the absence of bpy while in the bpy-catalysed path, Cr(VI)-bpy complex is suggested as the active oxidant. In the bpy-catalysed path, Cr(VI)-bpy complex receives a nucleophilic attack by the substrate to form a ternary complex which subsequently experiences a 2e-transfer redox decomposition leading to Cr(IV)-bpy complex and keto acid. Then the Cr(IV)-bpy complex participates in the oxidation of α-hydroxy acid in faster steps and ultimately is converted into the inert Cr(III)-bpy complex. In the uncatalysed path, Cr(VI)-substrate ester undergoes a redox decomposition through 2e-transfer at the rate determining step. The uncatalysed as well as the bpy-catalysed paths show first order dependence on both [α-hydroxy acid] and [Cr(VI)]. The bpy-catalysed path is first order in [bpy]. In the presence of surfactants like N-cetylpyridinium chloride and sodium dodecyl sulfate, the reaction orders remain unchanged. The former has been found to retard both the uncatalysed and bpy-catalysed paths while the latter shows rate accelerating effect for both the paths. The observed micellar effects have been explained by considering hydrophobic and electrostatic interactions between the reactants and surfactants in terms of the proposed mechanism.

Keywords: Kinetics, Reaction mechanisms, Oxidations, Micellar effects, Hydroxy acids

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To understand the mechanistic aspects of reduction of Cr(VI) to Cr(III), several kinetic studies of chromic acid oxidation of different types of organic substrates have been carried out by different workers1. Kinetic studies of oxidation of different types of organic substrate by halochromate have also been investigated by different workers2 to explore the effect of the substituent on the redox activity of Cr(VI). In this regard, micellar effect has been utilised by different workers as a powerful probe to explore the redox activity of chromium(VI)3. In the presence of chelating agents, the redox activity of chromic acid has been found to change drastically3,4. Different types of chelating agents like picolinic acid, 2,2´-bipyridyl (bpy), 1,10-phenanthroline (phen), oxalic acid, hydroxycarboxylic acids, etc., to catalyse the Cr(VI) oxidation of different types of organic substrates are quite important. 2,2´-Bipyridyl (bpy) is an efficient catalyst in chromic acid oxidation of different types of organic substrates. Though 2,2´-bipyridyl is not co-oxidised, it is gradually lost during the reaction through the formation of inert Cr(III)-bpy complex. Thus, bpy is not a true catalyst and is better described as a promoter. The present investigation aims to follow the kinetics of oxidation of α-hydroxy acid (malic acid and lactic acid) by chromic acid. The studies have been carried out in aqueous micellar media with a view to substantiate the mechanistic paths proposed from the observed micellar effects3,4,9.

Materials and Methods

All the chemicals were of AR grade. 2,2´-Bipyridyl (Qualigens, India) was used after repeated crystallisation from methanol (m.pt. 136ºC). Malic acid (SRL), lactic acid (SRL), K₂Cr₂O₇ (BDH), sodium dodecyl sulfate (SDS) (SRL), N-cetylpyridinium chloride (CPC) (SRL) and all other chemicals used were of highest purity available commercially. Solutions were prepared in doubly distilled water.

Solutions of the oxidant and reaction mixtures containing known quantities of the substrates (S)
(i.e., α-hydroxy acid), catalyst (bpy) (under the conditions $[S]_T \gg [Cr(VI)]_T$ and $[bpy]_T \gg [Cr(VI)]_T$), acid and other necessary chemicals were separately thermostated (± 0.1°C). The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture. Progress of the reaction was monitored by following the rate of disappearance of Cr(VI) by a titrimetric quenching technique as discussed earlier. The pseudo first order rate constants ($k_{obs}$) were calculated as usual. Under the experimental conditions, the possibility of decomposition of the surfactants by Cr(VI) was investigated and the rate of decomposition in this path was found to be kinetically negligible. To circumvent the solubility problem, different acids (HClO$_4$ and H$_2$SO$_4$) were used to follow the effects of the anionic surfactant (SDS) and cationic surfactant (CPC). The pseudo first-order rate constants ($k_{obs}$) were reproducible within the experimental error limit.

Under the kinetic conditions, [RCHOHCOOH]$_T \gg [Cr(VI)]_T$, the oxidised reaction mixture was completely neutralised by sodium bicarbonate and then extracted with ether. The ethereal layer was used for the detection of very small amounts of acetaldehyde while the aqueous layer was used to detect and estimate the main product, pyruvic acid. In both the cases, aqueous HCl solution of 2,4-dinitrophenylhydrazine was used to precipitate the hydrazones. The products were qualitatively checked by m.pt. of the hydrazones of pyruvic acid (m.pt. 218°C) and that of acetaldehyde (m.pt. 168°C). Under the experimental conditions, $[\alpha$-hydroxy acid]$_T \gg [Cr(VI)]_T$ and $[bpy]_T \gg [Cr(VI)]_T$, the overall stoichiometry of the reactions may be represented as follows (neglecting the formation of minor product acetaldehyde):

$$3\text{CH}_3\text{CHOHCOOH} + 2\text{HCrO}_4^- + 8\text{H}^+ \rightarrow 3\text{CH}_3\text{COCOOH} + 2\text{Cr(III)} + 8\text{H}_2\text{O} \quad \ldots \ldots (1)$$

$$3\text{CH}_3\text{(COOH)}\text{CHOHCOOH} + 2\text{HCrO}_4^- + 8\text{H}^+ \rightarrow 3\text{CH}_3\text{COCOOH} + 2\text{Cr(III)} + 3\text{CO}_2 + \text{H}_2\text{O} \quad \ldots \ldots (2)$$

**Results and Discussion**

In the presence and absence of bpy under the experimental conditions, the rate of disappearance of chromium(VI) shows a first order dependence on [Cr(VI)]. This dependence is also maintained in the presence of the surfactants, CPC and SDS. The pseudo first-order rate constants ($k_{obs}$) were evaluated from the linear plots of $\log$[Cr(VI)]$_T$ versus $t$.

The effect of [bpy] on $k_{obs}$ was followed in both aqueous H$_2$SO$_4$ and HClO$_4$ media. The plots of $k_{obs(T)}$ versus [bpy]$_T$ (Fig. 1) are linear with positive intercepts, which indicates the contribution of the uncatalysed path. This is also verified by carrying out an independent experiment in the absence of bpy. Thus, the observations may be formulated as follows:

$$k_{obs(T)} = k_{obs(a)} + k_{obs(c)} \quad \ldots \ldots (3)$$

$$k_{obs(c)} = k_{obs(T)} - k_{obs(a)} = k_{cat}[bpy]_T \quad \ldots \ldots (4)$$

Some representative values of $k_{cat}$ are given below:

For malic acid: $10^3 k_{cat(CPC)}$ (dm$^{-3}$ mol$^{-1}$ s$^{-1}$) = 14.0 ± 0.16 at 40°C for [Cr(VI)]$_T = 0.5 \times 10^{-3}$ mol dm$^{-3}$, $[\text{H}_2\text{SO}_4] = 1.0$ mol dm$^{-3}$, $[S]_T = 25 \times 10^{-3}$ mol dm$^{-3}$, $[\text{CPC}]_T = 6 \times 10^{-3}$ mol dm$^{-3}$, $[\text{bpy}]_T = (0 - 50) \times 10^{-3}$ mol dm$^{-3}$.

For lactic acid: $10^3 k_{cat(CPC)}$ (dm$^{-3}$ mol$^{-1}$ s$^{-1}$) = 18.0 ± 0.19 at 35°C for [Cr(VI)]$_T = 0.5 \times 10^{-3}$ mol dm$^{-3}$, $[\text{H}_2\text{SO}_4] = 0.5$ mol dm$^{-3}$, $[S]_T = 25 \times 10^{-3}$ mol dm$^{-3}$, $[\text{bpy}]_T = (0 - 30) \times 10^{-3}$ mol dm$^{-3}$, $[\text{CPC}]_T = 6 \times 10^{-3}$ mol dm$^{-3}$.

From the linear plot of $k_{obs}$ versus $[S]_T$, it is found that both the uncatalysed and catalysed paths show first-order in $[S]_T$.

$$k_{obs(a)} = k_{cat}[S]_T \quad \ldots \ldots (5)$$

$$k_{obs(c)} = k_{obs(T)} - k_{obs(a)} = k_{cat}[S]_T \quad \ldots \ldots (6)$$

Some representative values of $k_{cat}$ are given below:

![Fig. 1 — Dependence of $k_{cat(c)}$ on $[\text{bpy}]_T$ for the Cr(VI) oxidation of α-hydroxy acids. $[[\text{Cr(VI)}]_T = 0.5 \times 10^{-3}$ mol dm$^{-3}$, A: [malic acid]$_T = 25 \times 10^{-3}$ mol dm$^{-3}$, $[\text{H}_2\text{SO}_4] = 1.0$ mol dm$^{-3}$, $[\text{CPC}]_T = 6 \times 10^{-3}$ mol dm$^{-3}$, 40°C; B: [malic acid]$_T = 25 \times 10^{-3}$ mol dm$^{-3}$, $[\text{H}_2\text{SO}_4] = 1.0$ mol dm$^{-3}$, 40°C; C: [lactic acid]$_T = 25 \times 10^{-3}$ mol dm$^{-3}$, $[\text{H}_2\text{SO}_4] = 0.5$ mol dm$^{-3}$, 35°C; D: [malic acid]$_T = 25 \times 10^{-3}$ mol dm$^{-3}$, $[\text{HClO}_4] = 1.0$ mol dm$^{-3}$, 45°C.](image)
For malic acid: \(10^4 k_{(c) \text{(crp)}} \text{ (dm}^3\text{ mol}^{-1}\text{ s}^{-1}) = 5.0 \pm 0.12\) at 35°C for \([\text{Cr(VI)}]_T = 0.5 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{H}_2\text{SO}_4]_T = 1.0\) mol dm\(^{-3}\), \([\text{S}]_T = 0 \sim 70 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{CPC}]_T = 4 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{bpy}]_T = 15 \times 10^{-3}\) mol dm\(^{-3}\).

For lactic acid: \(10^4 k_{(c) \text{(SDS)}} \text{ (dm}^3\text{ mol}^{-1}\text{ s}^{-1}) = 9.0 \pm 0.19\) at 35°C for \([\text{Cr(VI)}]_T = 0.5 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{H}_2\text{SO}_4]_T = 0.5\) mol dm\(^{-3}\), \([\text{S}]_T = (0 \sim 100) \times 10^{-3}\) mol dm\(^{-3}\), \([\text{SDS}]_T = 4 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{bpy}]_T = 10 \times 10^{-3}\) mol dm\(^{-3}\).

The acid dependence was followed in aqueous HClO\(_4\) media at fixed \([\text{Cr(VI)}]_T\) and \([\text{S}]_T\). From the experimental fit, the observations are as given in Eqs (7) and (7a).

\[
k_{\text{obs(a)}} = k_{\text{H(a)}}[\text{H}^+] \quad \text{... (7)}
\]

\[
k_{\text{obs(c)}} = k_{\text{obs(T)}} - k_{\text{obs(a)}} = k_{\text{H(c)}}[\text{H}^+] \quad \text{... (7a)}
\]

Some representative values of \(k_{\text{H(c)}}\) are given below:

For malic acid: \(10^4 k_{\text{H(c) \text{(w)}}} \text{ (dm}^3\text{ mol}^{-1}\text{ s}^{-1}) = 1.5 \pm 0.01\) at 35°C for \([\text{Cr(VI)}]_T = 0.5 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{S}]_T = 35 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{bpy}]_T = 16 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{H}^+]_T = 0.25 \sim 1.25\) mol dm\(^{-3}\), \([\text{HClO}_4]_T + [\text{NaClO}_4]_T = 1.5\) mol dm\(^{-3}\).

For lactic acid: \(10^4 k_{\text{H(c) \text{(w)}}} \text{ (dm}^3\text{ mol}^{-1}\text{ s}^{-1}) = 2.67 \pm 0.01\) at 35°C for \([\text{Cr(VI)}]_T = 0.5 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{S}]_T = 20 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{bpy}]_T = 16 \times 10^{-3}\) mol dm\(^{-3}\), \([\text{H}^+]_T = (0.25 \sim 1.25)\) mol dm\(^{-3}\), \([\text{HClO}_4]_T + [\text{NaClO}_4]_T = 1.5\) mol dm\(^{-3}\).

Under the experimental conditions, polymerization of acrylonitrile was indicated under nitrogen atmosphere.

The reactions were carried out in aqueous sulfuric acid media (0.5-1.0 \(M\)), wherein, Cr(VI) mainly exist as \(\text{H}_2\text{CrO}_4\) and a small amount as \((\text{HO})\text{CrO}_2\text{(OS}_\text{3})\text{H}\), (i.e., chromyl sulfate). However, this distribution of Cr(VI) species does not complicate our studies because effect of different substances on the rate process was carried out at a fixed \([\text{H}_2\text{SO}_4]_T\). Effect of sulfuric acid was not studied to avoid the complication. To understand the effect of \(\text{H}^+, \text{HClO}_4\) was used. It is worth mentioning that \(\text{HClO}_4\) could not be used throughout the experiment because of the solubility problem of surfactants. The findings can be explained by considering the proposed mechanism (Schemes 1 and 2). Within the cyclic transition state (B in Scheme 1), Cr(VI) is reduced to Cr(IV). In Scheme 1, B denotes the cyclic chromic acid ester of the substrate. Under the experimental conditions, there were no kinetic and spectrophotometric evidences in favour of the proposed intermediate ester formation. However, this does not necessarily rule out the possibility of formation of the proposed intermediate\(^{10}\). In fact, if the equilibrium constants of the steps leading to the formation of the intermediate are very small, then there will be no kinetic evidence for the formation of the intermediate\(^{10}\). Then B experiences redox decomposition at the rate determining step through a 2e-transfer step, giving rise to \(\text{RCO}_2\text{H}\) and Cr(IV). For malic acid, \(\text{CH}_3\text{(CO}_2\text{H})\text{CO}_2\text{H}\) (a \(\beta\)-keto acid) undergoes further decarboxylation giving rise to the final product \(\text{CH}_3\text{CO}_2\text{H}\) (Scheme 1).

The Cr(IV) generated may subsequently participate in the faster reactions to be reduced to Cr(III) in

![Scheme 1](image-url)
different possible ways. Recent studies support the following path involving Cr(II) in which the substrate always acts as a 2e-reductant.

Cr(IV) + S → Products + Cr(II)
Cr(II) + Cr(VI) → Cr(III) + Cr(V)
Cr(V) + S → Products + Cr(III)

Cr(II) is produced from Cr(IV) through hydride transfer. Thus, the carbocationic centre generated is responsible for acrylonitrile polymerisation. It may be noted that in Rocek mechanism, the free radical (S•), produced through the 1e-oxidation of the substrate by Cr(IV) is supposed to be responsible for acrylonitrile polymerisation.

Scheme 1 gives the mechanistic steps for the oxidation of α-hydroxy acids in absence of bpy. Scheme 1 leads to the following rate law (assuming $K_1$ to be quite small under the present conditions). The factor 2/3 appears from the stoichiometry of the overall reaction.

$$k_{\text{obs(u)}} = \frac{2}{3}K_{1}[S]_{T}[H^+]$$

Here it is important to mention that for the substrates containing alcoholic -OH groups (e.g. sugars, hexitols, alkanols, diols etc.), the uncatalysed Cr(VI) oxidation path shows a second order dependence on [H⁺], while in the present case it shows a first order dependence on [H⁺] under comparable conditions. For the substrates containing the alcoholic –OH groups (the Cr(VI)–substrate ester mentioned above, i.e., B) produced at the preequilibrium step is not kinetically active and it needs further protonation on the oxygen centre of ‘Cr–O’ bond before its redox decomposition. This protonation favours electron flow towards the Cr(VI) centre. Consequently, Cr(VI) oxidation of such substrates shows a second order dependence on [H⁺]. In the present case, the proposed ester (i.e., B) does not require any further protonation for its redox decomposition and is itself kinetically active. The chelation by the carboxylate group in B favours the electron flow towards the Cr(VI) centre within the proposed cyclic transition state (see Scheme 1), thus showing a first order dependence on [H⁺].

Formation of a small amount of aldehyde can be explained by considering the carbon-carbon bond cleavage by Cr(IV) (Scheme 2). For malic acid (i.e., R), the aldehyde (HO$_2$CCH$_2$CHO) undergoes decarboxylation giving rise to CH$_3$CHO.

Scheme 3 explains the pathways of bpy-promoted Cr(VI) oxidation and it involves bpy coordination leading to a different intermediate (E), which is the active oxidant. Under the experimental conditions, the first-order dependence on [bpy]$_T$ is strictly maintained throughout the range of [bpy] used. Hence, it is reasonable to conclude that the equilibrium constant for the reaction leading to cyclic Cr(VI)-bpy complex is low. In the next step, the Cr(VI)-bpy complex reacts with the substrate to form a ternary complex (F), which experiences a redox decomposition at a rate-limiting step giving rise to the products and the Cr(IV)-bpy complex. The fate of Cr(IV)-bpy complex may be the same as in the case of uncatalysed path. Scheme 3 leads to the following rate law under the
steady-state condition of the proposed ternary complex (F):

\[ k_{\text{obs(c)}} = \frac{2}{3} K_3 K_2[S]_1[bpy]_1[H^+] \] ... (18)

The final fate of the Cr(III) species has been confirmed spectroscopically. The UV-visible spectra were recorded in the range 350-700 nm at regular intervals to follow the gradual development of the reaction intermediate (if any) and product spectrophotometrically. The gradual disappearance of Cr(VI)-species and appearance of Cr(III) species is seen with the isosbestic point at \( \lambda = 525 \) nm. Observation of this single isosbestic point indicates the very low concentration of the probable intermediates like Cr(V) and Cr(IV) under the present experimental conditions. In other words, it indicates the gradual decrease of Cr(VI) with the concomitant increase of Cr(III). Concentration of the intermediate species formed is too low to be detected spectrophotometrically. The characteristic part of electronic absorption spectrum of Cr(III) species lies in the range 360-600 nm. The colours of the final solutions of the uncatalysed and bpy-catalysed reaction are different due to the presence of different types of Cr(III) species. The colour of the final solution for the uncatalysed reaction (i.e. in absence of bpy) under the experimental condition is pale blue
explain the formation of Cr(III)-bpy product. In fact, Cr(VI) is labile remains present in the coordination sphere of higher present experimental conditions. It indicates that bpy independent experiment shows that within the final solution. The suggested Cr(III)-bpy complex is quite reasonable because of the favoured metal-to-ligand charge transfer. In fact, the vacant $\Pi^*$ of bpy favours the metal to ligand charge transfer. The existence of the charge transfer band at a much lower energy for the proposed Cr(III)-bpy complex is quite reasonable because of the favoured metal-to-ligand charge transfer. In fact, the vacant $\Pi^*$ of bpy favours the metal to ligand charge transfer. The existence of the charge transfer band (metal-to-ligand) at this lower energy for the bpy-catalysed reaction indirectly supports the proposition of the Cr(III)-bpy complex in the final solution. The suggested Cr(III)-bpy complex is not formed after the reduction of Cr(VI) to Cr(III) because Cr(III) is kinetically inert. In fact, Cr(VI) is labile and it is reasonable to consider the formation of Cr(VI)-bpy complex in a rapid pre-equilibrium step to explain the formation of Cr(III)-bpy product.

Plots of $k_{obs(T)}$ versus [CPC]$_T$, $k_{obs(A)}$ versus [SDS]$_T$, and $k_{obs(B)}$ versus [SDS]$_T$ indicate the rate enhancement at lower concentrations of SDS (Fig. 3). In $k_{obs(T)}$, the major contribution comes from the catalysed path. In the bpy-catalysed path, the rate acceleration is due to preferential partitioning of the positively charged Cr(VI)-bpy complex (by electrostatic attraction) and neutral substrate in the micellar surface (Stern layer). Thus, SDS allows the reaction to proceed in both aqueous and micellar interphases. The partitioning mode leads to higher local concentration of both the reactants at the micelle-water interphase compared to their stoichiometric concentrations. SDS permits the reaction in both the phases with a preferential rate enhancement in the micellar phase. At higher concentration, SDS retards the reaction. This is due to the dilution effect on the partitioned reactants in the micellar phase. Reactants are distributed over a large number of micelles.

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Retardation in higher concentration can be explained with the help of pseudo-phase ion exchange (PIE) model. The reaction is acid-catalysed and the corresponding exchange equilibrium between $H^+$ ion and $Na^+$ ion at the micellar surface is as given in Eq. (19).

$$H_W^+ + Na_M^+ \rightleftharpoons H_M^+ + Na_W^+ \quad \ldots (19)$$

Here the subscripts $W$ and $M$ denote the aqueous phase and micellar phase respectively. With the increase in [SDS]$_T$, the concentration of counterion (i.e. $Na^+$) also increases, which drives the equilibrium to the left. This factor retards the rate process at higher [SDS]$_T$. The dilution factor for the accumulated reactants in the micellar phase is also partly responsible for rate retardation at high surfactant concentration.

The shapes of the micelles and cmc values of surfactants are strongly dependent on the electrolyte concentration; electrolytes reduce the cmc values of SDS. The present kinetics studies have been carried out in strongly aqueous acid media and determination of cmc value is a difficult task under the present experimental conditions. This is why the micellar effects have been interpreted qualitatively. Here it is worth mentioning that analysis of the kinetic data in such cases can be done by Piszkiewicz model which does not require the cmc values. This model when applied in similar systems yields very low values of $n$ (cooperativity index) as compared to the aggregation number. This indicates the existence of catalytically productive submicellar aggregates.

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