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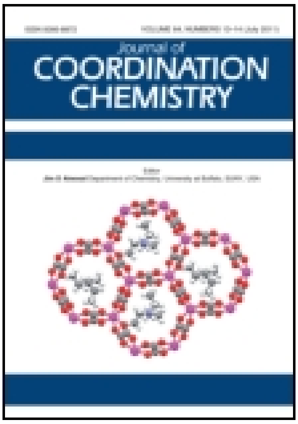

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Micellar catalysis on 1,10-phenanthroline promoted hexavalent chromium oxidation of ethanol

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Micellar catalysis on 1,10-phenanthroline promoted hexavalent chromium oxidation of ethanol

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The kinetics and mechanism of Cr(VI) oxidation of ethanol in the presence and absence of 1,10-phenanthroline in aqueous acid media have been carried out. Monomeric species of Cr(VI) are kinetically active in the absence of phen, while in the phen catalyzed path, the Cr(VI)-phen complex has been suggested as the active oxidant. In the catalyzed path, the Cr(VI)-phen complex participates in the oxidation of ethanol and ultimately is converted into the Cr(III)-phen complex. In the uncatalyzed path, the Cr(VI)-substrate ester experiences an acid catalyzed redox decomposition in the rate-determining step. The uncatalyzed path shows a second-order dependence on $[H^+]$, while the phen catalyzed path shows a first-order dependence on $[H^+]$. Both the uncatalyzed and phen-catalyzed paths show first-order dependence on $[\text{ethanol}]_T$ and $[\text{Cr(VI)}]_T$. The phen-catalyzed path is first order in $[\text{phen}]_T$. These observations remain unaltered in the presence of externally added surfactants. CPC inhibits the reactions while SDS catalyzes the reactions. The observed miceller effects have been explained by considering partitioning of the reactants between the miceller and aqueous phase.

Keywords: Chromium; 1,10-Phenanthroline; Ethanol; Micellar catalysis

1. Introduction

Chromium(VI) compounds are traditionally used as oxidizing agents in organic synthesis, mainly in the oxidation of alcohol to carbonyl compounds [1, 2]. Among the chelating agents, picolinic acid (PA), 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy), ethylenediaminetetraacetic acid (edta), oxalic acid, *etc*., several act as catalysts [3] in hexavalent chromium oxidation of different organic substrates. Picolinic acid has unique catalytic ability [4–12]. The structure of bipyridine and phenanthroline are comparable to picolinic acid in many respects and in particular, all chelating agents are heteroatomic nitrogen bases. Picolinic acid, bipyridine and phenanthroline are never co-oxidized along with the substrate, but act as an oxidation catalyst. During the reaction, similar to picolinic acid, bipy and phenanthroline are gradually lost due to the formation of inert Cr(III)-bipy and Cr(III)-phen complexes. Recently we reported bipyridine promoted Cr(VI) oxidation of dimethyl sulfoxide [13], D-fructose [14], D-glucose [15], hexitols [16], ethanol and propan-1-ol [17], ethane-1,2-diol [18] and propan-2-ol [19], but there are very few studies of 1,10-phenanthroline catalyzed Cr(VI)

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oxidation of organic substrates [14, 20, 21]. This article deals with micelle effects on 1,10-phenanthroline promoted Cr(VI) oxidation of ethanol. It has been observed [12–21] that micelles significantly influence the kinetic and mechanistic aspects of Cr(VI) oxidation of different organic substrates, and the observed micelle effect can substantiate the proposed reaction mechanism.

2. Experimental

Alcohol (E. Merck) was purified by refluxing with an excess of freshly burnt quicklime, followed by distillation, and the purity was checked by density measurement. $K_2Cr_2O_7$ (BDH, AR), cetylpyridinium chloride, CPC (SRL, AR), sodium dodecyl sulphate, SDS (SRL, AR) and all other chemicals used were of highest purity available commercially. Solutions of the oxidant and reaction mixture containing known quantities of the substrate (S) (i.e., alcohol), catalyst (phen) under the conditions $[S]_T \gg [Cr(VI)]_T$ and $[catalyst]_T \gg [Cr(VI)]_T$, acid and other necessary chemicals were separately thermostated ($\pm 0.10\,^{\circ}C$). The reaction was initiated by mixing requisite amounts of the oxidant with the reaction mixture. Progress of the reaction is monitored by following the rate of disappearance of Cr(VI). The concentration of Cr(VI) at different time intervals was measured by a titrimetric quenching technique using excess of standard Mohr's solution and unreacted Fe(II) was estimated by a standard Ce(IV) solution using ferroin indicator [6]. The pseudo-first order rate constants were calculated from the slopes of the plots of $\log[Cr(VI)]_t$ *versus* time (t), which were linear at least for three half-lives. The scanned spectra and spectrum after completion of the reaction were recorded with a UV-VIS spectrophotometer [UV-2450 (SHIMADZU)]. Quartz cuvettes of path length 1 cm were used. 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 kinetically negligible. Under the kinetic conditions $[CH_3CH_2OH]_T \gg [Cr(VI)]_T$, the alcohol was quantitatively oxidized to the carbonyl compound, which was identified by the preparation of 2,4-DNP derivatives. No positive test [22] for carboxylic acid due to further oxidation of the aldehydes was found, indicating no further oxidation occurred under the experimental conditions. In the presence of excess CH_3CH_2OH, oxidation of the product is kinetically insignificant. The overall stoichiometry of the reaction may be represented as

$$3CH_3CH_2OH + 2HCrO_4^- + 8H^+ \rightarrow 2Cr(III) + 3CH_3CHO + 8H_2O \qquad (1)$$

The color of the final solution under the experimental conditions is pale blue ($\lambda_{max} = 412\,nm$, $\varepsilon_{max} = 4.4\,M^{-1}\,cm^{-1}$ and 512 nm, $\varepsilon_{max} = 4.4\,M^{-1}\,cm^{-1}$) and the corresponding transitions are 512 nm for $^4A_{2g}$ (F) → $^2T_{2g}$ (F) and 412 nm for $^4A_{2g}$ (F) → $^2T_{1g}$ (F) of the Cr(III) species.

3. Results and discussion

3.1. *Dependence on $[Cr(VI)]_T$*

Under the experimental conditions $[ethanol]_T \gg [phen]_T \gg [Cr(VI)]_T$, both in the presence and absence of phen, the rate of disappearance of Cr(VI) shows a first-order dependence on $[Cr(VI)]_T$. This first-order dependence on Cr(VI) is also maintained in the presence of surfactants; (k_{obs}) has been evaluated from the linear plot of $\log[Cr(VI)]_T$ *versus* time (t) as usual.

3.2. *Dependence on [phen]$_T$*

Plots of k_{obs} *versus* $[phen]_T$ are linear ($r > 0.99$) with positive intercepts measuring the contribution of the relatively slower uncatalyzed path (figure 1). The pseudo-first order rate constants ($k_{obs(U)}$) directly measured in the absence of phen under the same conditions agree with those obtained from the intercepts of the plots of $k_{obs(T)}$ *versus* $[phen]_T$. The observation is formulated as follows.

$$k_{obs} = k_{obs(U)} + k_{cat}\,[phen]_T \tag{2}$$

In the presence and absence of surfactants (CPC and SDS) the above relationship was found to be true. During the progress of the reaction, phen is lost due to formation of an inert Cr(III)-phen complex. Under the conditions $[phen]_T \gg [Cr(VI)]_T$, during the progress of the reaction, $[phen]_T$ remains more or less constant.

3.3. *Dependence on [ethanol]$_T$*

From the plot of k_{obs} *versus* $[ethanol]_T$ (figure 2), the uncatalyzed and catalyzed paths show a first-order dependence on $[ethanol]_T$,

$$k_{obs(C)} = k_{obs(T)} - k_{obs(U)} = k_{S(C)}\,[S]_T \tag{3}$$

$$k_{obs(U)} = k_{S(U)}\,[S]_T \tag{4}$$

The above first-order dependence on $[ethanol]_T$ is also maintained in the presence of the surfactants CPC and SDS.

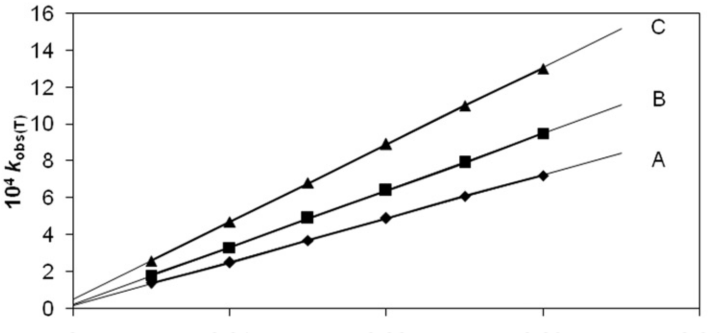


Figure 1. Dependence of $k_{obs(T)}$ on $[phen]_T$ for Cr(VI) oxidation of ethanol in aqueous H_2SO_4 at 35°C. $[ethanol]_T = 0.03\,mol\,dm^{-3}$, $[Cr(VI)]_T = 2 \times 10^{-4}\,mol\,dm^{-3}$, $[H_2SO_4]_T = 0.5\,mol\,dm^{-3}$, A: $[CPC]_T = 3 \times 10^{-3}\,mol\,dm^{-3}$; B: $[CPC]_T = [SDS]_T = 0\,mol\,dm^{-3}$; C: $[SDS]_T = 4 \times 10^{-2}\,mol\,dm^{-3}$.

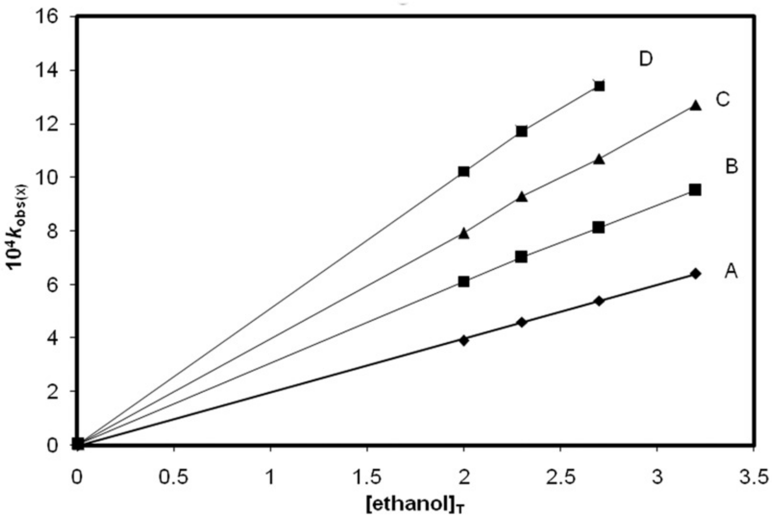


Figure 2. Dependence of $k_{obs(x)}$ (where x = U or T) on [ethanol]$_T$ for the Cr(VI) oxidation of ethanol in the presence (i.e., $k_{obs(T)}$ for B and D) and absence (i.e., $k_{obs(U)}$ for A and C) of 1,10-phenanthroline in aqueous H_2SO_4 at 30°C. $[Cr(VI)]_T = 3 \times 10^{-4}$ mol dm^{-3}. A: $[H_2SO_4] = 1.0$ mol dm^{-3}, $[CPC]_T = 2 \times 10^{-3}$ mol dm^{-3}; B: $[H_2SO_4]_T = 1.0$ mol dm^{-3}, $[phen]_T = 0.02$ mol dm^{-3}, $[CPC]_T = 3 \times 10^{-3}$ mol dm^{-3}; C: $[H_2SO_4]_T = 0.5$ mol dm^{-3}, $[SDS]_T = 4 \times 10^{-2}$ mol dm^{-3}; D: $[H_2SO_4]_T = 0.75$ mol dm^{-3}, $[phen]_T = 0.02$ mol dm^{-3}, $[SDS]_T = 3 \times 10^{-2}$ mol dm^{-3}.

3.4. *Dependence on [H$^+$]*

Acid dependence patterns for the uncatalyzed and catalyzed paths are different (figure 3). From the experimental fit, the observations are

$$k_{obs(U)} = k_{H(U)} [H^+]^2 \tag{5}$$

$$k_{obs(C)} = k_{H(C)} [H^+] \tag{6}$$

3.5. *Evidence for the formation of free radicals with acrylonitrile*

The presence of free radicals in the reaction mixture was evaluated by using the acrylonitrile monomer. The monomer solution (3.0 cm^3) was added to a reaction mixture (5.0×10^{-4} M Cr(VI), 5.0×10^{-2} M ethanol and 0.20 M $HClO_4$) and after 15 min a white precipitate appeared. The positive response indicates in situ generation of free radicals in the reaction mixture. Control experiments (with ethanol or oxidant only) did not show precipitate formation with mercuric chloride. A Cr(VI) solution (5.0×10^{-4} M) was added to a mixture of ethanol (5.0×10^{-2} M) and $HgCl_2$ (4.0×10^{-2} M) in a 50 cm^3 volume. The reaction mixture was heated to 50°C for 10 min. A white precipitate of Hg_2Cl_2 appeared as the reaction proceeded, indicating the formation of free radicals during the reaction. Control experiments did not show

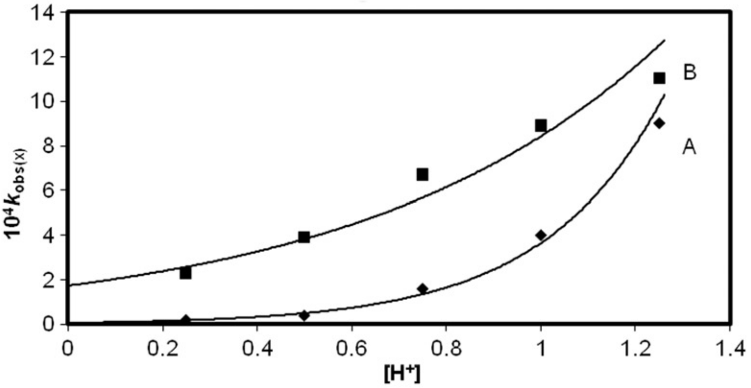


Figure 3. Dependence of $k_{obs(x)}$ (where x = U or T) on $[HClO_4]_T$ for the Cr(VI) oxidation of ethanol in the presence ($k_{obs(T)}$ for B) and absence ($k_{obs(U)}$ for A) of phenanthroline in aqueous $HClO_4$ at 20°C. $[HClO_4] + [NaClO_4] = 1.25$, $[ethanol]_T = 0.025\,mol\,dm^{-3}$, $[Cr(VI)]_T = 2 \times 10^{-4}\,mol\,dm^{-3}$, $[SDS]_T = 3 \times 10^{-2}\,mol\,dm^{-3}$, $[phen]_T = 0.025\,mol\,dm^{-3}$.

formation of the precipitate under the experimental conditions with either the oxidant or ethanol alone.

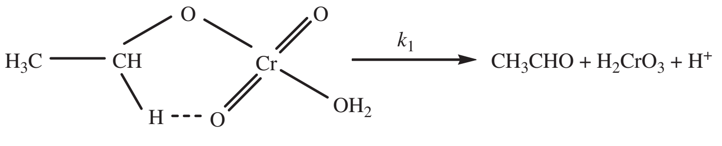
3.6. *Mechanism of the reaction*

The mechanism of the reaction can be divided in two sections: (i) uncatalyzed path and (ii) catalyzed path.

Uncatalyzed path:

$$CH_3CH_2OH + HCrO_4^- + H^+ \overset{K_1}{\rightleftharpoons} CH_3CH_2\text{-}O\text{-}CrO_2\text{-}OH\ (A) + H_2O \quad (7)$$

$$A + H_3O^+ \overset{K_2}{\rightleftharpoons} CH_3CH_2\text{-}O\text{-}CrO_2\text{-}\overset{+}{O}H_2\ (B) + H_2O \quad (8)$$

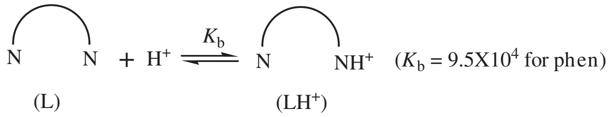


(9)

Scheme 1. Chromic acid oxidation of ethanol.

The uncatalyzed path (Scheme 1) for ethanol has already been established [17]. In Scheme 1, in the cyclic transition state (B), reduction of Cr(VI) to Cr(IV) is the rate-determining step. By considering the stoichiometry of the reaction, Scheme 1 leads to Scheme 2.

$$k_{obs(U)} = (2/3)\ K_1K_2k_1\ [CH_3CH_2OH]\ [H^+]^2 \quad (10)$$



$$\underset{(L)}{N\frown N} + H^+ \overset{K_b}{\rightleftharpoons} \underset{(LH^+)}{N\frown NH^+} \quad (K_b = 9.5X10^4 \text{ for phen}) \quad (11)$$

$$HCrO_4^- + 2\,H^+ + LH^+ \overset{K_3}{\rightleftharpoons} C_1 \quad (12)$$

$$C_1 + \underset{(S)}{CH_3CH_2OH} \overset{K_4}{\rightleftharpoons} C_2 + H^+ \quad (13)$$

$$C_2 \xrightarrow{k_2} P + Cr(VI)\text{-}L \quad (14)$$

$$Cr(IV)\text{-}L + S \xrightarrow{fast} S + Cr(III)\text{-}L \quad (15)$$

$$Cr(VI)\text{-}L + S \xrightarrow{fast} \text{Product (P)} + Cr(V)\text{-}L \quad (16)$$

$$Cr(V)\text{-}L + S \xrightarrow{fast} \text{Product (P)} + Cr(III)\text{-}L \quad (17)$$

(L = phen, S = ethanol)

Scheme 2. Cr(VI) oxidation of ethanol in the presence of phenanthroline.

For the phen-catalyzed path, Scheme 2 explains all the experimental findings. Scheme 2 leads to the following rate law

$$k_{obs(C)} = (2/3)\ K_3K_4k_2\ [S]_T[L]_T[H^+] \quad (18)$$

The formation of a Cr(III)-L complex indicates that a ligand heteroatomic N-base (L) undergoes complexation with the higher oxidation states (which are labile) of chromium. Because of the inertness of Cr(III) (t_{2g}^3), the ligand does not enter the Cr(III) coordination sphere produced after reduction of Cr(VI). However, phen readily forms the reactive cyclic Cr(VI)-L complex (C_1) which is the active oxidant [14, 20, 21]. Under the experimental conditions, first-order dependence on $[\text{phen}]_T$ is strictly maintained throughout the range of $[L]_T$ used. Hence, it is reasonable to conclude that the equilibrium constant for the reaction leading to the cyclic Cr(VI)-L complex (C_1) is low. In the next step, the Cr(VI)-L complex reacts with the substrate to form a ternary complex (C_L) which experiences a redox decomposition through a cyclic transition state. The rate-limiting step gives rise to the organic product and the Cr(IV)-L complex. Then the Cr(VI)-L complex participates in the next faster steps as discussed below:

Route I:

$$Cr(IV) + Cr(VI) \rightarrow 2\ Cr(V)$$
$$2\ Cr(V) + 2S \rightarrow 2\ Cr(III) + \text{Products}$$

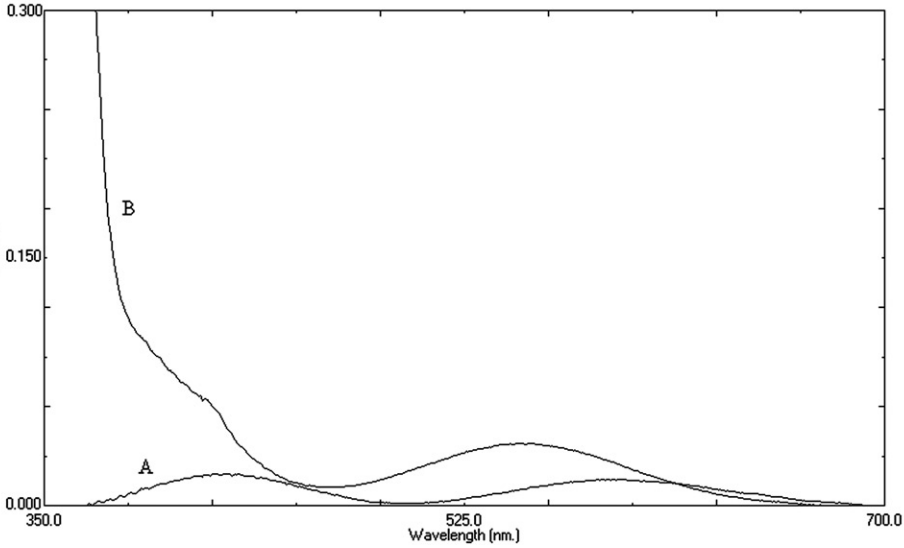


Figure 4. (A) Absorption spectrum of the reaction mixture (after completion of the reaction): $[\mathrm{Cr(VI)}]_T = 3.85 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{ethanol}]_T = 60 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{phen}]_T = 0\,\mathrm{mol\,dm^{-3}}$ (i.e., uncatalyzed path), and $[H_2SO_4] = 0.5\,\mathrm{mol\,dm^{-3}}$. (The spectrum of chromic sulfate is identical with this under the experimental condition.) (B) Absorption spectrum of the reaction mixture (after completion of reaction): $[\mathrm{Cr(VI)}]_T = 3.85 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{ethanol}]_T = 60 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{phen}]_T = 8 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ and $[H_2SO_4] = 0.5\,\mathrm{mol\,dm^{-3}}$.

Route II:

$$\mathrm{Cr(IV)} + \mathrm{S} \rightarrow \mathrm{Cr(III)} + \mathrm{S}^{\bullet}$$
$$\mathrm{Cr(VI)} + \mathrm{S} \rightarrow \mathrm{Cr(V)} + \mathrm{Products}$$
$$\mathrm{Cr(V)} + \mathrm{S} \rightarrow \mathrm{Cr(III)} + \mathrm{Products}$$

Route III:

$$\mathrm{Cr(IV)} + \mathrm{S} \rightarrow \mathrm{Cr(II)} + \mathrm{Products}$$
$$\mathrm{Cr(II)} + \mathrm{Cr(VI)} \rightarrow \mathrm{Cr(III)} + \mathrm{Cr(V)}$$
$$\mathrm{Cr(V)} + \mathrm{S} \rightarrow \mathrm{Products} + \mathrm{Cr(III)}$$

In the above-mentioned possible paths, S denotes the substrate acting as a $2\,e^-$ reductant and $S^{\bullet}$ stands for the partially oxidized substrate. In both the Watanable–Westheimer mechanism [23] (i.e., Route I) and the Perez-Bennito mechanism [24] (i.e., Route III), the title organic substrate acts in all steps as a $2\,e^-$ reductant, while it may act both as a $2\,e^-$ and $1\,e^-$ reductant in the Rocek mechanism [25] (i.e., Route II). In the Rocek mechanism [25], the free radical S^- is supposed to be responsible for acrylonitrile polymerization.

Chromium(VI) is ultimately converted into chromium(III) as is clear from figure 4. The scanned spectrum (figure 5) indicates the gradual disappearance of Cr(VI) species and appearance of Cr(III) species with an isobestic point at $\lambda = 530\,\mathrm{nm}$ for the uncatalyzed reaction and $\lambda = 522\,\mathrm{nm}$ for the catalyzed reaction. Observation of this single isobestic point indicates the very low concentration of Cr(V) and Cr(IV) intermediates under the present experimental conditions.

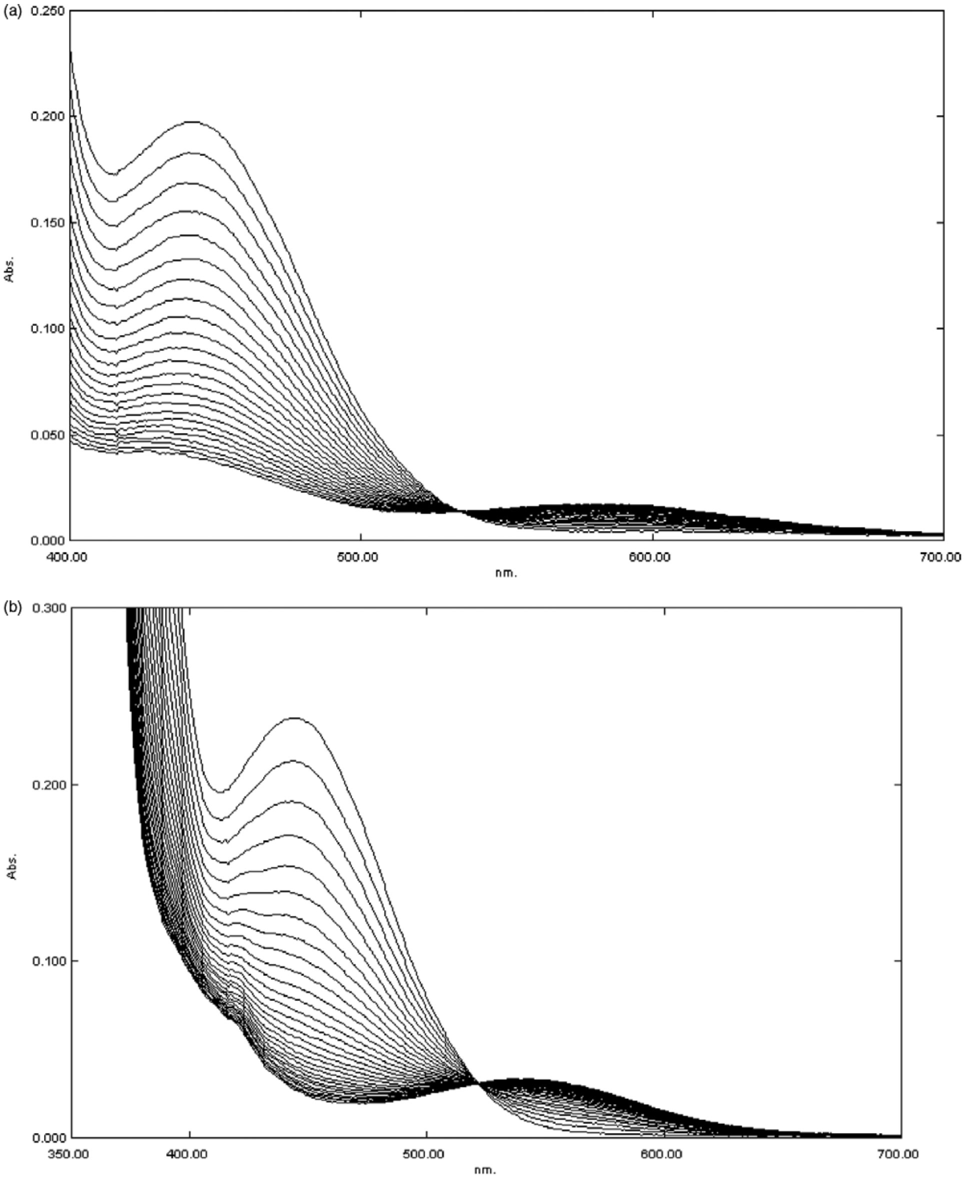


Figure 5. (a) Scanned absorption spectra of the reaction mixture at regular time intervals (5 min) up to 120 min. Concentrations at the beginning of the reaction: $[Cr(VI)]_T = 1.0 \times 10^{-3}\,mol\,dm^{-3}$, $[H_2SO_4] = 0.5\,mol\,dm^{-3}$, $[ethanol]_T = 0.1\,mol\,dm^{-3}$ and $T = 30°C$; (b) Scanned absorption spectra of the reaction mixture at regular time intervals (5 min) up to 120 min. Concentrations at the beginning of the reaction: $[Cr(VI)]_T = 1.0 \times 10^{-3}\,mol\,dm^{-3}$, $[phen]_T = 10 \times 10^{-3}\,mol\,dm^{-3}$ $[H_2SO_4] = 0.5\,mol\,dm^{-3}$, $[ethanol]_T = 0.1\,mol\,dm^{-3}$ and $T = 30°C$.

3.7. *Effect of CPC*

Cetylpyridinium chloride (CPC, representative cationic surfactant) retards both uncatalyzed and catalyzed paths. The plot of k_{obs} *versus* $[CPC]_T$ (figure 6) shows a continuous decrease and finally leveling off at higher concentration of CPC.

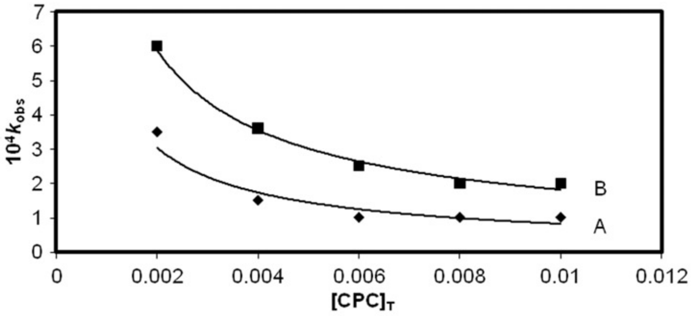


Figure 6. Effect of $[CPC]_T$ on k_{obs} for the Cr(VI) oxidation of ethanol in the presence (B) and absence (A) of 1,10-phenanthroline (phen) in aqueous H_2SO_4 media at 35°C. $[Cr(VI)]_T = 3 \times 10^{-4}\,mol\,dm^{-3}$, $[H_2SO_4] = 0.75\,mol\,dm^{-3}$, $[ethanol]_T = 0.02\,mol\,dm^{-3}$, $[phen]_T = 0.015\,mol\,dm^{-3}$.

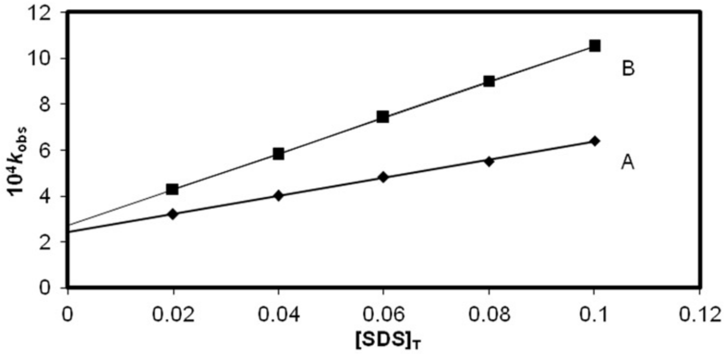


Figure 7. Effect of $[SDS]_T$ on k_{obs} for the Cr(VI) oxidation of ethanol in the presence (B, i.e., $k_{obs(T)}$) and absence (A, i.e., $k_{obs(U)}$) of 1,10-phenanthroline (phen) in aqueous H_2SO_4 media at 35°C. $[Cr(VI)]_T = 2 \times 10^{-4}\,mol\,dm^{-3}$, $[H_2SO_4] = 0.75\,mol\,dm^{-3}$, $[ethanol]_T = 0.035\,mol\,dm^{-3}$, $[phen]_T = 0.01\,mol\,dm^{-3}$.

This rate-retardation by surfactants has been previously reported [6–20]. In the uncatalyzed path, the neutral Cr(VI)-substrate ester (A) formed (7) can be partitioned in the miceller pseudo-phase of the surfactant, but the cationic surfactant repelling H^+ needed for the reaction (8) inhibits the reaction. The Cr(VI)-ester species (A) is likely to be present in the Stern layer. It may be noted that for the uncatalyzed reaction, H_2CrO_4 and/or substrate may also be partitioned in the miceller interphase. Simultaneous partitioning of both H_2CrO_4 and substrate is equivalent to the partitioning of the Cr(VI)-ester (A). In the phen-catalyzed path, CPC restricts the positively charged Cr(VI)-phen (C_1) (12) in the aqueous phase and thus the accumulated neutral substrate in the miceller phase (most probably in the Stern layer) cannot participate in the reaction and consequently the reaction rate is retarded. Thus in both the uncatalyzed and phen-catalyzed path the reaction is mainly restricted in the aqueous phase.

3.8. *Effects of SDS*

SDS (sodium dodecyl sulphate, a representative anionic surfactant) catalyzes the title reaction both in the presence and absence of phen (figure 7). In the phen-catalyzed path, the rate acceleration arises due to preferential partitioning of the positively charged Cr(VI)-phen complex (by electrostatic attraction) and neutral substrate in the miceller surface. Thus SDS allows the reaction to proceed in both aqueous and miceller interphases. Simultaneous partitioning of H_2CrO_4 and substrate is equivalent to partitioning of the Cr(VI)-substrate ester. Thus, it leads to a higher local concentration of both the reactants at the micelle-water interphase as compared to their stoichiometric concentrations. The H^+ ions needed for the reaction are also preferably attracted to the miceller phase. Thus SDS allows the reaction in both phases with a preferential rate enhancement in the miceller phase.

4. Conclusion

The Cr(VI)-phen complex is an active oxidant in the phen-catalyzed chromic acid oxidation of ethanol to give acetaldehyde. The reactions have been carried out in aqueous micelle media. The cationic surfactant (CPC) shows rate retarding effect, while the anionic surfactant (SDS) accelerates the rate both in the catalyzed and uncatalyzed paths. The micelle effects support the proposed mechanistic pathways. The state of the Cr(III)-species in the final solution has been detected by following the UV-visible spectra. In the uncatalyzed reaction, the species is simply Cr(III)-species (pale blue, $\lambda_{max} = 412\,nm$, $\varepsilon_{max} = 4.4\,M^{-1}cm^{-1}$ and 512 nm, $\varepsilon_{max} = 4.4\,M^{-1}cm^{-1}$), whereas for the phen-catalyzed path, the corresponding species is a Cr(III)–phen complex (pale violet color, $\lambda_{max} = 554\,nm$, $\varepsilon_{max} = 10\,M^{-1}cm^{-1}$). This Cr(III)-phen complex is not formed by interaction of 1,10-phenanthroline with the Cr(III)-species produced after reduction of Cr(VI), as Cr(III) (t_{2g}^3) is kinetically inert. From an independent experiment, it has been noted that under comparable conditions, the spectrum of a mixture containing $Cr(aq)^{3+}$ and 1,10-phenanthroline does not change within the reaction time (required for the present redox reaction initiated by Cr(VI) consistent with 1,10-phenanthroline not ligating with the Cr(III) center after its generation from Cr(VI). Existence of the Cr(III)-phen complex in the final solution supports the formation of Cr(VI)-phen complex in the pre-equilibrium step, as the Cr(VI) center is kinetically labile. This Cr(VI)-phen complex is finally reduced to the Cr(III)-phen complex. SDS can be used as catalyst for the production of acetaldehyde from ethanol.

Acknowledgments

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