

Micellar Catalysis on 1,10-Phenanthroline Promoted Chromic Acid Oxidation of Ethane-1,2-diol in Aqueous Media at Room Temperature

Sumanta K. Ghosh, Rumpa Saha*, Aniruddha Ghosh, Ankita Basu, Kakali Mukherjee, Indrajit Saha, and Bidyut Saha*

Homogeneous Catalysis Laboratory, Department of Chemistry, The University of Burdwan, Golapbag, Burdwan, Pin 713104, WB, India.

*E-mail: b_saha31@rediffmail.com; rumu.chem@gmail.com

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ABSTRACT. Under pseudo-first order conditions, the monomeric species of Cr(VI) was found to be kinetically active in the absence of phenanthroline (phen) whereas in the phen-promoted path, the Cr(VI)-phen complex undergoes a nucleophilic attack by ethane-1,2-diol to form a ternary complex which subsequently experience a redox decomposition leading to hydroxy ethanal and Cr(III)-phen complex. The effect of the cationic surfactant (CPC), anionic surfactant (SDS) and neutral surfactant (TX-100) on the unpromoted and phen-promoted path have been studied. Micellar effects have been explained by considering the preferential partitioning of reactants between the micellar and aqueous phase. Combination of TX-100 and phenanthroline will be the ideal for chromic acid oxidation of ethane-1,2-diol in aqueous media

Key words: 1,10-Phenanthroline, Ethane 1,2-diol, SDS, CPC, TX-100

INTRODUCTION

Micellar catalysis is the acceleration of chemical reactions by the micelles of surfactants and mainly caused by the change in the concentrations of reacting components when they pass from a solution into micelles.^{1,2} Micellar catalysis is very much important because it provides environmentally friendly media.⁴⁻⁷ Chromic acid is traditionally used as oxidizing agents in organic synthesis, particularly in the oxidation of alcohol to carbonyl compounds.³ Different chelating agents such as picolinic acid (PA), 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy) are used as promoter for chromic acid oxidation of different organic substrates in aqueous media. A variety of selective hexavalent chromium oxidizing agents such as pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), imidazolium dichromate (IDC) etc. have been developed for the oxidation of a wide range of compounds.⁸ All these reagents required some organic solvents like dichloromethane (CH₂Cl₂, DCM), acetone (CH₃COCH₃), dimethyl formamide (Me₂NCHO, DMF). These are hazardous for skin contact, eye contact and for ingestion or inhalation.⁹ Solvents in particular make a large contribution to the atmospheric burden. So we have selected water as a solvent to avoid such hazards.

EXPERIMENTAL

Materials and Reagents

Ethane 1,2-diol (98%, SRL, India), K₂Cr₂O₇ (99% AR, BDH), 1,10-phenanthroline (99.9%, Merck, India), sodium dodecyl sulfate (SDS) (AR, SRL, India), cetylpyridinium chloride (CPC) (98%, AR, SRL, India), TX-100 (98%, AR, SRL, India), H₂SO₄ (98%, Merck, India), HClO₄ (65%, Merck, India) and all other chemicals used were of highest purity available commercially.

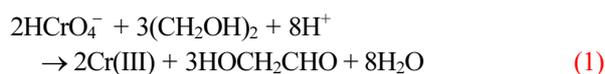
Procedure and Kinetic Measurements

Solutions of the oxidant and reaction mixtures containing known quantities of substrate (S) (ethane 1,2-diol), promoter 1,10-Phenanthroline (Phen) under the conditions $[S]_T \gg [Cr(VI)]_T$ and $[Phen]_T \gg [Cr(VI)]_T$, acid and other necessary chemicals were separately thermostated ($\pm 0.1^\circ C$). The reaction was initiated by mixing requisite amounts of the oxidant with the reaction mixture. Progress of the reaction was monitored by the following the decay of the Cr(VI). The concentration of Cr(VI) at different time interval 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.¹⁰ The pseudo-first order rate constant 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 scan spectra and spectrum after completion of the reaction were recorded with a UV-VIS spectrophotometer [UV-2450 (SHIMADZU)]. Quartz cuvettes of path length of 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.

Product Analysis and Stoichiometry

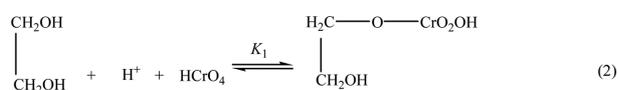
Under the experimental conditions, $[\text{ethane-1,2-diol}]_{\text{T}} \gg [\text{Cr(VI)}]_{\text{T}}$ and $[\text{phen}]_{\text{T}} \gg [\text{Cr(VI)}]_{\text{T}}$ (Subscript T stands for the total concentration) ethane-1,2-diol oxidised to hydroxyl ethanol confirmed by the melting point of hydrazone of hydroxy ethanal.¹¹ $[\text{ethane-1,2-diol}]_{\text{T}} = 0.015 \text{ mol dm}^{-3}$, $[\text{Cr(VI)}]_{\text{T}} = 0.001 \text{ mol dm}^{-3}$ and $[\text{phen}]_{\text{T}} = 0.015 \text{ mol dm}^{-3}$. In the experimental pH, H_2CrO_4 loses one proton and exist as HCrO_4^- . The overall stoichiometry of the reaction may be represented as:



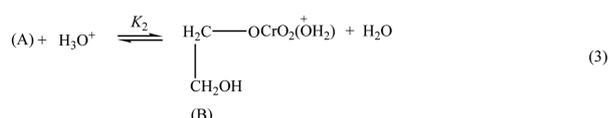
RESULTS AND DISCUSSIONS

On the basis of $[\text{H}^+]$ and $[\text{ethane-1,2-diol}]$ variation experiments the mechanism of unpromoted reaction is already established.¹² The first step is the formation of ester followed by protonation and finally decomposition of protonated ester to yield product. This type mechanism is previously reported.¹³⁻¹⁶

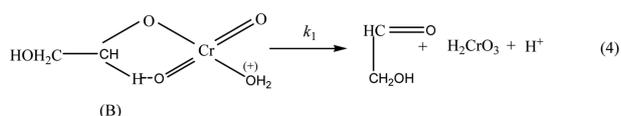
On the basis of $[\text{H}^+]$, $[\text{Phen}]$ and $[\text{ethane-1,2-diol}]$ variation experiments the mechanism of phen promoted reaction is given below. This type of phen promoted mechanism is previously reported.



(A)

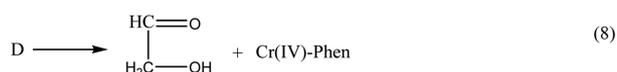
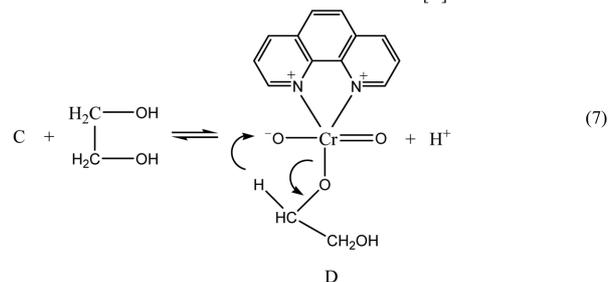
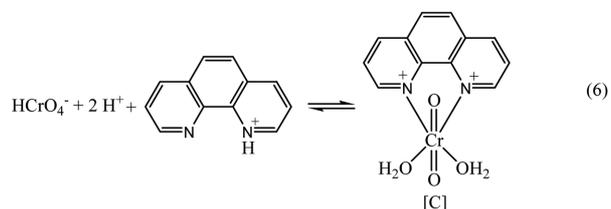
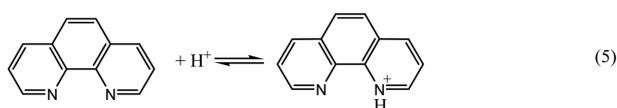


(B)



(B)

Scheme 1. Cr(VI) oxidation of ethane-1,2-diol in absence of phenanthroline.



Scheme 2. Cr(VI) oxidation of ethane-1,2-diol in presence of phenanthroline.

The colours of the final solutions in the absence of the promoter and in the presence of the promoter are different due to the presence of different types of Cr(III)-species. The colour of the final solution in the absence of the promoter under the experimental condition is pale blue ($\lambda_{\text{max}} = 412 \text{ nm}$ and 592 nm) and the corresponding transitions^{17,18} are 592 nm for ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and 412 nm for ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ of Cr(III) species. On the other hand, the colour of the final solution of the phen-catalysed reaction under the identical conditions is pale violet [$\lambda_{\text{max}} = 525 \text{ nm}$, for ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ of Cr(III) species]. The spectra of the final solution of without promoter reaction and pure chromic sulphate solution in aqueous sulphuric acid media are identical. It proves that the final Cr(III)-species is simply Cr(III)-species for the without promoter reaction while for the phen-promoter reaction; the final Cr(III)-species is a different species, which is Cr(III)-phen complex. For phen-promoted reaction, there is a blue shift (Fig. 1) for the peak due to the transition ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ compared to the final solution of the without promoter path. This blue shift is due to the presence of the strong field donor site, i.e. heteroaromatic N-donor site of phenanthroline. For the Cr(III)-phen complex, the peak due the transition ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ merges with a charge transfer band (Fig. 1). For Cr(III)-aqueous species, the band at 270 nm due to ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}$

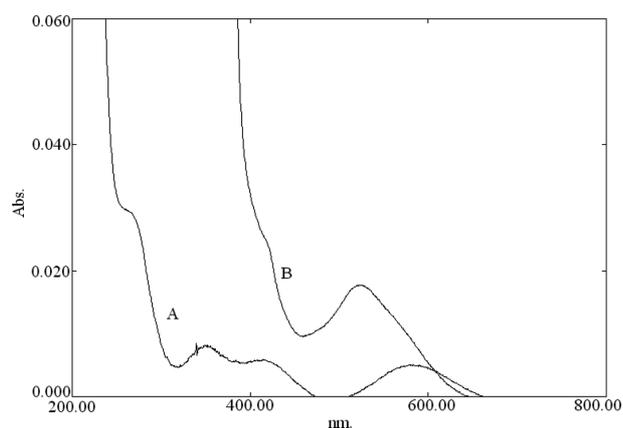


Fig. 1. (A) Absorption spectrum of unpromoted reaction mixture (after completion of reaction): $[\text{ethane-1,2-diol}]_T = 0.01 \text{ mol dm}^{-3}$, $[\text{Cr(VI)}]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$, $[\text{phen}]_T = 0 \text{ mol dm}^{-3}$. (The spectrum of the chromic sulfate is identical with this under the experimental condition.) (B) Absorption spectrum of the promoted reaction mixture (after completion of reaction): $[\text{ethane-1,2-diol}]_T = 0.01 \text{ mol dm}^{-3}$, $[\text{Cr(VI)}]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$, $[\text{phen}]_T = 0.005 \text{ mol dm}^{-3}$.

(P) transition appears as a shoulder on high energy charge transfer band.^{17,18} For Cr(III)-phen complex, the appearance of the charge transfer band at much lower energy for the proposed Cr(III)-phen complex is quite reasonable because of the favoured metal to ligand charge transfer. The vacant π^* of the phen favours the metal to ligand charge transfer. The existence of the charge transfer band (metal to ligand) at lower energy for the phen-promoted reaction may be the cause of rate enhancement.

The scanned spectrum (Fig. 2) indicates the gradual disappearance of Cr(VI) species and appearance of Cr(III) species with an isobestic point at $\lambda = 525 \text{ nm}$ for the without promoter reaction $\lambda = 515 \text{ nm}$ for the with promoter reaction. Observations of this single isobestic point indicates the very low concentration of Cr(V) and Cr(VI) intermediates under the present experimental condition. In presence of promoter, Cr(VI)-phen is the active oxidant^{4,5,17} (Fig. 3).

Partition of ethane-1,2-diol is not equal to all types of surfactants (Fig. 4) due to different extent of hydrophobic portion of cationic (CPC), anionic (SDS) and neutral (TX-100) surfactants. Hydrophobic portion is large in case of TX-100 than CPC. SDS has smallest portion of hydrophobic region. The partition of ethane-1,2-diol will be maximum in TX-100 and be minimum in SDS.

Active oxidant Cr(VI)-phen complex reacts with the substrate to form a ternary complex which experience a redox decompositions in a rate limiting step^{4-7,17,18} giving rise to organic product. Positively charged active oxidants are preferably accumulated in the anionic micellar phase

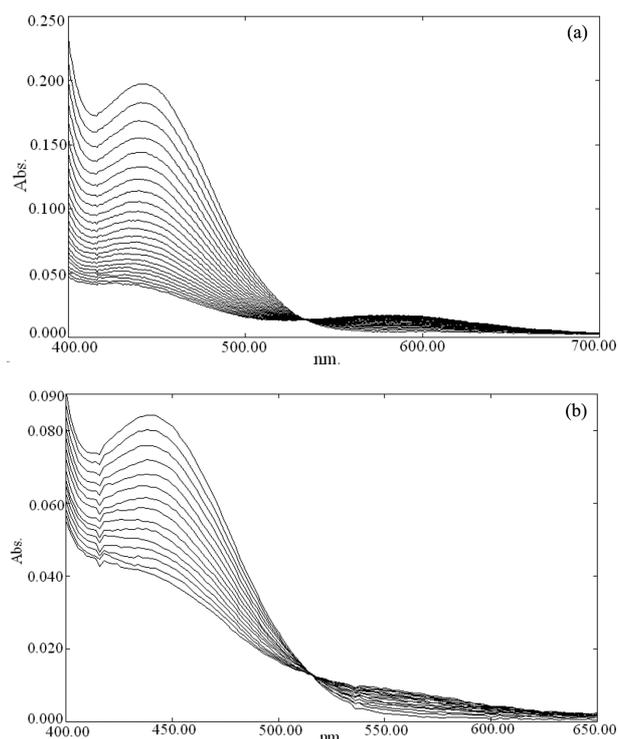


Fig. 2. (A) Scanned absorption spectra of the reaction mixture at regular time intervals (12 min). Concentrations at the beginning of the reaction: $[\text{ethane-1,2-diol}]_T = 0.01 \text{ mol dm}^{-3}$, $[\text{Cr(VI)}]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$, $[\text{phen}]_T = 0 \text{ mol dm}^{-3}$. (B) Scanned absorption spectra of the reaction mixture at regular time intervals (3 min). Concentrations at the beginning of the reaction: $[\text{ethane-1,2-diol}]_T = 0.01 \text{ mol dm}^{-3}$, $[\text{Cr(VI)}]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$, $[\text{phen}]_T = 0.005 \text{ mol dm}^{-3}$.

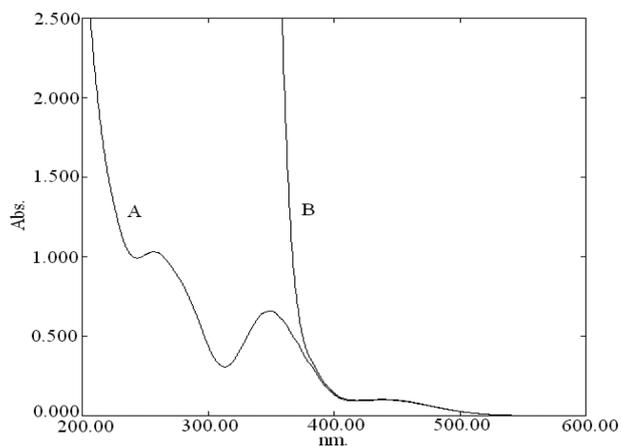


Fig. 3. Absorption spectrum of reaction mixture with (B) and without phen (A) (in absence of substrate): $[\text{ethane 1,2-diol}]_T = 0 \text{ mol dm}^{-3}$, $[\text{Cr(VI)}]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$, $[\text{phen}]_T = 0.005 \text{ mol dm}^{-3}$.

of SDS due to electronic attraction. Considering the both facts, in presence of TX-100, the reaction simultaneously goes on in both in the micellar phase and aqueous phase

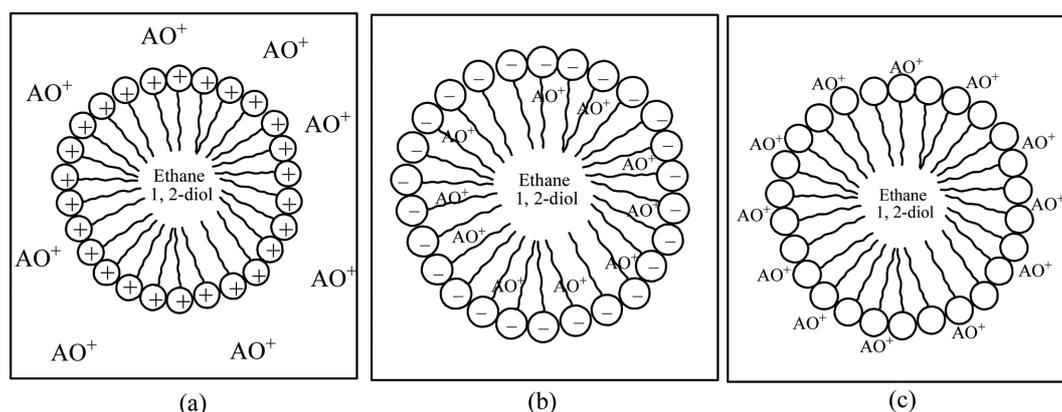


Fig. 4. Schematic representation of partitioning of substrate and active oxidant [$\text{AO}^+ = \text{Cr(VI)-Phen complex}$] in (a) Cationic surfactant, (b) Anionic surfactant and (c) Neutral surfactant.

Table 1. Reaction completion time (87.5%) in presence and absence of promoter and catalyst

T_{com} (hours)	Promoter	Micellar catalyst
358.69	Absent	Absent
9.5	Absent	SDS ($2 \times 10^{-2} \text{ mol dm}^{-3}$)
30.72	Absent	TX-100 ($2 \times 10^{-2} \text{ mol dm}^{-3}$)
2.59	Phen ($0.005 \text{ mol dm}^{-3}$)	Absent
2.54	Phen ($0.005 \text{ mol dm}^{-3}$)	SDS ($2 \times 10^{-2} \text{ mol dm}^{-3}$)
3.92	Phen ($0.005 \text{ mol dm}^{-3}$)	CPC ($2 \times 10^{-3} \text{ mol dm}^{-3}$)
1.19	Phen ($0.005 \text{ mol dm}^{-3}$)	TX-100 ($2 \times 10^{-2} \text{ mol dm}^{-3}$)

$[\text{Cr(VI)}]_{\text{T}} = 5 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{ethane-1,2-diol}]_{\text{T}} = 0.01 \text{ mol dm}^{-3}$

and the rate is accelerated in the micellar phase because of the preferential accumulation of the reactants in the micellar phase. This type of observation is previously reported.^{19,20} In the presence of CPC, although the substrate is partitioned in the micellar phase, the approach of the active oxidants Cr(VI)-phen complex are repelled. Thus in the presence of CPC, the reaction is restricted to the aqueous phase which is depleted in the concentration of the substrate. This leads to the rate retardations compare to CPC. The catalytic effect of SDS is in between TX-100 and CPC.

CONCLUSION

Under pseudo-first order conditions, the monomeric species of Cr(VI) was found to be kinetically active in the absence of phenanthroline (phen) whereas in the phen-promoted path, the Cr(VI)-phen complex undergoes a nucleophilic attack by ethane-1,2-diol to form a ternary complex which subsequently experience a redox decomposition leading to hydroxy ethanal and Cr(III)-phen complex. Combination of TX-100 and phenanthroline will be

the ideal for chromic acid oxidation of ethane-1,2-diol in aqueous media.

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