# Micellar Effect on the Electron Transfer Reaction of Sulphur Containing Amino Acid, L-Cysteine with Chromium (Vi) Complex

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**Abstract- Kinetics and mechanism of electron transfer from L-cysteine (RSH) to pyridinium chlorochromate (VI) have been reported in aqueous acid media in the absence and the presence of anionic micelle, sodium dodecyl sulphate (SDS) and cationic micelle cetyl trimethyl ammonium bromide(CTAB) . The observations are consistent with a rate law and mechanism which involves an equilibrium interaction of a protonated PCC species with the substrate, prior to rate determining electron transfer in variable acid-depndent steps; the formation of the disulphide product (R-S-S-R) identified by FTIR, is presumed to take place in subsequent rapid and kinetically inconsequencial steps. The computed activation parameters appear to be in line with the proposed mechanism..The kinetics of electron transfer follow 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. Activation parameters have been evaluated, which are consistent with the mechanism. The kinetics of the PCC – RSH reaction in acid medium is found to be strongly catalysed by SDS upto $[SDS]_0 \approx 3x10^{-2}$ mol $dm^{-3}$, beyond which there is progressive retardation in the oxidation rate with increasing $[SDS]^0$ , this may be due to the medium effect caused by the presence of high dielectric SDS. The micellar effects on the oxidation rate in the presence of CTAB or Triton X-100 were not very pronounced.**

## INTRODUCTION

Many industrially important processes occur on the surfaces of solid catalysts and nearly all biological reactions take place at gas-liquid interfaces or on an enzyme surface which itself may be bound to a membrane. The properties of these catalytic surfaces are critically depend on the detailed surface structure. The molecule of a surface active agent consists of a long chain hydrocarbon moiety and a polar or ionic head group. It is essentially the hydrophobic and hydrophilic part of the molecule (ion) which impart special properties to the surface active agents. In recent years there has been a great upsurge of interest on mechanistic studies of the reactions of amino acids with transition metal complexes due to their biological relevance[1-10] with the focal point of research in the field of biochemistry, biology and medicine. Since most biological processes occur at interfaces, structure, dynamics and reactivity of biomoleculeus differ at an interface than those observed in the bulk. Keeping this in view the present reaction has been studied in aqueous as well as micellar media.

## EXPERIMENTAL

Pyridinium chlorochromate was prepared by reported method. Sodium dodecyl sulphate (SDS), Ccetyl trimethyl ammonium bromide (CTAB),TritonX-100 are used as anionic, cationic and neutral micelle

## KINETIC MEASUREMENTS

The progress of the reaction was monitored by following the decrease in absorbance ($A_t$) at 425 nm(Fig.1) with time using conventional mixing technique. $A_\infty$ 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).

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_{obs}.t \qquad (1)$$

where $A_t$ and $A_\infty$ are the 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

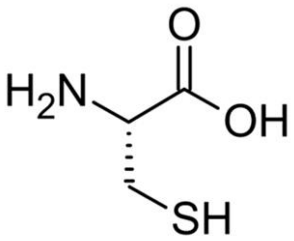
order rate constant ($k_{obs}$) was calculated by the least square method from the above relationship. The redox reactions were followed for about 3 half lives. The reported rates data represent as an average of duplicate runs were reproducible to within ± 3%.

## STOICHIOMETRY AND REACTION PRODUCTS

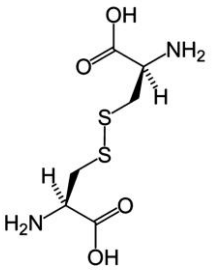
The reaction mixture containing substrate and PCC in the ratio 1:10, I = 0.3 ($NaClO_4$) mol $dm^{-3}$, was allowed to undergo complete reaction in aqueous perchloric acid medium, the unreacted chromium (VI) and product chromium (III) were estimated. From the above experimental findings it was observed that 2 moles of PCC reacted with 6 moles of cysteine to generate disulfanyl-propionic acid (cystine) and $Cr^{3+}$(aq). The stoichiometry of the above reaction is explained by equation (2)

$$6\,\text{Cysteine} + 2\,\text{PCC} \rightarrow 3\,\text{Cystine} + 2\text{Cr}(H_2O)_6^{+3} \qquad (2)$$

In order to get the reaction product, PCC (0.2 mol), cysteine (0.02 mol) were mixed at $[H^+]$ = 0.2 mol $dm^{-3}$. The volume of the made solution was made 50 ml. The reaction mixture was warmed for a quick completion of the reaction. The mixture was refrigerated overnight. A crystalline product was formed, it was washed with diethyl ether and the product was dried in a desiccator. The yield of the product was 70%. The FTIR spectra of cysteine and the product were recorded with a Perkin Elmer (UK) FTIR spectrophotometer.



(2-amino-3-sulfanylpropanoic acid)



(Product Cystine)

(2-Amino-3-(2-amino-2-carboxy-ethyl) disulfanyl-propanoic acid)

## RESULTS AND DISCUSSION

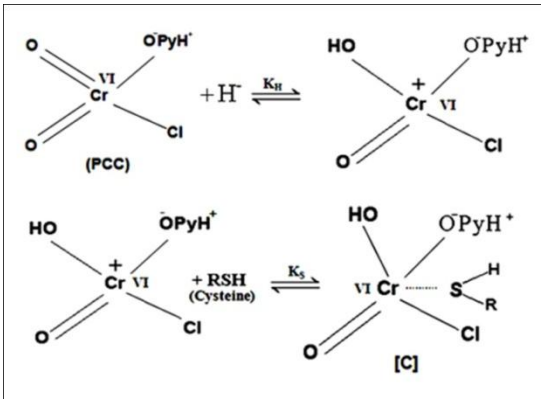
The electron transfer reaction between L-cysteine and PCC has been studied over the range 2.0 $\leq 10^{-3}$ $[\text{cysteine}]_T \leq 6.0$, 0.01 $\leq [H^+] \leq$ 0.2, 298 K $\leq$ T $\leq$ 318K and I = 0.3 mol $dm^{-3}$ ($NaClO_4$)

The UV-Vis spectral scan of the reaction mixture of L-cysteine and PCC are displayed (Fig.1.a) over the range 200$\leq \lambda$ (nm) 600. The shifting of absorption maxima from 350 nm to 425 nm indicates the formation of an intermediate species between cysteine and PCC. The said intermediate was found to decay with increasing time. After a long interval (approximately 24 hrs) the peak at 425 nm vanished completely and two new peaks appeared (Fig. 1.b) at 410 nm and 566 nm which corresponded to the spectrum of $Cr(H_2O)_6^{3+}$ [12].

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

**Mechanism:**

Scheme – I




$$[C] \xrightarrow[\text{Slow}]{k_1} \text{Cr(V)} + R - S^{\cdot} + H^+$$

$$[C] \xrightarrow[\text{Slow}]{k_2} \text{Cr(V)} + R - S^{\cdot} + 2H^+$$

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

$$2\text{Cr (V)} + 2\text{RS}. \xrightarrow{\text{fast}} 2\text{Cr (IV)} + \text{R - S - S - R}$$

$$\text{Cr (VI)} + \text{Cr (IV)} \xrightarrow{\text{fast}} 2\text{ Cr (V)}$$

$$\text{Cr (V)} + 2\text{RSH} \xrightarrow{\text{fast}} \text{Cr (III)} + R–S–S–R + 2H^+$$

Cr (III) is the Cr $(H_2O)_6^{3+}$ species in aqueous acidic medium.

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

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

The reaction is showing approximately first order dependence on [RSH]. At relatively higher $[H^+]$, $K_H$ $[H^+]$ >> 1 and $K_S$ [RSH] >> 1 at finite $[H^+]$ concentration , the equation (3) is reduced to equation(4)

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

The values of $k_1$ and $k_2$ can be computed from plots of $k_{obs}$ / [RSH] vs $[H^+]^2$ and are listed in Table 5 from which activation parameters are calculated as

$\Delta H^{\neq}$ =30.25±0.25, 29.60±0.62 kJ $mol^{-1}$and $\Delta S^{\neq}$ = -159.66±0.83 , 127.09±2.17 $JK^{-1}$ $mol^{-1}$ for $k_1$ and $k_2$ paths respectively. The values of activation parameters appear to be more or less compatible with the mechanism proposed.[13, 14]

**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 coworkers[15] have indicated that the surface of the protein is similar to a micellar surface. Thus the study of such reactions in a micellar medium is thought to throw more light on the details of electron transfer reaction in the biological systems. Many researchers[16-21]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 at varying [SDS] = 0.01 to 0.07 mol $dm^{-3}$ in temperature range of 303 K ≤ T ≤318 K. The rate data are collected and are displayed in Fig.2. The curve shows increase of rate with increase of SDS beyond its CMC [CMC of SDS = 0.007 mol $dm^{-3}$][22] and reaches a maxima at [SDS] = 0.03 mol $dm^{-3}$. The rate of reaction decreases when [SDS] goes above 0.03 mol $dm^{-3}$.Similar phenomena are observed at four different temperatures in the range 303 K to 318 K.

The variation of 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- II[23].

$$\begin{array}{ccc} [Cr(VI]_w + [D_n] & \xrightarrow{K_{SB}} & [Cr(VI]_m \\ + & & + \\ [RSH]_w & & [RSH]_m \\ \downarrow k_w & \text{product} & k_2^m \uparrow \end{array}$$

Scheme –II

The observed 1st order rate constant of overall reaction in micellar medium is given by equation (7).

Rate = $k_{obs}$ [Substrate]

$$k_{obs} = \frac{k_w[O]_w + k_2^m K_{SB}[D_n][O]_m}{1+K_{SB}[D_n]} \quad (7)$$

Where is the second order rate constant in micellar pseudo- phase which is defined in terms of the local molarity of oxidant.

$[O]_m$ ⟶ Concentration of oxidant in micellar medium.

$k_w$ ⟶ Second order rate constant in aqueous phase.

$K_{SB}$ ⟶ Substrate binding constant.

$$k_{SB} = \frac{[S_m]}{[S_w][D_n]}$$

where $[D_n] = [D_T] - CMC$

$[D_n]$ ⟶ micellarized surfactant.

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

$$K_{SB}[D_n] << 1$$

The equation (7) becomes equation (8)

$$k_{obs} = k_w + k_2^m K_{SB}[D_n] \quad (8)$$

This equation shows the linear dependence of rate constants with an increase of surfactant. This explains the increased part of the curve in

Fig. 6.

By assuming the rate in micellar pseudo-phase is zero i.e. $k_2^m = 0$ equation (7) is reduced to equation (9).

$$k_{obs} = \frac{[k_w]}{1+K_{SB}[D_n]} \quad (9)$$

The above equation explains the decrease of rate with an increase of the surfactant at [surfactant] > 0.03 mol $dm^{-3}$. Similar micellar effect has been reported by Bunton[24,25] and Richardson[26] for the oxidation of organic sulphides with periodates, 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 to concentrate on the micellar surface which assists speeding up of the reaction. After reaching the maximum value, rate decreases probably because the concentration of substrate available in the aqueous phase is small so small that the rate falls with with increase in SDS.

**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 TritonX -100 carried out at 303 K varying [TritonX - 100] = 0.01 to 0.08 mol $dm^{-3}$ at constant [oxidant] and [substrate]. The rate data are collected and displayed in Fig.3. The marginal retardation effect was observed upto 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) from a sulphur containing amino acid, cysteine [RSH], follow 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 (cystine) (R-S-S-R) in the reaction. The organic disulphide product cystine 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) species and cysteine, it is probably outer sphere electron transfer process.

[3] The kinetics of the PCC – RSH reaction in acid medium is found to be strongly catalysed by SDS upto $[SDS]_0 \approx 3x10^{-2}$ mol $dm^{-3}$, beyond which there is progressive retardation in the oxidation rate with increasing $[SDS]_0$. This may be due to the medium effect caused by the presence of high dielectric SDS.

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

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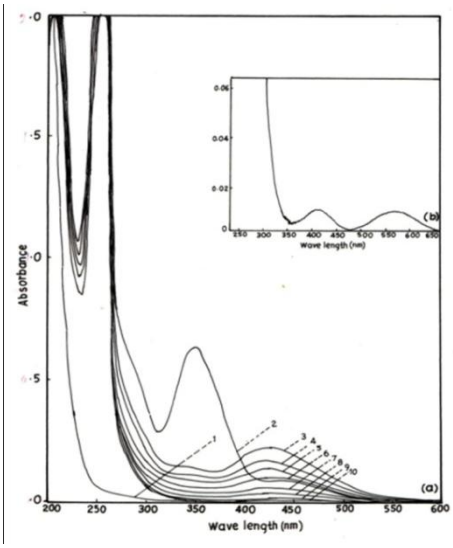


Fig. 1. a) UV"Vis spectral scan of reaction mixture of L-cysteine and PCC in $HClO_4$ media [cysteine] = 4 x $10^{-3}$ mol $dm^{-3}$(1), [PCC] = 4 x$10^{-4}$ mol dm-$^{3}$(2), [ $H^+$] = 0.1 mol $dm^{-3}$, I = 0.3 mol $dm^{-3}$ ($NaClO_4$), immediate after mixing (3). After 15 minutes $\Delta$ t = 5 minutes (curves 5-9).After 2 hours (10)

b) Inset : Spectra after 24 hrs, 303 K.

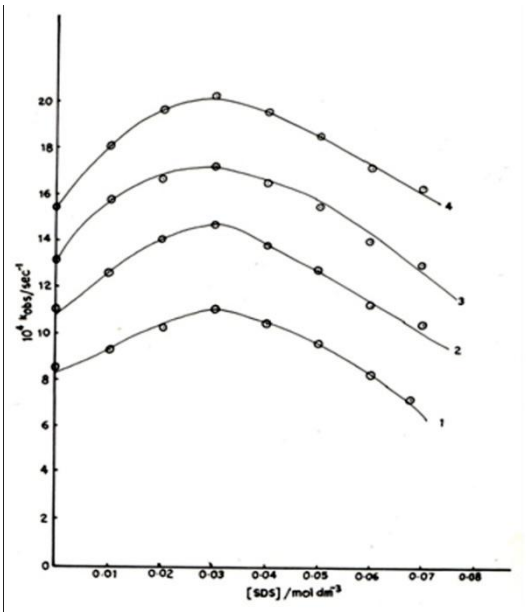


Fig 2 . Plots of $k_{obs}$/ $s^{-1}$ versus [SDS]/ mol $dm^{-3}$ at different temperatures 303 K (1), 308 K (2), 313 K (3) , 318 K (4) [PCC] = 5 x $10^{-4}$ mol $dm^{-3}$, [cysteine] = 4 x $10^{3}$ mol $dm^{-3}$,[$H^+$] = 0.05 mol $dm^{-3}$

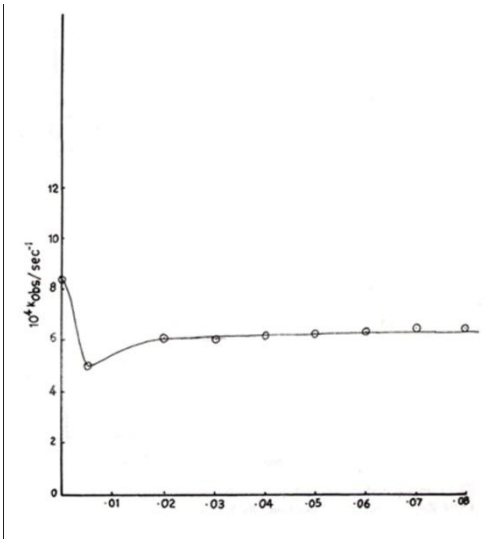

Fig 3. Plot of $k_{obs}$ versus [Triton X-100] [PCC]= 5x$10^{-4}$ mol $dm^{-3}$, [cysteine] = 4 x $10^{-3}$ mol $dm^{-3}$ [$H^+$]=0.05 mol $dm^{-3}$ at 303K