

# Hetero-aromatic Nitrogen Base Promoted Cr(VI) Oxidation of Butanal in Aqueous Micellar Medium at Room Temperature and Atmospheric Pressure

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**Abstract** The kinetics of the oxidation of butanal by chromic acid in aqueous and aqueous surfactant (sodium dodecyl sulfate, SDS, Triton X-100 (TX-100) and *N*-cetylpyridinium chloride, CPC) media have been investigated in the presence of a promoter at 303 K. The pseudo-first-order rate constants ( $k_{obs}$ ) were determined from a logarithmic plot of absorbance as a function time. The rate constants were found to increase with introduction of heteroaromatic nitrogen base promoters such as picolinic acid (PA), 2, 2'-bipyridine (bipy) and 1,10-phenanthroline (phen). The product, butanoic acid, was characterized by <sup>1</sup>H-NMR. Three promoters PA, bpy and phen are used in combination with SDS, TX-100 and CPC surfactants showing an increase in the rate of oxidation compared to the unpromoted pathway. The mechanism of the reaction path has been proposed with the help of kinetic results and spectroscopic studies. The observed net enhancement of rate effects has been explained by considering the hydrophobic and electrostatic interaction between the surfactants and reactants. The TX-100 and PA combination is suitable for butanal oxidation.

Keywords Kinetics · Oxidation · Butanal, Cr(VI) · Micellar effects

## **1** Introduction

Oxidation is a fundamental transformation in organic synthesis and will likely play a significant role in the growth of value-added chemicals from biomass. However, direct conversion of butanal to butanoic acid is still a challenge. Butanoic acid has many potential applications in different industries, and currently there is a great interest in using it as a

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precursor to biofuels. Biofuels in general offer many advantages including sustainability, a reduction of greenhouse gas emissions, and security of supply. In addition, butanoic acid can be used to produce ethyl butyrate and butyl butyrate, both of which can be used as fuels. In addition to its use as a biofuel, butanoic acid has also many applications in the pharmaceutical and chemical industries [1].

The oxidation of butanal by several oxidants has been reported earlier [2]. A similar version for the oxidation of butanal to butanoic acid in aqueous micellar medium is not known. The dichromate anion  $(Cr_2O_7^-, Cr^{6+})$  is commonly used to oxidize butanal. Upon reaction with butanal, the chromium (VI) in dichromate (yellow) is reduced to  $Cr^{3+}$  and this species is observed in solution with the appearance of a blue color. The kinetic aspects of oxidation of different aldehydes by several higher valent metal ions including Cr(VI) have been studied by different workers under different conditions [3–7].

The mechanistic aspects of oxidation of different aliphatic and aromatic aldehydes by different transition metal ions in aqueous acid media have been reported [8–10]. Various chelating agents are known to catalyze the Cr(VI) oxidation of different organic substrates. In this regard, picolinic acid (PA) is unique and quite efficient. A diversity of selective chromium (VI) oxidizing agents, including pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), imidazolium dichromate (IDC), etc. have been developed, which allow for the oxidation of a large range of compounds [11]. All these reagents required organic solvents such as dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, DCM), acetone (CH<sub>3</sub>COCH<sub>3</sub>) or dimethyl formamide (Me<sub>2</sub>NCHO, DMF) which are hazardous in the case of skin contact (irritant, permeator), eye contact (irritant), ingestion or inhalation. Solvents in particular make a large negative contribution to the environment. So we have selected water as a solvent to avoid such hazards. Simple chromic acid oxidation of aldehydes is a very slow process [12, 13, 22]. Three representative surfactants (anionic, cationic and neutral) and three promoters containing pyridine moieties: picolinic acid, 2,2'-bipyridine, and 1,10-phenanthroline are used for the oxidation of butanal.

Although water is an eco-friendly solvent for reactions, due to solubility problems with organic substrates, researchers select aggregated surfactant media which have two different parts: one is hydrophobic and another is hydrophilic. Aggregated surfactant media are composed of different nano sized aggregates, including micellea, vesiclea, large unil-amellar vesiclea, etc., above the critical micelle concentration (CMC) in aqueous medium. Among these, micelles catalyze several reactions, including oxidative transformations, hydroformylation, Diels–Alder reactions, several organic synthesis, etc. [14]. In this study we have selectively chosen three different types of surfactants: cationic (cetyl pyridinium choloride, CPC), anionic (sodium dodecylsulfate, SDS), and nonionic (octylphenol-polyoxyethylene ether, TX-100).

The promoters are used as chelating agents and found to be similar in reactivity as they contain one or two hetero atoms, i.e., nitrogen in the aromatic ring. Naturally, they are strong bases and act as an effective oxidation catalysts. One of the key conclusions from our work is that the effects of both surfactant head groups and of the surfactant tails need to be taken into account to fully reproduce medium effects as reported by a variety of kinetic and spectroscopic probes of the micellar pseudophase [15]. In the present work, some preliminary investigations into effects on the rate of oxidation reaction in micellar medium are reported and, for this study, several kinetics measurements were performed. Product identification was by different spectroscopic studies. This work essentially involved determination of the rate of the reaction and establishing the proposed mechanism of the

reaction. Dynamic light scattering (DLS) can be used. This oxidation takes place in environmentally friendly aqueous medium rather than hazardous organic solvents.

### 2 Experimental

### 2.1 Materials and Reagents

All chemicals used were of analytical reagent (AR) grade. Butanal (99.0 %, SRL, India),  $K_2Cr_2O_7$  (99.9 %, BDH),  $H_2SO_4$  (98 %, Merck), picolinic acid (99 %, Sigma Aldrich), 2, 2'-bipyridine (99 %, Spectrochem, India), 1,10-phenanthroline (99.5 %, Merck), sodium dodecyl sulfate (SRL, India), *N*-cetylpyridinium chloride (98.0 %, SRL, India), Triton X-100 (98.0 %, HIMEDIA) and double distilled water for the preparation of required solutions. All other used chemicals have been purchased in their highest purity state available commercially.

#### 2.2 Instrumentation

<sup>1</sup>H-NMR spectra have been recorded on a Bruker Ascend 500 MHz spectrometer at ambient temperature. UV–vis spectra have been recorded on a UV-1601PC (SHIMADZU) spectrometer equipped with a temperature controller (TCC SHIMADZU). The balance used was a Sartorius BSA224S-CW. The solutions have been prepared using a Digital Ultrasonic Cleaner CD 4820 sonicator and a Z206A, Hermle Labortechnik GmbH centrifuge. DLS studies have been investigated in a Malvern Zetasizer Nano ZS-90 instrument.

#### 2.3 Procedure and Kinetics Measurements

Solutions of the oxidant and reaction mixtures containing known quantities of the substrate (butanal =  $75 \times 10^{-4} \text{ mol·dm}^{-3}$ ), promoter (picolinic acid =  $150 \times 10^{-4} \text{ mol·dm}^{-3}$ , 2,2'-bipyridine =  $125 \times 10^{-4} \text{ mol·dm}^{-3}$ , 1,10-phenanthroline =  $75 \times 10^{-4} \text{ mol·dm}^{-3}$ ) under the kinetics conditions [butanal]\_T  $\gg$  [Cr(VI)]\_T and [promoter]\_T  $\gg$  [Cr(VI)]\_T. The reactions were followed under pseudo-first-order conditions, using an excess of butanal over Cr(VI). Reactant solutions were previously thermostated and transferred into 1 cm path length cell immediately after mixing. Experiments were performed using 0.5 (mol·dm<sup>-3</sup>) H<sub>2</sub>SO<sub>4</sub> at 30 °C [16]. The pseudo-first-order rate constant were calculated from the slopes of the plot of  $\log_{10}$ [Cr(VI)]<sub>T</sub> 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-1601PC (SHIMADZU)]. Under experimental conditions, the possibility of decomposition of the surfactants by Cr(VI) was investigated and the rate of decomposition in this path was negligible.

#### 2.4 Product Analysis and Stoichiometry

Product analysis was carried out under mineral acid ( $[H_2SO_4] = 0.5 \text{ mol} \cdot dm^{-3}$ ) catalyzed conditions in butanal. Keeping the concentration of butanal in excess over the oxidizing reagent (dichromate), the two solutions were mixed and sulfuric acid was added to maintain the solution pH at 2. Under our experimental conditions,  $[butanal]_T \gg [Cr(VI)]_T$ 



Fig. 1 The <sup>1</sup>H NMR spectrum of butanoic acid in CDCl<sub>3</sub> solvent

(T = total concentration). In the case of the oxidation of butanal by Cr(VI), after keeping the reaction mixtures,  $K_2Cr_2O_7$  and sulfuric acid in proper composition for 72 h in water at room temperature, the volume of the reaction mixture was reduced to 20 % under vacuum. The butanoic acid produced was first separated from the reaction mixture by fractional distillation.

Estimation of the un-reacted Cr(VI) showed that 1 mol of each butanal consumed 1 mol of Cr(VI) for oxidation to take place, on the assumption that all the butanal was consumed for the oxidations to take place. Our present work was intended to find the best combination of promoter and micellar catalyst in the presence of which the reaction occurs most rapidly. The overall stoichiometry of the oxidation can be represented as:

 $3 CH_3 CH_2 CH_2 CHO + 2 H CrO_4^- + 8 H^+ \longrightarrow 3 CH_3 CH_2 CH_2 COOH + 2 Cr(III) + 5 H_2 OH_2 CH_2 CHO_4 + 2 H CrO_4^- + 8 H^+ - 2 H CrO_4 + 2 H CrO_4$ 

## 2.4.1 <sup>1</sup>H NMR Spectrum

The <sup>1</sup>H NMR spectrum (Fig. 1) of the separated product was recorded at 500 MHz in CDCl<sub>3</sub>. Chemical shifts (ppm) are internally referenced to the TMS signal (0 ppm) in all cases and are listed in Table 1.

# 2.5 Determination of the Size of Aggregates by Dynamic Light Scattering (DLS)

DLS is the most versatile and useful techniques for measuring the sizes, size distribution and shapes of nanoparticles. The hydrodynamic diameters ( $D_h$ ) of TX-100 micelles with reactant were determined by DLS. DLS characterization was performed to obtain micelle/ vesicle size and morphology on a DLS instrument with a capillary cell. Size measurements were performed at a 90° angle, in triplicate. DLS analyzes the velocity distribution of particle movement by measuring dynamic fluctuations of light scattering intensity caused by the Brownian-motion of the particle. The light scattering study was done with TX-100 surfactant by taking its concentration above its CMC value in acidic medium.

<b>Table 1</b> Chemical shift valuesfor different protons of butanoic	Butanoic acid	Moiety	Chemical shift ( $\delta$ ppm)	Multiplicity
acid		$\begin{array}{c} \mathrm{CH}_3\\ \mathrm{CH}_2\\ \mathrm{CH}_2\\ \mathrm{OH} \end{array}$	0.96 1.62 2.25 10.8	3H, triplet 2H, multiplet 2H, triplet 1H, singlet

#### **3** Result and Discussion

All the kinetic measurements were carried out at 30 °C. The reaction rate increases linearly with increasing butanoic acid concentration showing that the reaction is first order with respect to butanoic acid. The rate of oxidation increases linearly with the acidity of the solution [8]. The pseudo-first-order rate constants ( $k_{obs}$ , s<sup>-1</sup>) were determined from the slopes of plots of  $\ln(A_{450})$  against time (*t*), where  $A_{450}$  is the absorbance at 450 nm. The  $t_{1/2}$  values are directly calculated in Table 1 by using the relation  $t_{1/2} = \ln 2/k_{obs}$  (Fig. 2).

The data in Table 2 show the  $k_{obs}$  for SDS, CPC and TX-100 micelle catalyzed reactions to be greater than for the corresponding non-catalyzed reaction. This observation is also true for promoted path compared to the unpromoted path. It was observed that the reactions of organic compounds were significantly enhanced in the aqueous micellar solutions of ionic surfactants.

The reaction mixtures were scanned in the range of 200–800 nm in the presence and absence of promoter and surfactant at regular time intervals (3 min) to follow the gradual development of the reaction intermediates (if any) and the product. The scanned spectra (Fig. 3a-g) indicate the gradual disappearance of Cr(VI) species and appearance of Cr(III). The same also appeared for micellar catalyzed reactions in the presence and absence of promoter.

The colors of the final solutions in the absence and presence of promoters are different due to the presence of different types of Cr(III) species. The color of the final solution in the absence of the promoter under the experimental condition is pale blue ( $\lambda_{max} = 407$  nm and 584 nm) and the corresponding transitions [17–19] are 584 nm for  ${}^{4}A_{2g}$  (F)  $\rightarrow {}^{4}T_{2g}$  (F) and 407 nm for  ${}^{4}A_{2g}$  (F)  $\rightarrow {}^{4}T_{1g}$  (F) of Cr(III) species (Fig. 4a). The spectra of the final





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– None		$1.216\pm0.03$	1.58
None			
		$2.808 \pm 0.04$	0.685
None		$13.23\pm0.07$	0.145
None		$9.128 \pm 0.01$	0.210
SDS	400	$1.415\pm0.04$	1.36
CPC	20	$0.33\pm0.02$	1.44
TX-100	200	$1.558\pm0.06$	1.23
CPC	20	$4.975\pm0.04$	0.38
CPC	20	$4.51\pm0.08$	0.42
CPC	20	$5.39\pm0.01$	0.357
SDS	400	$4.233\pm0.04$	0.45
SDS	400	$5.26\pm0.03$	0.365
SDS	400	$6.306\pm0.03$	0.305
TX-100	200	$16.26\pm0.01$	0.118
TX-100	200	$14.46\pm0.05$	0.133
TX-100	200	$14.5\pm0.03$	0.132
	None None SDS CPC TX-100 CPC CPC CPC SDS SDS SDS TX-100 TX-100 TX-100 TX-100 Ddtdm <sup>-3</sup> HsSO <sub>1</sub> = 0.5	None         None         SDS       400         CPC       20         TX-100       200         CPC       20         CPC       20         CPC       20         CPC       20         SDS       400         SDS       400         SDS       400         SDS       400         TX-100       200         TX-100       200         TX-100       200         Dd.dm <sup>-3</sup> HeSO = 0.5 mol/dm <sup>-3</sup>	None $13.23 \pm 0.07$ None $9.128 \pm 0.01$ SDS $400$ $1.415 \pm 0.04$ CPC $20$ $0.33 \pm 0.02$ TX-100 $200$ $1.558 \pm 0.06$ CPC $20$ $4.975 \pm 0.04$ CPC $20$ $4.51 \pm 0.08$ CPC $20$ $5.39 \pm 0.01$ SDS $400$ $4.233 \pm 0.04$ SDS $400$ $5.26 \pm 0.03$ SDS $400$ $6.306 \pm 0.03$ TX-100 $200$ $14.46 \pm 0.05$ TX-100 $200$ $14.5 \pm 0.03$

**Table 2** Pseudo-first-order rate constant ( $k_{obs}$ ) and half life of the reaction in the presence and absence of promoter and non-functional micellar catalyst

 $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, H_2SO_4 = 0.5 \text{ mol·dm}^{-3}, [butanal]_T = 75 \times 10^{-3} \text{ mol·dm}^{-3}, and temperature = 30 °C$ 

solution in the absence of promoter and pure chromic sulfate solution in aqueous sulfuric acid media are identical. On the other hand, the color of the final solutions with promoters, under the identical conditions, is pale violet ( $\lambda_{max} = 541$  nm for the phen promoted reaction, 543 nm for the bipy promoted reaction and 561 nm for the PA promoted reaction) for  ${}^{4}A_{2g}$  (F)  $\rightarrow {}^{4}T_{2g}$  (F) of Cr(III) species (Fig. 4). For the promoted reaction, there is a blue shift for the peak due to the transition  ${}^{4}A_{2g}$  (F)  $\rightarrow {}^{4}T_{2g}$  (F) compared to the final solution without promoter. This blue shift is due to the presence of the strong field donor site, i.e. heteroaromatic N-donor site of the promoters. For Cr(III) aqueous species, the band at 260 nm due to the  ${}^{4}A_{2g}$  (F)  $\rightarrow {}^{4}T_{1g}$  (P) transition appears as a shoulder on the high energy charge transfer band [17–20]. The scanned spectrum (Fig. 3c) indicates the gradual disappearance of Cr(VI) species and appearance of Cr(III) species with an isobestic point at  $\lambda = 518$  nm for the promoter reaction (phen promoted scan). Observations of this single isobestic point indicate the very low concentration of Cr(IV) and Cr(V) intermediates under the present experimental condition. In the presence of promoter, Cr(VI)–A, Cr(VI)– phen and Cr(VI)–bipy are the active oxidants [21, 22] (Fig. 5).

#### 3.1 Mechanism of the Reaction and Rate Law

#### 3.1.1 Mechanism of the Oxidation Process by Unpromoted Path

The unpromoted path is drawn on the basis that the reaction follows first order dependency on  $[Cr(VI)]_T$ ,  $[butanal]_T$  and second order dependency on  $[H^+]$  is already established [23, 24] (Scheme 1).





**Fig. 3 a** Scanned absorption spectra of the reaction mixture at regular time intervals (3 min) [butanal]<sub>T</sub> = 75 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> = 5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, temperature = 30 °C. **b** Scanned absorption spectra of the reaction mixture at regular time intervals (3 min) [butanal]<sub>T</sub> = 75 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> = 5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, [PA] = 150 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> = 5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, [PA] = 150 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, temperature = 30 °C, isosbestic point = 520 nm. **c** Scanned absorption spectra of the reaction mixture at regular time intervals (3 min) [butanal]<sub>T</sub> = 75 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> = 5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, [TX-100] = 2 × 10<sup>-2</sup> mol·dm<sup>-3</sup>, [PA] = 150 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, temperature = 30 °C, isosbestic point = 518 nm. **d** Scanned absorption spectra of the reaction mixture at regular time intervals (3 min) [butanal]<sub>T</sub> = 75 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> = 5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, [TX-100] = 2 × 10<sup>-2</sup> mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> = 5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, [TX-100] = 2 × 10<sup>-2</sup> mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> = 5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, [TX-100] = 2 × 10<sup>-2</sup> mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> = 5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, [TX-100] = 2 × 10<sup>-2</sup> mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> = 5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, [TX-100] = 2 × 10<sup>-2</sup> mol·dm<sup>-3</sup>, [Phen] = 75 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, temperature = 30 °C, isosbestic point = 513 nm. **e** Scanned absorption spectra of the reaction mixture at regular time intervals (3 min) [butanal]<sub>T</sub> = 75 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> = 5 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, [Phen] = 75 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>]<sub>T</sub> = 0.5 mol·dm<sup>-3</sup>, [Phen] = 75 × 10<sup>-4</sup> mol·dm<sup>-3</sup>, temperature = 30 °C, isosbestic point = 513 nm.



**Fig. 4** *a* Absorption spectrum of unpromoted reaction mixture (after completion of reaction): [butanal]<sub>T</sub> =  $75 \times 10^{-4}$  mol·dm<sup>-3</sup>, [Cr(VI)]<sub>T</sub> =  $5 \times 10^{-4}$  mol·dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 0.5 mol·dm<sup>-3</sup> (the spectrum of chromic sulfate is identical with this under the experimental conditions). Absorption spectra of the promoted reaction mixture (after completion of reaction); *b* [PA]<sub>T</sub> =  $150 \times 10^{-4}$  mol·dm<sup>-3</sup>; *c* [bipy]<sub>T</sub> =  $125 \times 10^{-4}$  mol·dm<sup>-3</sup>; *d* [phen]<sub>T</sub> =  $75 \times 10^{-4}$  mol·dm<sup>-3</sup>



**Fig. 5** Absorption spectra of reaction mixture with and without promoter (in the absence of substrate): *a*  $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3};$ *b* $<math>[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3}, [PA]_T = 0.015 \text{ mol·dm}^{-3};$ *c* $<math>[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3}, [D_2SO_4] = 0.5 \text{ mol·dm}^{-3};$ *d* $<math>[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}, [H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mol·dm}^{-3}; d$   $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol·dm}^{-3}; H_2SO_4] = 0.5 \text{ mo$ 

#### 3.1.2 Mechanism of the Oxidation Process by Promoted Path

Promoted paths are drawn on the basis that the reaction follows first order dependency on  $[Cr(VI)]_T$ ,  $[butanal]_T$  and  $[promoter]_T$ . For bipyridine and phenanthroline first order

$$CH_{3}CH_{2}CH_{2}CH_{0} + HCrO_{4}^{-} + H^{+} \underbrace{K_{1}}_{C} CH_{3}CH_{2}CH_{2}CH (OH)O-CrO_{2}(OH) + H_{2}O$$
(Neutral ester)
$$CH_{3}CH_{2}CH_{2}CH (OH)O-CrO_{2}(OH) + H^{+} \underbrace{K_{2}}_{C} CH_{3}CH_{2}CH_{2}CH (OH)O-CrO_{2}(OH_{2}^{+})$$
(Neutral ester)
$$CH_{3}-CH_{2$$



dependency on  $[H^+]$  and zero order dependency on  $[H^+]$  for picolinic acid is observed (not shown in the paper).

Scheme 2 leads to the following rate law:

$$k_{obs(c)} = (2/3) \left( K_3 K_a k_3 k_1 [butanal]_T [PA]_T [H^+]^2 \right) / (k_{-3} + k_1) (K_a + [H^+])$$
  
= a[butanal]\_T [PA]\_T [H^+] (1)

where,  $a = (2/3) (K_3 K_a k_3 k_1)/(k_{-3} + k_1)$ 

$$k_{\text{obs}(c)} = (2/3)k_2K_3K_4[\text{butanal}]_T[\text{bipy}]_T[\text{H}^+]$$
(2)

$$k_{\text{obs}(c)} = (2/3)k_3K_5K_6[\text{butanal}]_{\text{T}}[\text{phen}]_{\text{T}}[\text{H}^+]$$
(3)

Partition of neutral ester (Scheme 1) and neutral butanal (Fig. 6a, b) are equally probable for all types of surfactants (Schemes 3, 4).

#### 3.2 DLS Explanation of Micellar Aggregate

Figure 7 shows that, in case of TX-100, the size or diameter of micelles change when butanal is added to the micellar medium. This helps us to understand that an interaction occurs between the substrate (butanal) and TX-100 within the "Stern layer" of micelle. The overall charge of the TX-100 micelle is neutral; therefore TX-100 interacts with the aggregates and substrate molecules reside in the "Stern layer" of the micelle. The size of TX-100 was 5.6 nm as found in the plot. Upon interaction of substrate (butanal) with the outer surface of the aggregates the diameter of the TX-100 micelle increases from 5.6 to 7.6 nm.

# 3.3 High Resolution Transmission Electron Microscope (HR-TEM) Images of TX-100 Micelles

The HR-TEM was done at 20 kV acceleration voltage using lacey carbon coated Cu grid of 300 mess size in the HR-TEM microscope (JEOL JEM 2100). Samples were prepared by placing sample mixture drops directly on the copper grids using a micropipette. The reactants, including the surfactant present in the aqueous mixture, were allowed to settle. TEM pictures (Fig. 7) are presented which illustrate the multiple morphologies of the



$$Cr(IV)-PA + CH_3CH_2CH_2CHO \xrightarrow{Cr(VI)} CH_3CH_2CH_2COOH + Cr(III)-PA$$

Scheme 2 Chromic acid oxidation of butanal in the presence of picolinic acid



Fig. 6 Schematic representation of neutral ester and H<sup>+</sup> in a neutral surfactant, b anionic surfactant

aggregates made from the surfactant TX-100. Also, the micrograph suggests a relatively narrow size distribution of the micelle diameters but a widely variable length. TEM images of blank TX-100 micelles and Cr(VI) + TX-100 micelles were taken (Fig. 8). From



C (Active oxidant)



$$Cr(IV)$$
-bpy +  $CH_3CH_2CH_2CHO$   $\xrightarrow{Cr(VI)}$   $CH_3CH_2CH_2COOH + Cr(III)$ -bpy

Scheme 3 Chromic acid oxidation of butanal in presence of 2, 2'-bypiridine

Fig. 8a, b it can be observed that the TX-100 micelle is roughly spherical in aqueous acid media. Small holes are seen in the micellar surface when Cr(VI) is added to the TX-100 aqueous acidic medium. So, we can say that incorporation of Cr(VI) takes place inside the micelle.

#### 4 Analysis of Catalytic Role of TX-100

In a micellar system, with TX-100 as the substrate, both the oxidant and the butanal are found to be partitioned between the aqueous and the micellar pseudophase. Thus, the reaction may proceed according to Scheme 5.

The attractive electrostatic interaction between the negatively charged polar head groups and positively charged active oxidant is increased, leading to a decrease in the free energy, which are advantages in regards to the energy requirement for the redox reaction. The types of interaction occurring between SDS micelles and reactants determine the locus



 $Cr(IV)-phen + CH_3CH_2CH_2CHO \xrightarrow{Cr(VI)} CH_3CH_2CH_2COOH + Cr(III)-phen$ 

Scheme 4 Chromic acid oxidation of butanal in the presence of 1,10-phenanthroline

of the solubilization phenomenon at the micellar interface, in between the hydrophilic head groups and the first few carbon atoms of the hydrophobic fragment (commonly referred to as the palisade layer) and finally in the core of the micelle. Therefore, the polar –CHO functional groups of butanal are mainly solubilized in the outer region of the micelle, whereas the non-polar aliphatic framework is preferentially located in the inner portions of the micelles (Fig. 9). Most of the micellar mediated reactions occur either inside the Stern layer or at the interfacial junction region of Stern and Guoy–Chapman layers. In the presence of cationic CPC micelles, hydrophilic negatively charged ions (HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and anionic reactive species such as HCrO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) will compete for binding to the micelle by exchanging the bound (chloride) counter ions in the case of normal micelle formation by CPC, but cationic species (H<sup>+</sup>; positively charged chromium(VI) species are most



**Fig. 7** Variation of particle size distribution of TX-100 micelles/vesicles determined by dynamic light scattering (DLS). The average particle sizes for only (*closed square*) TX-100 is 5.6 nm and butanal incorporated (*closed circle*) TX-100 is 7.5 nm. [butanal] =  $5 \times 10^{-4}$  mol·dm<sup>-3</sup>, [TX-100] =  $2 \times 10^{-2}$  mol·dm<sup>-3</sup>



Fig. 8 TEM image of (a) blank TX-100 micelle in the presence of acid; (b) TX-100 micelle in the presence of Cr(VI) and acid



W = aqueous medium, M = micellar medium, S = substrate (butanal), O = oxidant

Scheme 5 Portioning of the oxidant and substrate between the aqueous phase and the micellar pseudo phase

Fig. 9 Schematic representation of partitioning of substrate and active oxidant  $[AO^+ = Cr(VI) - PA \text{ complex}]$  in neutral surfactant



likely at the acid concentration used in this work) will also take part in the inter-micellar aqueous phase, due the to micelle formation by CPC. The enhancement of the rate of reaction for CPC micelles is low compared to those of the SDS and TX-100 micelles as repulsion takes place between the cationic CPC micelle and positively charged Cr(VI) species. SDS micelles have an aggregation number around sixty and are roughly spherical in shape. TX-100 is larger in size than SDS. The non-ionic surfactant TX-100 has a larger core than SDS, so the active oxidant Cr(VI)–PA complex interacts better with the TX-100 micelle (Fig. 9). There are also hydrophobic interactions between the active oxidants and the micelles. On the other hand the negative charges on the SDS micelles are partially neutralized in the presence of excess  $H^+$ . So smaller number of active oxidants come in contact with the sodium dodecylsulfate Stern layer due to columbic attraction. So the steric factor and hydrophobic interaction play dominant roles and the rate of oxidation is fastest in the presence of the combination of PA and TX-100.

Therefore, the reaction rate follows the order:

$$k_{\text{obs}}(\text{TX} - 100) > k_{\text{obs}}(\text{SDS}) > k_{\text{obs}}(\text{CPC}) > k_{\text{obs}}(\text{water})$$

#### 5 Interaction of Butanal with the CPC micelles

Butanal interactions with CPC monomers were examined by the chemical shifts in the CPC protons, particularly those on and near the pyridyl ring. Addition of the CPC above the CMC ( $2 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ , with butanal ( $75 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ ) displayed distinct upfield shifts in the proton peaks situated near the pyridyl ring, verifying the positioning of butanal close to the pyridyl ring. Importantly, the chemical shifts in the proton signals of CPC from normal micelles and that in the presence of butanal are noticeably different. This is an indication that the CPC micelles are modulated by the presence of butanal, assuming the interaction of the butanal–CPC complex above the CMC. On the other hand, similar NMR measurements with butanal and CPC (1.2 mmol·dm<sup>-3</sup>, above the CMC of CPC), displayed

Table 3 Chemical shift values           for different protons of CPC		CPC	CPC + butanal
	Aromatic proton		
	(a, a') CH protons	8.983	8.926
	(b, b') CH protons	8.605	8.604
	(C)-CH protons	8.132	8.146
	Aliphatic proton		
	$\beta$ -CH <sub>2</sub> proton	1.980	1.931
	Bulk proton	1.279	1.241
	-		



Fig. 10 The <sup>1</sup>H-NMR spectrum of CPC and butanal in  $D_2O$  solvent (*Inset* The <sup>1</sup>H-NMR spectrum of CPC only in  $D_2O$  solvent)

	TX-100	TX-100 + butanal
T <sub>8</sub> CH protons	7.173	7.244
T <sub>7</sub> CH protons	6.799	6.865
T <sub>6</sub> CH protons	3.998	4.072
T <sub>5</sub> CH protons	3.724	3.834
T <sub>4</sub> CH protons	3.549	3.623
T <sub>3</sub> CH protons	1.630	1.699
T <sub>2</sub> CH protons	1.258	1.321
T <sub>1</sub> CH protons	0.683	0.882

**Table 4**Chemical shift valuesfor different protons of TX-100

broader proton peaks, having only small changes in the chemical shifts of the pyridyl protons [25]. The corresponding proton NMR signals are assigned in Table 3 (Fig. 10).

## 6 Interaction of Butanal with the TX-100 Micelles

Butanal interactions with TX-100 monomers were examined by the chemical shifts in the TX-100 protons in D<sub>2</sub>O. TX-100 has 8 different protons denoted:  $T_1$ ,  $T_2$ ,  $T_3$ ,  $T_4$ ,  $T_5$ ,  $T_6$ ,  $T_7$ , and  $T_8$ . Addition of the TX-100 surfactant, above the CMC (2 × 10<sup>-2</sup> mol·dm<sup>-3</sup>, with



**Fig. 11** The <sup>1</sup>H-NMR spectrum of TX-100 and Butanal in  $D_2O$  solvent (*Inset* The <sup>1</sup>H NMR spectrum of TX-100 only in  $D_2O$  solvent)

butanal ( $75 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ ) displayed distinct downfield shifts of the 8 protons of TX-100. Therefore in TX-100 medium the butanal molecule stays at Stern-layer of the micelle [26]. The corresponding proton NMR signals are assigned in Table 4 (Fig. 11).

## 7 Conclusion

The electron transfer kinetics of butanal to butanoic acid have an important role in lab based and industrial transformation reactions. The reaction is accelerated by addition of the surfactants TX-100, SDS and CPC. The non-ionic micelles of TX-100 are better catalysts than the anionic SDS micelles and cationic CPC micelles. The combination of PA and TX-100 is the best choice for chromic acid oxidation of butanal in aqueous media and is capable of increasing the oxidation rate by up to  $\sim 14$  fold.

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