

Sodium dodecylsulphate-catalyzed hetero-aromatic nitrogen base-promoted chromium(VI) oxidation of 2-propenol to 2-propenal in aqueous media

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Abstract A kinetic study of homogeneously micelle-catalyzed, hetero-aromatic *N*base (2-picolinic acid, 2,2'-bipyridine and 1,10-phenanthroline)-promoted oxidation of 2-propenol by chromium(VI) in sulfuric acid medium was carried out at 303 K. The pseudo first-order rate constant (k_{obs}) of the oxidation reaction is directly proportional to [H⁺] and [promoters], which indicates that the reaction is first order with respect to H⁺ and promoters. The reaction was conducted at four different temperatures from which the activation parameters were calculated. Proton nuclear magnetic resonance (¹H-NMR) studies were performed to detect the location of reactant molecules in nanometersized micelles. From the observed kinetic results, a suitable mechanism consistent with the rate law has been proposed. The micelles produced a catalytic effect in the entire range of sodium dodecylsulphate (SDS) concentrations used, and the effect is explained by pseudo-phase ion exchange. The combination of 2,2'-bipyridine (bipy) and SDS exhibited a 15-fold rate enhancement of Cr(VI) oxidation of 2-propenol to 2-propenal.

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Graphical Abstract Ultraviolet-visible (UV-Vis) spectrum of reaction mixture for the Cr(VI) oxidation of 2-propenol with varying solution colour at different reaction times. Right: Location of reactant molecule in the micellar pseudophase region.



Keywords 2-Propenol · Chromium(VI) · SDS · Kinetics · Promoter

Introduction

Chromium has both beneficial and detrimental properties. The two oxidation states of chromium are naturally occurring; one is trivalent chromium and another is hexavalent chromium. The behavior of chromium species depends strongly on their oxidation states: Cr(III) is essential for human nutrients, whereas most hexavalent compounds are toxic, several of which even cause lung cancer [1, 2]. From an economical point of view, there are several advantages of chromium application in a wide array of chemical industries [3, 4], such as the production of stainless steel, the refractory industry, electroplating, chromium pigments of paints and textiles and some wood preservation. These applications contrast with its chromium's external effects as a hazardous pollutant. As compared to other high valency transition metals like Cerium(IV), Vanadium(V), Manganese(VII), and Osmium(VIII), the E⁰ of HCrO₄^{-/}/Cr³⁺ couple (1.33 V) is high enough to oxidize most organic functional groups [5–9]. The oxidation of various organic compounds by Cr(VI) was found to be more pronounced in the presence of metal ions, micellar catalyst and promoters [8–13].

We used 2-propenol as an organic substrate which is oxidized to 2-propenal by the powerful oxidant Cr(VI) with subsequent reduction to non-toxic Cr(III). 2-propenol is the simplest unsaturated alcohol containing two different functional groups: $-CH=CH_2$ and -OH groups at the terminal carbon. The oxidized product 2-propenal is widely used in chemical industry as an intermediate in the manufacture of chemical compounds, colloidal metals, plastics, and perfumes [14]. The most important use of 2-propenal is as an aquatic biocide to control the growth of bacteria, fungi, algae and mollusks in cooling-water systems.

Kinetic studies on the oxidation of 2-propenol with different oxidants such as potassium permanganate, quinaldinium chlorochromate, vanadium(V), bromate(V), cerium(IV), chloramine-T, diperiodatonickelate(IV), etc. have been reported [15-21]. The reported literature followed only simple oxidation kinetics and rate law with probable mechanisms. In this paper, our target is to speed up the oxidation reaction in a simple kinetic way by using different hetero-aromatic N-base promoters and homogeneous micellar medium. We are also interested in determining the role of promoters on the reaction rate by discerning the actual mechanism and location of the reactant molecules inside the nanometer-sized micelle. The promoters used, 2-picolinic acid (PA), 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen), are well known for chromium(VI) oxidation of organic substances. Micellar media has several important roles in the field of organic chemistry and in various fields of research, e.g., solar energy conversion, nanoparticle synthesis, and drug delivery in biological systems [22, 23]. Another critical role of micellar media is to supervise different chemical reactions as multifunctional nano-reactors. A substantial volume of research on the systematic kinetics of micelles and their effects on various organic reactions has been reported during the past few decades [24].

To achieve the target, several kinetic measurements were performed. Product identification was characterized by different spectroscopic studies. Micellar medium as a nano-reactor in combination with different promoting agents is a very efficient facilitator of rapid 2-propenol oxidation. From the view point of green chemistry, water would be the perfect solvent to carry out chemical reactions, provided that the reactants, as well as products, are soluble in water and no polluting waste waters are dispersed into the environment. This oxidation procedure also takes place in environmentally friendly aqueous medium rather than in hazardous organic solvents.

Experimental section

Materials and solution preparation

2-propenol, sulfuric acid and $Cr_2(SO_4)_3$ were purchased from Hi-Media (Mumbai, India). 2-picolinic acid and D_2O were purchased from Sigma Aldrich (USA). 1,10phenanthroline and 2,2'-bipyridine were purchased from Merck (Mumbai, India). Potassium dichromate was purchased from BDH Chemical (Mumbai, India), sodium dodecylsulfate from Fischer Scientific (Mumbai, India) and other required chemical reagents of analytical (AR) grade were used without further purification. Double distilled water was used to prepare reaction mixtures in each case, and for other studies, unless other systems are mentioned specifically.

Kinetic measurements

Kinetics measurements were carried out by monitoring the spectral changes over a range of 250-650 nm on a UV-Vis spectrophotometer (Shimadzu UV-3600) with

fully thermostatted cell compartments. Reaction mixtures were previously thermostatted and transferred into a cell of 1 cm path-length immediately after mixing, and disappearance of Cr(VI) was monitored to 85 % conversion. The pseudo first-order conditions were attained by maintaining a large excess (~15 times) of 2-propenol over the dichromate. Experiments were performed at 303 K unless otherwise stated. Pseudo first-order rate constants (k_{obs}) were calculated from the slopes of plots of -ln(A₄₅₀) versus time (t), which were linear (Fig. S1). The half life ($t_{1/2}$) values were directly calculated by using relation $t_{1/2} = (\ln 2/k_{obs})$. No other reactant or product had any significant absorbance at this wavelength.

Product analysis and stoichiometry

Under experimental conditions, [2-propenol]_T \gg [Cr(VI)]_T (T = total concentration), 2-propenol oxidized to 2-propenal (separated from mixture by fractional distillation), as confirmed by a 2,4-dinitrophenylhydrazine (DNP) test [19]. After completion of the reaction, the mixture solution was treated with an excess of a saturated solution of 2,4-DNP in dilute H₂SO₄ medium. After storage in an ice bath for approximately 1 h, the precipitate was filtered off, dried and recrystallized from ethanol. The micellecatalyzed reactions were performed in the presence of promoters in the same manner as mentioned before. The infrared (IR) spectrum of the 2,4-DNP derivative of the product (Fig. S2) was recorded by the a Perkin-Elmer FTIR spectrometer (model RX1). The characteristic IR bands of the oxidized product at 1615 cm⁻¹ support the formation of corresponding aldehydes (Table S1). The observed IR spectrum of the 2-propenal-DNP derivative was similar to previous literature [25].

To determine the stoichiometry of the oxidation reaction, several reaction mixtures taking [chromium(VI)] \gg [2-propenol] (7.5 \times 10⁻³ mol dm⁻³ oxidant: 1.5–6.0 \times 10⁻³ mol dm⁻³ reductant) at fixed [H⁺] (0.5 mol dm⁻³) were prepared and kept for 24 h at 303 K. After completion of the reaction, the unconsumed oxidant was determined spectrophotometrically. The overall stoichiometry of the reaction may be represented as:

$$3CH_2 = CH - CH_2 - OH + 2HCrO_4^- + 8H^+ = 3CH_2 = CH - CHO + 2Cr^{III} + 8H_2O$$

Test for free radicals

During oxidation of the aldehyde in an atmosphere of nitrogen, attempts at inducing polymerization with the addition of acrylonitrile were unsuccessful. Further, the addition of acrylonitrile did not affect the rate. This indicates that one-electron oxidation, giving rise to free radicals, is unlikely in this reaction.

¹H-NMR measurements

¹H NMR experiments were performed on a Bruker spectrometer (Ascend 400). All measurements were performed at 303 K. Samples were prepared in D_2O . SDS solutions were pre-equilibrated for 10 min before measurements.

Results and Discussion

UV–Vis spectrophotometric study

During the reaction, the yellow-orange colour of the dichromate solution of Cr(VI) quickly disappeared and a green coloured solution was obtained (Fig. 1). The orange color of the dichromate was reduced to green Cr(III). The gradual production of the Cr(III)-aqua complex was confirmed spectrophotometrically. In the unpromoted path, the final color that appeared as green ($\lambda_{max} = 579$ nm Fig. 1) was quite different from the color found in the promoted path, which was pale violet. In the unpromoted path, the two bands were observed due to the transitions $\lambda_{max} = 581$ nm for ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ and $\lambda_{max} = 408$ nm (appeared as shoulder) for ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$ of Cr(III), respectively [26, 27]. The spectra of the final solution produced in the unpromoted path after completion of the reaction and the spectra of the pure chromic sulfate solution in aqueous sulfuric acid media were almost similar (Fig. 1), but were different in the promoted reaction path due to the presence of different types of Cr(III) species. This simply suggests that the final Cr(III) species are a Cr(III)-promoter complex in which the promoter behaves as a ligand. PA, bipy and phen as a ligand contain one or more heteroatom, i.e., nitrogen donor sites are in the aromatic ring with vacant π^* (antibonding) M.O., highly assisting the metal-toligand charge transfer (MLCT).

Cr(VI) oxidation of 2-propenol in aqueous acid media may generate three possible oxidized products: 2-propenal, 2-propenoic acid and glycerol (Scheme 1). Fractional distillation products from the reaction mixture were divided into two parts. The first part was treated with freshly prepared permanganate solution. The



Fig. 1 UV–Visible spectrum with corresponding colours of the reaction mixture $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$, $[2\text{-propenol}]_T = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$ at 303 K. [The green spectrum, for pure Cr(III) solution, is almost identical to the spectrum after completion of the reaction.]



Scheme 1 Possible oxidized product from Cr(VI) oxidation of 2-propenol



Fig. 2 Scanned absorption spectra of the reaction mixture in the presence of SDS (8.0 mol dm⁻³) at regular time intervals. $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$, $[2-propenol]_T = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$ at 303 K. *Inset* Similar scanned absorbance spectra in absence of SDS and promoter

pink KMnO₄ colour disappeared, indicating that the product included an unsaturated component. The second part was treated with freshly prepared 2,4-DNP solution and dil H_2SO_4 , yielding a hydrazone product. The presence of orange hydrazone confirms the presence of the >C=O group. Previously we stated that the reaction occurred under a pseudo first-order condition, i.e., formation of 2-propenal from single-step oxidation of 2-propenol is possible, but oxidation of 2-propenol to 2-propenol by Cr(VI) in acidic media only produces 2-propenal. Product analysis studies ruled out the possibility of an attack on the double bond. Again, the IR spectrum of this hydrazone (Fig S2, Table S1) superimposed on the spectrum of a corresponding hydrazone of a standard sample of 2-propenal.

Promoter [10 ⁴ mol dm ⁻³]		Micellar catalyst [10 ³ mol dm ⁻³]		$10^4 \times k_{\rm obs} [{\rm s}^{-1}]$	t _{1/2} [h]
_		_		3.308 ± 0.04	0.582
PA	5	_		4.698 ± 0.01	0.410
PA	10	-		5.428 ± 0.04	0.354
PA	15	-		5.616 ± 0.02	0.342
PA	20	-		5.998 ± 0.06	0.321
PA	30	-		6.468 ± 0.03	0.297
PA	40	-		7.163 ± 0.02	0.269
Bipy	5	-		6.068 ± 0.05	0.317
Bipy	10	-		9.331 ± 0.05	0.206
Bipy	15	-		11.900 ± 0.02	0.162
Bipy	20	-		13.600 ± 0.01	0.141
Bipy	30	-		18.600 ± 0.04	0.103
Bipy	40	-		26.700 ± 0.05	0.072
Phen	5	-		4.920 ± 0.06	0.391
Phen	10	_		5.661 ± 0.06	0.340
Phen	15	-		6.151 ± 0.05	0.313
Phen	20	-		7.418 ± 0.04	0.259
Phen	30	_		8.716 ± 0.01	0.221
Phen	40	-		10.100 ± 0.02	0.191
-		SDS	4	3.251 ± 0.03	0.592
-		SDS	6	3.863 ± 0.05	0.498
-		SDS	8	4.285 ± 0.04	0.449
-		SDS	12	4.148 ± 0.04	0.464
-		SDS	16	4.132 ± 0.02	0.466
-		SDS	20	3.990 ± 0.06	0.482
PA	20	SDS	14	6.090 ± 0.02	0.316
PA	30	SDS	14	8.015 ± 0.04	0.240
PA	40	SDS	14	9.387 ± 0.05	0.205
Bipy	20	SDS	14	31.372 ± 0.05	0.061
Bipy	30	SDS	14	42.367 ± 0.04	0.045
Bipy	40	SDS	14	49.552 ± 0.01	0.038
Phen	20	SDS	14	5.438 ± 0.03	0.354
Phen	30	SDS	14	6.985 ± 0.04	0.275
Phen	40	SDS	14	9.125 ± 0.06	0.211

Table 1 k_{obs} and half life of the reaction in the presence and absence of a promoter and non-functional micellar catalyst

 $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}, [H_2SO_4] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}, [2\text{-propenol}]_T = 1.5 \times 10^{-3} \text{ mol dm}^{-3}, PA = 2\text{-picolinic acid, bipy} = 2,2'\text{-bipyridine, phen} = 1,10\text{-phenanthroline, Temp} = 303 \text{ K}$

The reaction mixture was scanned in the range of 300–600 nm in both the presence and absence of a promoter and surfactant at regular time intervals to follow the gradual development of the reaction intermediates (if any) and the product. The

scanned spectra in Fig. 2 indicates the gradual disappearance of Cr(VI) species at a wavelength of 450 nm.

The reaction kinetics were found to obey the Michaelis–Menten equation with respect to [2-propenol]; that is, a complex formed between the oxidant and substrate prior to the rate determining step. The spectrum with an isosbestic point at $\lambda_{\text{max}} = 533$ nm (Fig S3) shows the intermediate complex subsequently decomposed into the products.

The kinetic data (k_{obs} and $t_{1/2}$) in Table 1 shows k_{obs} for the SDS-catalyzed reaction to be greater than that of the corresponding non-catalyzed reaction. In the case of the promoted path, this observation was also true as compared to the unpromoted path. From Fig. 3, it was found that the k_{obs} value increased with SDS concentration, up to 8 mol dm⁻³, after which the k_{obs} value decreased to some extent. For each promoter, we followed the reaction in the concentration range (5–40) × 10⁻⁴ mol dm⁻³. In this oxidation, bipy is the best promoter, as compared to the other two promoters (PA and phen) used (Table 1; Fig. 4).

Effect of [2-propenol]

The pseudo first-order rate constants k_{obs} (s⁻¹) were measured (Table S2) at constant [Cr(VI)] (5 × 10⁻⁴ mol dm⁻³), [H⁺] (0.5 × 10⁻³ mol dm⁻³) and temperature (303 K). The k_{obs} values thus obtained were found to increase with an increasing concentration of 2-propenol (Fig. 5).



Fig. 3 Effect of [SDS] on the oxidation reaction. $[2\text{-propenol}]_T = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$, $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$, Temp = 303 K



Fig. 4 Effect of [promoter] on the oxidation reaction. $[2\text{-propenol}]_T = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$, $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$, Temp = 303 K



Fig. 5 Effect of [2-propenol] on the oxidation reaction. $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2SO_4] = 0.5 \times 10^{-3} \text{ mol dm}^{-3}$, Temp = 303 K

Effect of [H⁺]

The effect of $[H^+]$ on the rate of 2-propenol oxidation was studied at constant Cr(VI) and substrate (2-propenol) concentrations. The results obtained show that the pseudo first-order rate constant of oxidation increased significantly with an increase in the $[H^+]$ of the reaction medium.

The plot of k_{obs} against [H⁺] was found to be linear (Fig. 6). This shows that the reactions were acid-catalyzed. As the sulfuric acid concentration increased in the reaction mixture, the [H⁺] increased, but there was also a corresponding increase in [HSO₄⁻]. If the rate is proportionally dependent on the [HSO₄⁻] to a great extent, the overall effect of adding sulfuric acid would increase the rate.

Effect of temperature

Oxidation of the 2-propenol was carried out at different temperatures, ranging from 293 K to 313 K, maintaining constant concentrations of 2-propenol, Cr(VI) and H⁺. The pseudo first-order rate constant increased with an increase in temperature for uncatalyzed, SDS-catalyzed and bipy-promoted paths, as shown in Table 2. The Arrehenius parameters (that is, E_a) were calculated using the Eyring equation

$$\ln\left[\frac{k_{\rm obs}h}{K_{\rm B}T}\right] = -\frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R}$$
$$\Delta H^{\neq} = E_{\rm a} - RT$$

The energy of activation E_a for uncatalysed, catalysed and promoted paths (Table 3) as $k_{obs(bipy)} \gg k_{obs(SDS)} \gg k_{obs(u)}$. The E_a values clearly suggest that SDS and bipy act as catalysts and provide new reaction paths with lower activation energy. The variation of the activation parameters in SDS micelles compared to water is as expected because one may expect stabilization of the transition state owing to the presence of micelles that assist the reaction path. The negative value of $\Delta S^{\#}$ indicates formation of a complex in the reaction, and the complex is more ordered than the reactants [28]. The observed large decrease in $\Delta S^{\#}$ further



Fig. 6 Effect of $[H^+]$ on the oxidation reaction. $[2\text{-propenol}]_T = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$, $[Cr(VI)]_T = 5 \times 10^{-4} \text{ mol dm}^{-3}$, Temp = 303 K

Temperature	Without surfactant and promoter $10^4 \times k_{obs} [s^{-1}]$	With SDS $10^4 \times k_{\rm obs} [{\rm s}^{-1}]$	With promoter $10^4 \times k_{\rm obs} [{\rm s}^{-1}]$
293 K	1.150	2.357	18.400
298 K	2.335	3.270	22.000
303 K	3.308	4.364	26.700
308 K	4.331	5.200	29.386
313 K	5.485	6.892	32.841
Thermodynamic paramete	ers		
$\Delta H^{\#} (kJ mol^{-1})$	54.795	37.322	19.617
$\Delta S^{\#} (J \ K^{-1} \ mol^{-1})$	-131.772	-186.573	-229.962
$\Delta G^{\#} (kJ mol^{-1})$	94.722	93.854	89.296
$E_a (kJ mol^{-1})$	2573.937	2556.464	2538.759

Table 2 Temperature effect and thermodynamic activation parameters for the oxidation of 2-propenol by Cr(VI)

$$\label{eq:cr(VI)} \begin{split} \hline [Cr(VI)]_T &= 5 \times 10^{-4} \quad \text{mol } dm^{-3}, \quad [H_2SO_4] = 0.5 \times 10^{-3} \quad \text{mol } dm^{-3}, \quad [2\text{-propenol}]_T = 1.5 \times 10^{-3} \ \text{mol } dm^{-3}, \quad \text{SDS} = 14 \times 10^{-3} \ \text{mol } dm^{-3}, \quad \text{Promoter } (bipy) = 4 \times 10^{-3} \ \text{mol } dm^{-3} \end{split}$$

Uncertainties in the thermodynamic parameters $\Delta H^{\#}, \ \Delta S^{\#}, \ \Delta G^{\#}$ and Ea are $\leq \pm 0.1 \ kJ \ mol^{-1}, \pm 0.1 \ J \ K^{-1} \ mol^{-1}, \pm 0.1 \ kJ \ mol^{-1}$ and $\pm 0.1 \ kJ \ mol^{-1}$, respectively

Table 3 Proton NMR shifts δ (ppm) of SDS in the presence of2-propenol

2-Propenol	a 5.168 α-CH ₂	b 5.912 β- CH ₂	c 4.195 Bulk -CH ₂	Terminal-CH ₃
SDS	3.982	1.634	1.250	0.850
SDS + 2-propenol	4.000	1.656	1.274	0.845
$\Delta\delta$ (shift in ppm)	0.018	0.022	0.024	0.005

strengthens the point. A meaningful, mechanistic explanation of the apparent values of $\Delta S^{\#}$ and $\Delta H^{\#}$ is not possible because the k_{obs} does not represent a single elementary kinetic step; it is a function of true rate constants.

Location of reactant molecule inside the micelle

Aggregated surfactant media of any type consist of several solubilization sites where the reactant molecules prefer to occur through different type of interactions [29–31]. Actually, an aqueous surfactant solution looks like a micro-heterogeneous media and is considered a two-phase system, namely, an aqueous phase and a micellar pseudophase. Due to the different properties of the micellar pseudo-phase, it is not possible to precisely locate the exact site of the reaction but, at least, the location of the reactants can be considered. It is well established that most of the micellar reactions involving an ionic and a neutral reactant, as well as ionic micelles, are believed to take place either inside the Stern layer or at the interface between the micellar surface and the bulk solvent water.

To explain micellar catalysis, some authors consider exchange of the reactants between the micelles. This exchange is a function of the thickness of the layer where the substrate and the surfactant are located. Taking into account that, for both H^+ and Na^+ (for the SDS case) ions, there is no difference between the specific interactions with the surfactant head group, all the H^+ can be considered located in the micellar interface. Changes in the micro-environment of the surfactant solution can be easily monitored by the analysis of the ¹H NMR spectrum of the micelle. The ¹H-NMR spectra of SDS alone and in the presence of 2-propenol are represented in Fig. 7a, b, respectively. The signals for four different protons of SDS, i.e., α -CH₂, β -CH₂, 9 bulk methylene (bulk-CH₂) and the terminal methyl proton (–CH₃), in



Fig. 7 a ¹H-NMR spectrum of SDS in D₂O. **b** ¹H-NMR spectrum of SDS in the presence of 2-propenol in D₂O. [*Inset*]: ¹H-NMR spectrum of 2-propenol in D₂O. [SDS] = 12×10^{-3} mol dm⁻³, [2-propenol] = 1×10^{-2} mol dm⁻³

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¹H-NMR spectrum are given in Table 3. In the presence of 2-propenol, the δ value for the terminal -CH₃ protons is not shifted much, whereas a significant downfield shift for α -, β - and bulk-CH₂ protons of SDS were found. The $\Delta\delta$ value clearly indicates that the α -protons of SDS are shielded more by the –OH group of 2-propenol. This suggests that the 2-propenol molecule containing hydrophilic groups (–OH) does not enter the micellar core of SDS; however, it resides in the stern layer region through ion–dipole interactions. Here, it should be noted that 2-propenol is highly polar and tends to solubilizes in the vicinity of the micellar surface of SDS due to ion interactions or polar interactions [31].

Reaction mechanism and rate law

Aqueous solutions of chromic acid contain mainly $HCrO_4^-$ species [32]. It has already been reported that chromium(VI) oxidation of organic substrate (like alcohol, aldehyde, etc.) occurs via formation of a neutral ester [4, 7, 12, 13] through binding of the substrate by $HCrO_4^-$. The neutral ester protonated by H^+ ion, present in the reaction medium, subsequently decomposes to give the product. The oxidation mechanism in the unpromoted path is given in Scheme 2.

According to the stoichiometry equation, we get

$$-\frac{1}{2}\frac{d[HCrO_4^-]}{dt} = \frac{1}{3}\frac{d[2 - \text{propenol}]}{dt}$$

On the basis of the mechanism in Scheme 2, the following rate equation is derived:

$$K_{obs(u)} = -\frac{d\ln[\text{HCrO}_4^-]}{dt}$$
$$= \frac{2}{3}k_1K_1K_2[2 - \text{propenol}]_T[\text{H}^+]^2$$

The promoted path of Cr(VI) oxidation of 2-propenol in acid media is not like the unpromoted path. Chromium(VI) was reported to form chromate esters with ligands containing O-, N- and S-atoms [9, 13, 26]. Promoters containing such atoms used in this study behaved as a ligand.

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

$$CH_{2}=CH$$

$$CH_{2}=CH$$

$$CH_{2}=CH$$

$$CH_{2}=CH-CHO + CrO_{2} + H^{+} + H_{2}O$$

$$CH_{2}=CH-CHO + CrO_{2} + H^{+} + H_{2}O$$

Scheme 2 Chromium(VI) oxidation of 2-propenol in absence of a promoter

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The promoters bipy/PA/phen promote acid-catalyzed Cr(VI) oxidation of organic substrates explicitly in an aqueous solution. The mechanistic pathway involves ratelimiting formation of the "active oxidant" through complexation between $HCrO_4^-$ and the promoter [4, 7, 12, 13]. In general, active oxidant species bearing a positive charge tend to bind with 2-propenol through the –OH group, forming a ternary complex, and subsequently decomposing to 2-propenal and Cr(IV)-promoter species at the rate determining step. Afterward, Cr(IV)-promoter species rapidly reduce to the Cr(III)-promoter via Cr(VI) and 2-propenol. The mechanism for overall oxidation of 2-propenol to 2-propenal by Cr(VI) in the presence of a promoter are proposed in Scheme 3 [13, 26].

In this kinetic study, it was found that bipy, containing N atoms as donor, is the best among the three promoters used. It has been observed that the orange-yellow colour of Cr(VI) rapidly disappears to blue-violet in the presence of bipy. In the presence of PA and phen, the orange-yellow colour disappeared quickly, but not as rapidly as in the bipy pathway. Bipy, like PA and phen, also forms an active oxidant species by combining with $HCrO_4^-$, but in the ternary complex, electron transfer from 2-propenol to the active oxidant species occurs more easily in the case of bipy than that of PA and phen. The active oxidant Cr(VI)-bipy, containing two positively



Scheme 3 Chromium(VI) oxidation of 2-propenol in the presence of a promoter

charged nitrogen atoms, plays a crucial role in the rate enhancement process compared to the one positively charged nitrogen atom in the Cr(VI)-PA complex.

The observed pseudo first-order rate constant for the Cr(VI) oxidation of 2-propenol in sulfuric acid media (Table 2; Fig. 5) follows $k_{obs(bipy)} \gg k_{obs(phen)} \gg k_{obs(PA)} \gg k_{obs(u)}$. This observation matches well with earlier reports [33–35].

Effect of 'micelle' and 'promoter with micelle' media on the reaction rate

SDS, as an anionic surfactant, preferably attracts cationic species in its outer stern layer region. The protonated ester produced from the neutral ester is cationic in nature [33, 34], which, therefore, is attracted by the outer surface of the negatively charged head group of the SDS micelle. A slight acceleration of the reaction rate was observed when the reaction was performed in the presence of anionic SDS compared to that of aqueous medium. 2-propenol is a neutral molecule with its polar –OH groups preferably partitioned between the aqueous phase and the stern layer (or close proximity of head groups) of the SDS micelle. The limited presence of a reactant towards the outer surface of the micelle results in a slight rate acceleration. In fact, in the presence of SDS, the reaction occurs simultaneously in both the micellar and aqueous phase (Scheme 4).

In this study, the maximum rate acceleration was found when promoters were used in addition to micelles. The active oxidants, Cr(VI)-PA, Cr(VI)-bipy and Cr(VI)-phen complexes, react with 2-propenol to form a ternary complex which undergoes redox decomposition in a rate-limiting step [26, 27], giving rise to the final product, 2-propenal. Formation of the active oxidant (reaction intermediate, Scheme 3) during the progress of the reaction was already confirmed by obtaining the ¹H NMR spectra in our previous report [36]. The positively charged active oxidants (AO⁺) preferably accumulated in the anionic stern layer region of SDS through electrostatic attraction, as shown in Scheme 5. The counter-ions (Na⁺) of the SDS micelle were exchanged by the AO⁺ and H⁺ ions and they were arranged



Scheme 4 Schematic representation of the oxidation reaction occurring in the aqueous and micellar pseudophase



Scheme 5 Location of reactant molecule inside the micelle in the presence of a promoter

in an ordered manner, resulting the negative $\Delta S^{\#}$ value. Incorporation of reactant species in the SDS micelle can be regarded both as having micro-environmental effects on the micelle and solubilization effects. Our kinetic experiment shows maximum rate acceleration was obtained when combining an SDS-catalyzed and bipy-promoted pathway than when using an SDS-phen or an SDS-PA pathway. Combination of SDS and bipy in the reaction mixture leads to almost a 15-fold rate acceleration compared to the uncatalyzed and unpromoted paths. Therefore, we can say that bipy in the presence of SDS is the best promoter for the oxidation of 2-propenol by Cr(VI). A table comparing our results (Table S3) explains the selection of suitable catalysts and promoters over the other oxidants used previously in 2-propenol to 2-popenal conversion [19–21, 37].

Conclusion

The main target of our study was to carry out the oxidation of 2-propenol to 2-propenal in aqueous micellar media rather than in an hazardous solvent. It is a growing and challenging preference that synthetic chemists carry out organic transformations using "green" aqueous solutions. In this context, the use of water as a solvent features many benefits; not only is water innocuous, but it can also potentially improve reactivities and selectivities of organic transformations, and simplify the work up procedures. Micelles act as nano-reactors and efficiently increase the effective local concentration of reactants inside its surface. The ¹H-NMR studies

established that the stern region of micellar reactor is the most probable location of reactants in this oxidation process. It is interesting to note that the rate of oxidation increased drastically when SDS was used as the micellar catalyst in combination with the bipy promoter at a particular concentration. The pseudo first-order rate constants of the oxidation reaction between Cr(VI) and 2-propenol vary in magnitude in the order of $k_{(Aqs)} < k_{(SDS)} < k_{(PA)} < k_{(phen)} < k_{(bipy)} < k_{(phen+SDS)} < k_{(PA+SDS)}$ $\ll k_{(bipy+SDS)}$. The aldehyde product was confirmed by a conventional 2,4-DNP test and IR studies of the DNP derivative. In conclusion, the overall investigation of the present work is simple, cost effective and eco-friendly, as compared to previous research. Micellar catalysis by SDS in association with a bipy promoter exhibited a remarkable ~16-fold rate enhancement as compared to that of the uncatalyzed reaction pathway. Considering all the above facts, it is quite reasonable to select a combination of SDS micelles and bipy as *hetero-aromatic nitrogen* base promoters as being the most effective and suitable for chromic acid oxidation of 2-propenol to 2-propenal in aqueous media.

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