

Kinetics and mechanism of electron transfer to pyridinium chlorochromate (VI) from sulfur containing amino acid, L-cysteine in aqueous and micellar media

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The electron transfer reaction of L-cysteine (RSH) with pyridinium chlorochromate (PCC) has been studied spectrophotometrically over the range $2.0 \leq 10^3 [\text{RSH}] \leq 6.0$; $0.01 \leq [\text{H}^+] \leq 0.2$; $298 \leq T \leq 318 \text{ K}$ and $I = 0.3 \text{ mol dm}^{-3}$ (NaClO_4). The electron transfer reaction has also been carried out in the presence of anionic, cationic and neutral micelle. The reaction in acid medium is strongly catalyzed by changing $[\text{SDS}]_T$ (sodium dodecyl sulfate) up to $3 \times 10^{-2} \text{ mol dm}^{-3}$, beyond this concentration of SDS, the rate is retarded. The cationic and neutral micelle has a small effect on the rate. ΔH^\ddagger (kJ mol^{-1}) and ΔS^\ddagger ($\text{JK}^{-1} \text{ mol}^{-1}$) values for the k_1 and k_2 paths are 30.20 ± 0.25 , -159.65 ± 0.83 and 29.60 ± 0.62 , -127.09 ± 2.17 , respectively. The negative activation entropy is indicative of the ordered transition state for the electron transfer reaction. Formation of 2-amino-3-(2-amino-2-carboxy-ethyl) disulfanyl-propanoic acid as product is strongly supported by IR spectra.

Keywords: kinetics mechanism, electron transfer, pyridinium chlorochromate, cysteine, micellar media.

INTRODUCTION

In recent years there has been a great upsurge of interest on mechanistic studies of reactions of amino acids with transition metal complexes, due to their biological relevance¹⁻⁸. Amino acids are important biomolecules which are not only building blocks of proteins but they also function as chemical messengers in bringing about communication between cells. This prompted us to undertake the present study which includes interaction of sulfur containing amino acid, cysteine with Cr(VI) in the form of pyridinium chlorochromate (PCC). L-cysteine is an important amino acid which has three active donor sites of O, N and S. It would be interesting to know which active site of cysteine will interact with Cr (VI) during the electron transfer process. Since most biological processes occur at interfaces, structure, dynamics and the reactivity of biomolecules differ at an interface than those observed in the bulk. Keeping this in view the present study was carried out both in the aqueous and micellar media.

EXPERIMENTAL

Raw materials

Analytical grade chemicals were used. Pyridinium chlorochromate (PCC) was synthesised as reported earlier⁹. Ionic strength was maintained at $I = 0.3 \text{ mol dm}^{-3}$ by using the freshly prepared NaClO_4 solution. Solutions of different concentrations were prepared by proper dilution of the stock solution, fresh solutions were used for kinetic measurements. The strength of stock NaClO_4 solution was estimated by a combined ion-exchange alkalimetric procedure. The resin Dowex 50 W X8 (Na^+ form) was used for ion-exchange experiments.

Fresh solutions were prepared using double distilled water in an all-quartz distillation apparatus containing KMnO_4 solution.

Sodium dodecyl sulphate (SDS), N-cetyl-N,N,N trimethyl Ammonium Bromide (CTAB) and the commercial surfactant, Triton X-100 were used as anionic, cationic and neutral micelles, respectively. The stock micellar solution of the strength of 1.0 mol dm^{-3} was prepared by dissolving the required amount of the surfactant in the double distilled water. The acetic acid used was purified by the reported procedure¹⁰.

Kinetic measurements

The kinetics of the reaction between cysteine and PCC in the aqueous and micellar medium were studied spectrophotometrically under the pseudo-first order conditions with an excess of cysteine using a CECIL 7200 (UK) UV-Visible spectrophotometer with a thermostatic bath for temperature control with an accuracy of $\pm 0.1^\circ\text{C}$. The progress of the reaction was monitored by the following decrease in absorbance at 425 nm with time using a conventional mixing technique. A_∞ was measured after the completion of the reaction (approximately after 24 hours of mixing) when the absorbance became almost constant.

The plot of $\ln (A_t - A_\infty)$ versus t was found to be linear as indicated in the equation (1).

$$\ln (A_t - A_\infty) = \ln (A_0 - A_\infty) - k_{\text{obs}} \cdot t \quad (1)$$

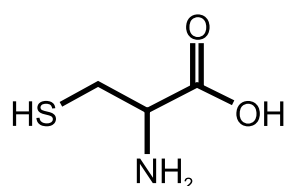
Where A_t and A_∞ are absorbances of the reaction mixture at time t and at equilibrium respectively. The correlation coefficients (R^2) of the plots used to determine k_{obs} were found to be 0.99. The pseudo-first order rate constant (k_{obs}) was calculated by the least squares method from the above relationship. The redox reactions were followed for about 3 half lives. The reported rate data represent as an average of duplicate runs were reproducible to within $\pm 3\%$.

Stoichiometry and identification of product

The reaction mixture containing PCC and cysteine in the molar ratio 1:10 was warmed at 318 K to complete the reaction. The unreacted chromium (VI) and product chromium (III) were estimated¹¹. From the above experimental findings it was observed that 2 moles of PCC reacted with 6 moles of cysteine to generate disulfanylpropionic acid (cystine) and Cr^{3+} (aq). The stoichiometry of the above reaction is explained by equation (2).

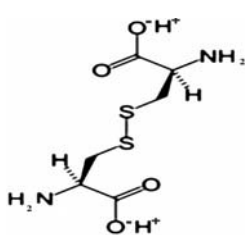
$$6 \text{ Cysteine} + 2 \text{ PCC} \rightarrow 3 \text{ Cystine} + 2 \text{ Cr}(\text{H}_2\text{O})_6^{+3} \quad (2)$$

In order to get the reaction product, PCC (0.2 mol), cysteine (0.02 mol), were mixed at $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$. The volume of the made solution was 50ml. The reaction mixture was warmed for a quick completion of the reaction. The mixture was refrigerated over night. A crystalline product was formed, it was washed with diethylether and the product was dried in a desiccator. The yield of the product was 70%. The FTIR spectra of cysteine and the product (Fig. 1) were recorded with a Perkin Elmer (UK) FTIR spectrophotometer. A broad strong peak around at 3564 cm^{-1} in the product may be assigned to stretching $\nu_{\text{N-H}} (-\text{NH}_3^+)$, as compared to 3177 cm^{-1} and 2962 cm^{-1} in L-cysteine. The shifting to higher frequency is probably due to an association of water molecule with the product. Two NH_3^+ bending bands and a strong absorption peak of carboxylate ion are mixed up and a broad band is observed at 1613 cm^{-1} in the product compared to 1586, 1544, 1423 cm^{-1} peaks in L-cysteine. The overtone band at 2079 cm^{-1} in L-cysteine is shifted to 2017 cm^{-1} in the product, weak band at 2551 cm^{-1} in cysteine due to S-H stretching is absent in the product suggesting that cysteine dimerises to disulfanyl-propanoic acid having S-S linkage. Strong and broad peak of 1093 cm^{-1} and a sharp peak of 630 cm^{-1} in the product correspond to 1063 cm^{-1} and 692 cm^{-1} in the cysteine (I) and is due to free NH_2 twisting and rocking¹². Formation of disulfanyl-propanoic acid (II) as product is strongly supported by the IR spectra.



(I)

(Cysteine Substrate)



(II)

(Product disulfanyl-propanoic acid)

RESULTS AND DISCUSSION

The electron transfer reaction between L-cysteine and PCC has been studied over the range $2.0 \leq 10^3 [\text{cysteine}]_{\text{T}} \leq 6.0$; $0.01 \leq [\text{H}^+] \leq 0.2$, $298 \text{ K} \leq T \leq 318 \text{ K}$ and $I = 0.3 \text{ mol dm}^{-3}$ (NaClO_4).

The UV-VIS spectral scan (Fig. 2) of the reaction mixture of L-cysteine and PCC over the range $200 \leq \lambda(\text{nm}) \leq 600$ shows shifting of absorption maxima from 350 nm to 425 nm, indicating the formation of an intermediate species between cysteine and PCC. The said intermediate was found to decay with the increasing time. After a long interval (approximately 24 hrs) the peak at 425 nm vanished completely and two new peaks appeared (Fig 2) at

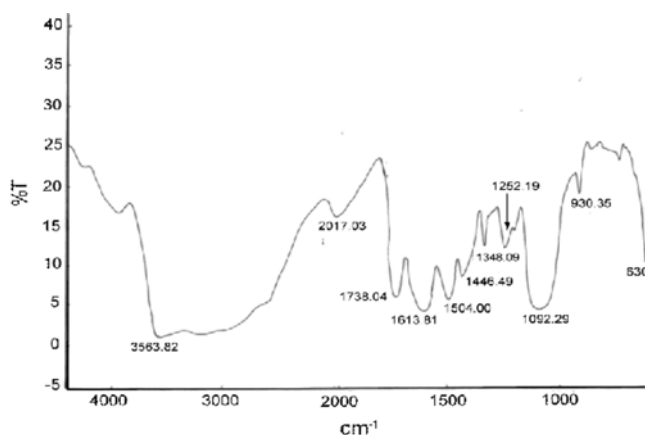


Figure 1. The FTIR spectra of the product (disulfanylpropanoic acid)

410 nm and 566 nm which corresponded to the spectrum of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ¹³.

The k_{obs} of the above reactions are listed in Table 1. Plots of k_{obs} versus L-cysteine were linear with finite positive intercepts. The rate of the reaction was also seen to increase with increasing $[\text{H}^+]^2$ at constant [cysteine] (Fig. 3).

The pseudo – first order rate constants ($10^4 k_{\text{obs}}(\text{s}^{-1}) = 6.46 \pm 0.29$) at 303 K were almost not affected by varying [PCC] in the range from 3×10^{-3} to $8 \times 10^{-3} \text{ mol dm}^{-3}$ at $[\text{H}^+] = 0.05 \text{ mol dm}^{-3}$ indicating the fact that the reaction is the first order in $[\text{Cr}(\text{VI})]_{\text{T}}$.

In order to know what type of species are involved in the rate determining step, the reaction was investigated by changing the ionic strength of the medium in the range 0.1 to 0.5 mol dm^{-3} keeping $[\text{PCC}]_{\text{T}} = 5.0 \times 10^{-4}$ and $[\text{cysteine}]_{\text{T}} = 4.0 \times 10^{-3}$ constant at $[\text{H}^+] = 0.05 \text{ mol dm}^{-3}$. $10^4 k_{\text{obs}}(\text{s}^{-1}) = 6.63 \pm 0.09$, did not change appreciably. This indicates that probably charged and uncharged species are involved in the rate determining step.

The effect of relative permittivity was studied at 303 K by varying aqueous [acetic acid] 20% to 70%, when $[\text{PCC}] = 5.0 \times 10^{-4}$, $[\text{Complex}] = 4.0 \times 10^{-3}$, $I = 0.3 \text{ mol dm}^{-3}$ $10^4 k_{\text{obs}}(\text{s}^{-1})$ changed from 6.4 to 22.4 when % of HAC vary from % and dielectric constant changed 81.50 to 38.50. This indicates a probable polar character for the transition state as

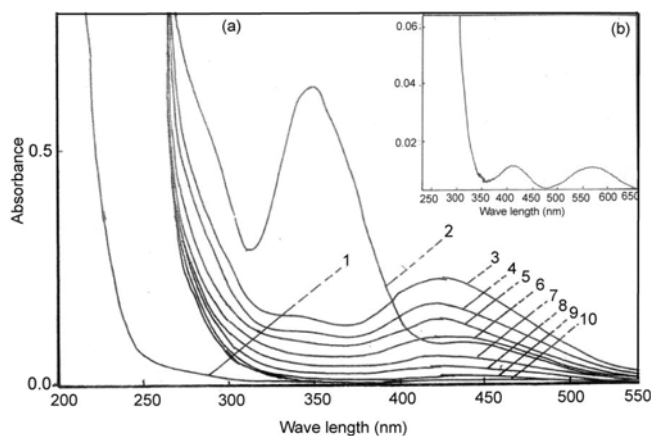


Figure 2. UV-VIS spectral scan of reaction mixture of L-cysteine and PCC, $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$, $I = 0.3 \text{ mol dm}^{-3}$ (NaClO_4) at 303K (a)(1) [cysteine] = $4 \times 10^{-3} \text{ mol dm}^{-3}$, (2) [PCC] = $4 \times 10^{-4} \text{ mol dm}^{-3}$, (3) immediate after mixing, (4) after 15 minutes, (5-9) $\Delta t = 5$ minutes, (10) after 2 hours. (b) Inset: Spectral scan after 24 hrs, 303 K

Table 1. Pseudo-first order rate constant (k_{obs}) data at different temperatures 298K–318 K, $[\text{PCC}] = 5 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, I (ionic strength) = $0.3 \text{ mol} \cdot \text{dm}^{-3}$ (NaClO_4)

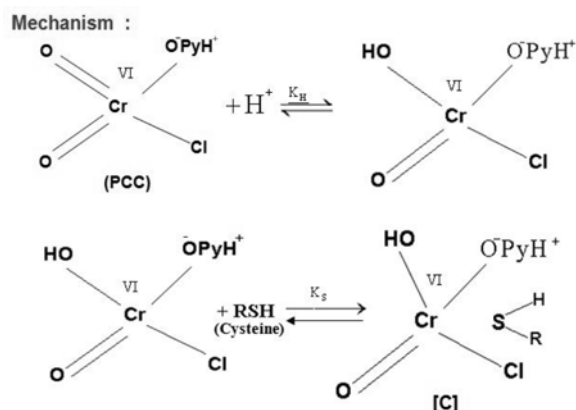
$[\text{H}^+]$ (mol dm^{-3})	$10^3 [\text{cysteine}]$ (mol dm^{-3})	$10^4 k_{\text{obs}} (\text{s}^{-1})$				
		298K	303K	308K	313K	318K
0.01	2.0	2.54	3.30	4.40	5.50	6.60
	3.0	2.98	4.00	5.40	7.40	9.25
	4.0	3.53	4.75	6.50	9.08	11.20
	5.0	3.69	5.32	7.47	11.00	14.00
	6.0	4.63	6.37	8.934	12.80	16.00
0.05	2.0	6.505	7.63	8.77	9.90	11.80
	3.0	6.88	8.27	9.97	12.00	14.10
	4.0	7.097	8.65	10.60	13.28	15.40
	5.0	7.572	9.50	12.00	15.30	18.20
	6.0	7.658	9.97	13.13	17.52	21.30
0.15	2.0	9.33	12.00	15.36	19.60	24.40
	3.0	14.29	16.55	19.16	22.20	25.10
	4.0	17.48	19.30	21.53	24.30	25.80
	5.0	19.22	21.50	24.01	26.80	29.50
	6.0	21.48	24.50	27.96	31.97	35.60
0.2	2.0	11.34	15.00	20.13	27.48	33.60
	3.0	14.78	19.00	25.20	31.20	39.93
	4.0	19.75	23.90	29.03	35.43	41.20
	5.0	22.49	26.60	31.48	37.30	42.90
	6.0	25.49	31.00	37.85	46.85	54.20

compared to the reactants or an ion-dipolar interaction in the rate determining step. The plot of k_{obs} versus $1/D$ was linear with a positive slope ($R^2 = 0.99$).

The reaction mixture was mixed with acrylonitrile monomer and kept for 2 hrs in an inert atmosphere. On diluting with methanol, a white precipitate was formed indicating the presence of free radicals in the reaction. However, the blank experiments with each reactant alone in the presence of acrylonitrile did not produce any precipitate.

The reaction rate was measured at five different temperatures (298K–318K) with varying substrate concentrations (Table 1) keeping other variables constant. The rate constant (k_{obs}) was found to increase with increasing temperature. Activation parameters (ΔH^\ddagger , ΔS^\ddagger) (Table 2) were calculated by using Eyring equation. The values of activation parameters (ΔH^\ddagger , ΔS^\ddagger) are favourable for electron transfer reaction.

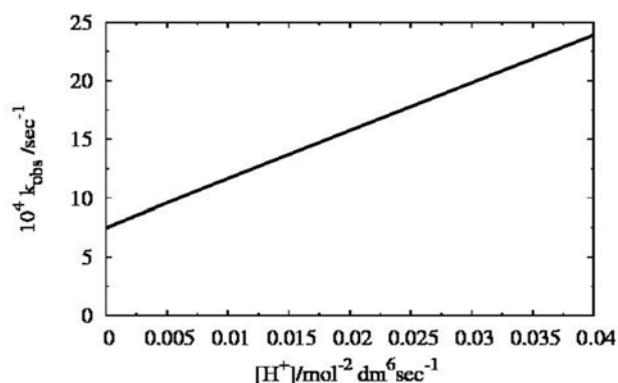
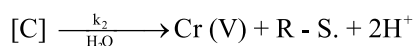
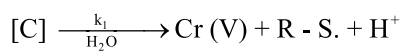
Basing on stoichiometry and identification of the product, the probable mechanism may be delineated as in Scheme I.



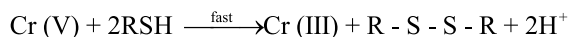
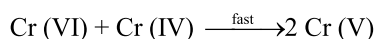
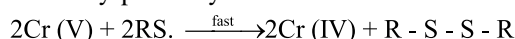
Scheme I

Table 2. Calculated values of k_1 , k_2 and activation parameters using temperature range 298K–318K

Temperature (T)	Acid Independent Path $10^2 k_1 (\text{s}^{-1})$	Acid Dependent Path $k_2 (\text{s}^{-1})$
298	14.86	9.37
303	18.07	11.47
308	22.40	14.07
313	27.45	17.36
318	32.79	20.67
$\Delta H^\ddagger (\text{kJ mol}^{-1})$	30.20 ± 0.25	29.60 ± 0.62
$\Delta S^\ddagger (\text{JK}^{-1} \text{mol}^{-1})$	-159.65 ± 0.83	-127.09 ± 2.17

**Figure 3.** The plot of k_{obs} versus $[\text{H}^+]^2$, $[\text{PCC}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{cysteine}] = 4 \times 10^{-3} \text{ mol dm}^{-3}$, $I = 0.03 \text{ mol dm}^{-3}$ at 303 K

Where k_1 and k_2 are acid independent and acid dependent paths of electron transfer reactions respectively. Rapid and kinetically unimportant steps of the product formation may probably be visualized as follows.



Cr (III) is the $\text{Cr (H}_2\text{O)}_6^{3+}$ species in aqueous acidic medium.

The rate law corresponding to the above mechanism is indicated by equation (3).

$$\frac{\text{rate}}{[\text{PCC}]_0} = k_{\text{obs}} = \frac{K_H K_S [\text{H}^+] [\text{RSH}] (k_1 + k_2 [\text{H}^+])}{(1 + K_S [\text{RSH}]) (1 + K_H [\text{H}^+])} \quad (3)$$

The reaction is showing approximately first order dependence on $[\text{RSH}]$.

At relatively higher $[\text{H}^+]$, $K_H [\text{H}^+] \gg 1$ and $K_S [\text{RSH}] \gg 1$ at finite $[\text{H}^+]$ concentration, the equation (3) is reduced to equation (4)

$$\frac{k_{\text{obs}}}{[\text{RSH}]} \approx k_1 + k_2 [\text{H}^+]^2 \quad (4)$$

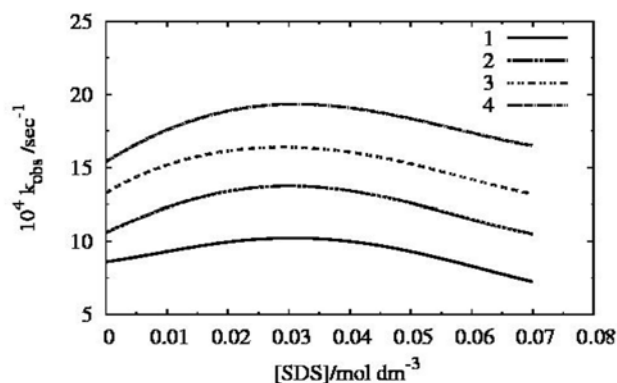


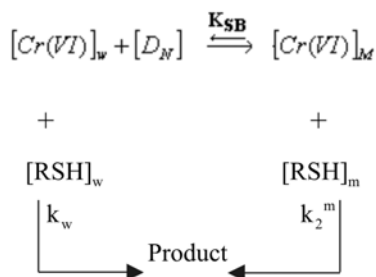
Figure 4. The plots of k_{obs} versus [SDS] at 303 K (1), 308 K (2), 313 K (3), 318 K (4) [PCC] = 5×10^{-4} mol dm $^{-3}$, [cysteine] = 4×10^{-3} mol dm $^{-3}$, [H $^{+}$] = 0.05 mol dm $^{-3}$

The values of k_1 and k_2 can be computed from plots of $k_{\text{obs}}/[\text{RSH}]$ vs $[\text{H}^{+}]^2$ and are listed in Table 2. From which activation parameters are calculated.

The values of activation parameters appear to be more or less compatible with the mechanism proposed^{14, 15}.

Micellar effects on electron transfer reaction

Micellar effect on the rate of oxidation reaction between PCC and cysteine was studied using SDS, CTAB and Triton X-100. Recently Zewail and co-workers¹⁶ have indicated that the surface of the protein is similar to a micellar surface. Thus the study of such reactions in micellar medium is thought to throw more light on the details of the electron transfer reaction in the biological systems. Many researchers^{17 - 22} have also studied the micellar and reverse micellar effects on different electron transfer reactions.



Effect of SDS

The kinetics of oxidation of cysteine with pyridinium chlorochromate was carried out in presence of SDS by changing [SDS] from 0.01 to 0.07 mol dm $^{-3}$ in temperature range of 303 K–318 K. The curve (Fig. 4) shows an increase of the rate with increase of [SDS], beyond its CMC [CMC of SDS = 0.007 mol dm $^{-3}$]²³ it reaches a maxima at [SDS] = 0.03 mol dm $^{-3}$, the rate of reaction decreases when [SDS] goes above 0.03 mol dm $^{-3}$.

The variation of the rate constant with [SDS] is explained using the assumption that the surfactant is distributed between the aqueous and micellar pseudo-phase designated as subscripts w and m respectively as shown in Scheme II²⁴. Scheme II

The observed first order rate constant of the overall reaction in micellar medium is given by equation (5).

$$\text{Rate} = k_{\text{obs}} [\text{substrate}]$$

$$k_{\text{obs}} = \frac{k_{\text{w}} [\text{O}]_{\text{w}} + k_2^{\text{m}} K_{\text{SB}} [\text{D}_n] [\text{O}]_{\text{m}}}{1 + K_{\text{SB}} [\text{D}_n]} \quad (5)$$

Where k_2^{m} is the second order rate constant in the micellar pseudo – phase which is defined in terms of the local molarity of the oxidant.

$[\text{O}]_{\text{m}}$ – concentration of oxidant in micellar medium.

k_{w} – second order rate constant in aqueous phase.

K_{SB} – substrate binding constant.

$$K_{\text{SB}} = \frac{[\text{S}_m]}{[\text{S}_w][\text{D}_n]}$$

Where $[\text{D}_n] = [\text{D}_T] - \text{CMC}$

$[\text{D}_n]$ – micellised surfactant.

S_m and S_w denote substrate in the aqueous and micellar pseudo – phase respectively. As micellar pseudo – phase occupies only a small fraction (2–3)% of total solution volume, it can be assumed that

$$K_{\text{SB}} [\text{D}_n] \ll 1$$

The equation (5) becomes equation (6)

$$k_{\text{obs}} = k_{\text{w}} + k_2^{\text{m}} K_{\text{SB}} [\text{D}_n] \quad (6)$$

Which shows a linear increase of the observed rate constant with an increase of [surfactant]. This explains the rate increase part of the curve in Fig. 4.

By assuming the rate in the micellar pseudo-phase is zero i.e. $k_2^{\text{m}} = 0$, equation (5) is reduced to equation (7).

$$k_{\text{obs}} = \frac{[k_{\text{w}}]}{1 + K_{\text{SB}} [\text{D}_n]} \quad (7)$$

The above equation explains the decrease of the rate with an increase of the [surfactant] at [surfactant] > 0.03 mol dm $^{-3}$. A similar micellar effect has been reported by Bunton^{25, 26} and Richardson²⁷ for the oxidation of organic sulfides with peroxomonosulphate and bicarbonate-activated hydrogen peroxide respectively. This is probably due to an effect where cationic substrate and PCC are taken up by the anionic micelle on the micellar surface which assists in speeding up of the reaction. After reaching the maximum value, the rate decreases probably because the concentration of the substrate available in the aqueous phase is small.

Effect of CTAB

Rate measurement in the presence of CTAB could not be made even in a very low concentration (0.001 – 0.005) mol dm $^{-3}$ due to the cloudiness of the reaction mixture.

Effect of Triton X-100

Rate measurements in the presence of neutral micelle Triton X-100 was carried out at 303 K with varying [Triton X-100] from 0.01 to 0.08 mol dm $^{-3}$ at constant [oxidant] and [substrate]. The marginal retardation effect was observed up to 0.03 mol dm $^{-3}$ concentration of the neutral micelle probably due to structural changes of the micelle.

Conclusion

The following clear cut conclusions can be drawn from the study:

1. The kinetics of electron transfer to PCC (a Cr VI species) for a sulfur containing amino acid, cysteine [RSH], follows a pseudo-first order decay of the Cr (VI) species, a near unity dependence of rate on [RSH], a small acid

independent and a strongly $[H^+]^2$ dependent paths, are observed.

2. The derived rate law and the proposed mechanism coherently explain the kinetic observations for the product formation of disulfanyl-propanoic acid (R-S-S-R) in the reaction. The organic disulphide product is identified by FTIR. The magnitude of the activation parameters are consistence with the proposed mechanism. Negative activation entropy is indicative of the ordered transition state for the reaction. Since there is no evidence of the formation of the bridge between Cr (VI) and cysteine, it is probably outersphere electron transfer process.

3. The kinetics of the PCC – RSH reaction in acid medium is found to be strongly catalysed by SDS upto $[SDS]_0 \approx 3 \times 10^{-2} \text{ mol dm}^{-3}$, beyond which there is progressive retardation in the redox rate with increasing $[SDS]_0$, this may be due to the medium effect caused by the presence of high dielectric of SDS.

4. The micellar effects on the oxidation rate in the presence of CTAB or Triton X-100 were not very pronounced.

Acknowledgements

Authors are thankful to Professor Ramakrushna Panda, Ex- Professor of Chemistry, Berhampur University for his help and co-operation.

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