Journal of the Korean Chemical Society
2013, *Vol. 57, No. 4*
Printed in the Republic of Korea
http://dx.doi.org/10.5012/jkcs.2013.57.4.425

Rate Enhancement by Micelle Encapsulation for Oxidation of L-Glutamic Acid in Aqueous Media at Room Temperature

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(Received January 14, 2013; Accepted June 26, 2013)

ABSTRACT. Oxidation of glutamic acid is performed in aqueous acid media at 30 °C under the kinetic condition $[\text{glutamic acid}]_T >> [Cr(VI)]_T$. Effect of combination of micellar catalyst (SDS, TX-100) and promoter (PA, bpy, phen) has been studied. Among the promoters phen accelerates the reaction most in aqueous media. But the rate acceleration is small in the case. Combination of promoter and catalyst produces much better result. Maximum rate enhancement occurs in presence of the combination of bpy and SDS.

Key words: Oxidation, Micelle, Catalyst, Promoter

INTRODUCTION

The oxidation of biologically important amino acid is very important because it may reveal the mechanism of amino acid metabolism. Amino acids are oxidized by variety of oxidizing reagent under different experimental conditions.[1–2] Chromate is a very strong oxidizing agent in acidic media. Oxidation of methionine, cysteine by Cr(VI) is reported.[3–4] Present work deals with the oxidation of glutamic acid by Cr(VI) in acidic media. Glutamic acid is one of the most essential amino acid. It is required for a variety of body function. Glutamate is a key molecule in cellular metabolism and it is an important intermediate in citric acid cycle.[3] It also acts as an excitatory neurotransmitter in central nervous system[4,5] and used for detoxification of ammonia from brain.[6] In this work chromic acid oxidizes glutamic acid to succinic semi aldehyde. Chromic acid is chosen as the oxidant because the other Cr(VI) containing oxidizing agent like PCC, PDC etc. dissolves in chloroform, dichloromethane, acetone etc. But these solvents are not environmental friendly. Thus the toxic effects of organic solvents are avoided. Again by this oxidation toxic Cr(VI) is reduced to non toxic Cr(III).[7–9] But the rate of the reaction is extremely slow in aqueous media. Here surfactants are used to increase the rate of the reaction. The catalytic behavior of surfactant is well known.[7–15] They dissolve in water at very low concentration but above a certain concentration they forms micelle. After the formation of micelle the reactant is partitioned between the micellar phase and aqueous phase. When the effective concentration of the reactant is greater in the small micellar core than the bulk then rate enhancement occurs. Rate of a slow reaction can also be accelerated by the use of promoter. Among the different chelating agents, picolinic acid (PA), 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy) are widely used as promoter for Cr(VI) oxidation of various substrates.[6,10–18] They are not co-oxidised with the substrate rather they form Cr(III)-promoter complex at the end of the promoted reaction. In this case glutamic acid is oxidized to succinic semialdehyde.

EXPERIMENTAL

Material and Reagents

L-glutamic acid (HIMEDIA), Picolinic acid (AR, BDH), 1,10-phenanthroline (AR, Spectrochem, India), $K_2Cr_2O_7$ (AR, BDH), sodium dodecyl sulphate (AR, SRL), TX-100 (AR, SRL) and all other chemicals used were of highest purity available commercially. Solutions were prepared in doubly distilled water.

Kinetics and Measurements

The oxidation reaction of L-glutamic acid to succinic semialdehyde is initiated by mixing requisite amount oxidant to the reaction mixture. Under the kinetic condition $[\text{glutamic acid}]_T >> [Cr(VI)]_T$ and at 30°C the reaction follows pseudo first order kinetics. Progress of the reaction is monitored spectrophotometrically by measuring the absorbance of Cr(VI) at different time interval at 450 nm. Pseudo first order rate constants (k_{obs}) are determined from the slope of linear plot (*Figs*. 1 and 2) of $\ln(A_{450})$ vs time (t). From the magnitude of k_{obs}, the half lives of the reactions

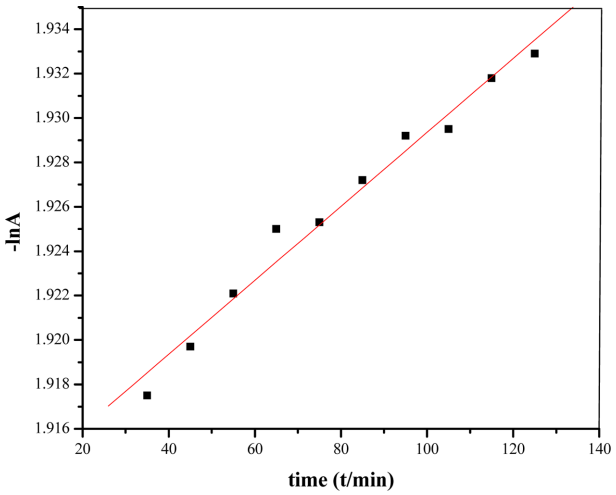


***Figure* 1.** Plot of –lnA vs time (t) for unpromoted and uncatalysed reaction $[\text{L-glutamic acid}]_T = 75 \times 10^{-4}$ mol dm^{-3}, $[Cr(VI)]_T = 5 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, Temp = 30 °C.

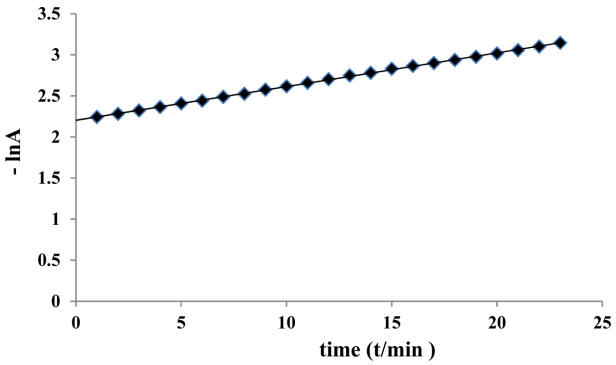


***Figure* 2.** Plot of –ln A vs time (t) in presence of the combination of promoter PA and surfactant TX-100. $[\text{L-glutamic acid}]_T = 75 \times 10^{-4}$ mol dm^{-3}, $[Cr(VI)]_T = 5 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[PA]_T = 150 \times 10^{-4}$ mol dm^{-3}, $[TX\text{-}100]_T = 3 \times 10^{-2}$ mol dm^{-3}, Temp = 30 °C.

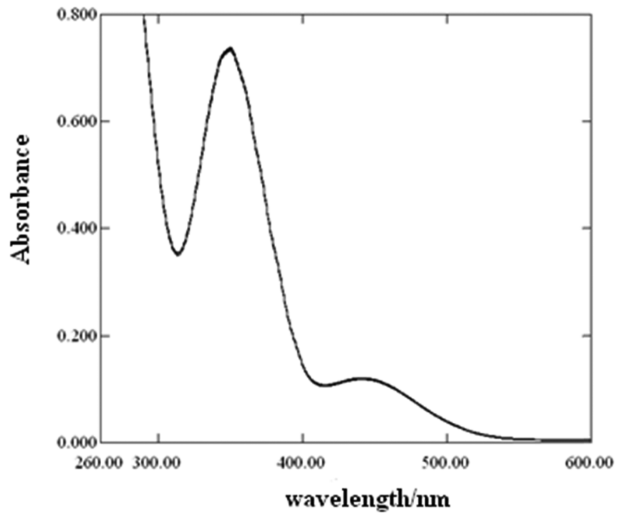


***Figure* 3.** Scanned absorption spectra of the reaction in absence of promoter at regular time interval (20 min). $[\text{L-glutamic acid}]_T = 75 \times 10^{-4}$ mol dm^{-3}, $[Cr(VI)]_T = 5 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, Temp = 30 °C.

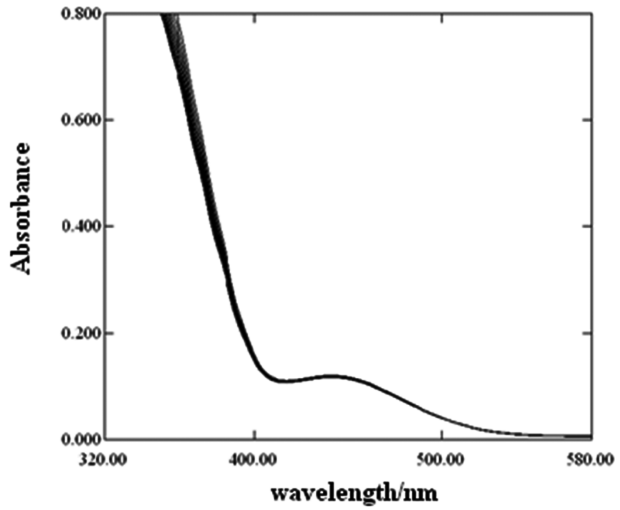


***Figure* 4.** Scanned absorption spectra of the reaction mixture at regular time interval (3 min). $[\text{L-glutamic acid}]_T = 75 \times 10^{-4}$ mol dm^{-3}, $[Cr(VI)]_T = 5 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[bpy]_T = 125 \times 10^{-4}$ mol dm^{-3}, Temp = 30 °C.

are determined.

In case of unpromoted reaction in aqueous medium the scanned spectra (*Fig*. 3) indicates the gradual disappearance of Cr(VI). But the rate of disappearance is very slow as is seen from *Fig*. 3. In case of promoted reaction also no significant rate change occurs. *Fig*. 4 shows the scanned spectra of bpy promoted reaction in aqueous media. In micellar media rate is greater. The surfactants SDS produces better result (*Fig*. 5). But in presence of the combination of promoter and catalyst much greater rate is obtained and sharp isobestic points are seen in the scanned spectra. In presence of the combination of bpy and TX-100 isobestic point appears at $\lambda = 517$ nm (*Fig*. 6) and for phen and SDS isobestic point is at $\lambda = 519$ nm (*Fig*. 7). Single isobestic point indicates that Cr(IV) and Cr(V) intermediates are formed in very small amount under the experimental condition. For unpromoted reaction the colour of the solution after completion of reaction is pale blue ($\lambda_{max} = 580$ nm, and 436 nm) (*Fig*. 8) and the corresponding transition are 580 nm for $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and 436 nm for $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ of Cr(III) species. The spectrum of this solution is identical with the chromic sulphate solution in sulphuric acid media. In case of promoted reaction colour of the final solution is pale violet. The spectrum of this solution is slightly different from the unpromoted

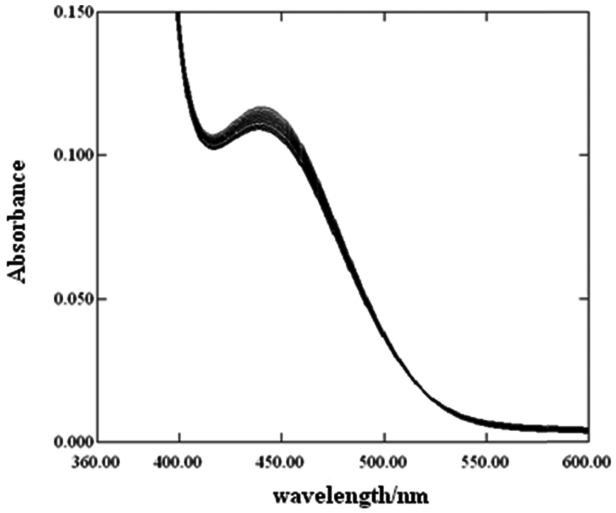


***Figure* 5.** Scanned absorption spectra of the reaction mixture at regular time interval (5 min). [L-glutamic acid]$_T$ = 75 × 10^{-4} mol dm^{-3}, [Cr(VI)]$_T$ = 5 × 10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5 mol dm^{-3}, [TX-100]$_T$ = 3 × 10^{-2} mol dm^{-3}, Temp = 30 °C.

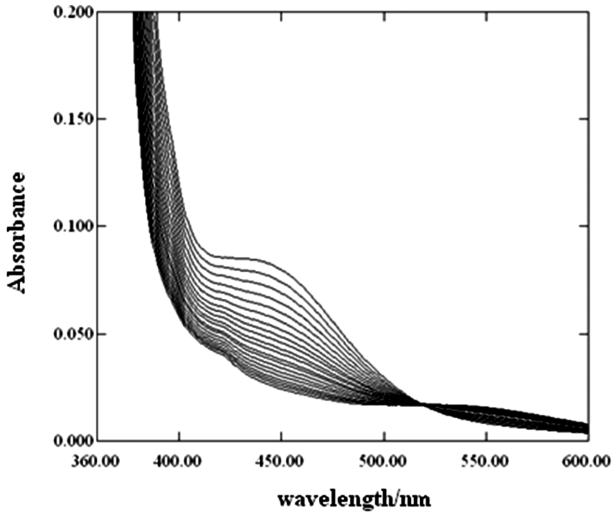


***Figure* 7.** Scanned absorption spectra of the reaction mixture at regular time interval (5 min). [propan-2-ol]$_T$ = 75 × 10^{-4} mol dm^{-3}, [Cr(VI)]$_T$ = 5 × 10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5 mol dm^{-3}, [SDS]$_T$ = 4 × 10^{-2} mol dm^{-3}, [Phen]$_T$ = 75 × 10^{-4} mol dm^{-3}, Temp = 30 °C.

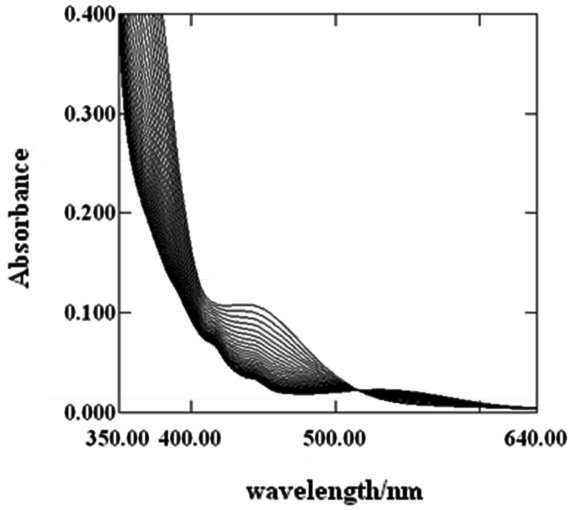


***Figure* 6.** Scanned absorption spectra of the reaction mixture at regular time interval (5 min). [L-glutamic acid]$_T$ = 75 × 10^{-4} mol dm^{-3}, [Cr(VI)]$_T$ = 5 × 10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5 mol dm^{-3}, [TX-100]$_T$ = 3 × 10^{-2} mol dm^{-3}, [bpy]$_T$ = 125 × 10^{-4} mol dm^{-3}, Temp = 30 °C.

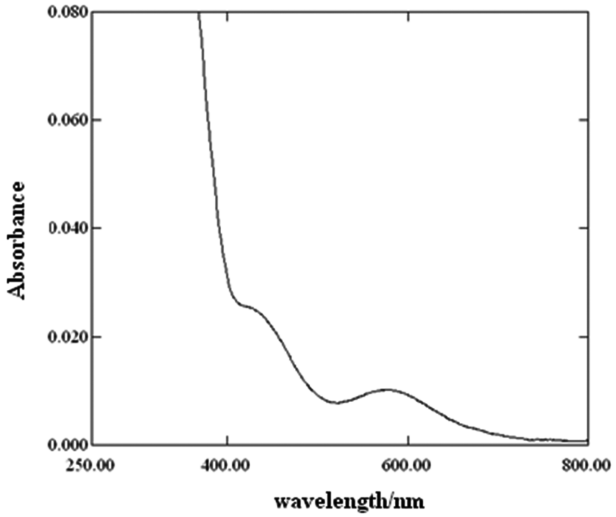


***Figure* 8.** Absorption spectrum of unpromoted reaction mixture (after completion of reaction): [L-glutamic acid]$_T$ = 75 × 10^{-4} mol dm^{-3}, [Cr(VI)]$_T$ = 5 × 10^{-4} mol dm^{-3}, [H_2SO_4] = 0.5 mol dm^{-3}, Temp = 30 °C.

reaction because here Cr(III)-promoter complex is formed. In the overnight spectrum (*Fig*. 9) of bpy catalysed reaction a blue shift is seen for $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition. This is due to the presence of strong field ligand bpy. The same is true for other two promoters also (*Fig*. 9). Both for unpromoted and promoted reaction a charge transfer band appears. But for promoted reaction charge transfer band appears at much lower energy due to favored metal to ligand charge transfer. Vacant π^* orbitals of promoters favour metal to ligand charge transfer.

Test for Free Radicals

To test for free radical, the reaction mixture containing stabilizer free acrylonitrile was kept for 24 h in an inert atmosphere. On diluting the reaction mixture by methanol and no precipitate was observed. It indicates that no free radicals are formed during the reaction.

PRODUCT ANALYSIS

Stoichiometry

Under the experimental condition the stoichiometry of

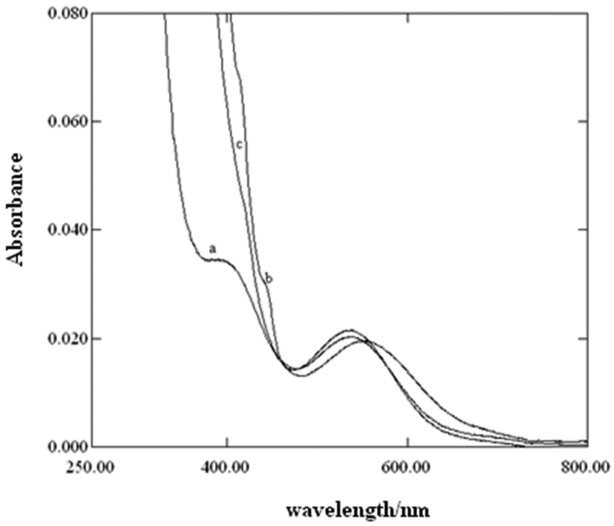


***Figure* 9.** Absorption spectrum of promoted reaction mixtures (after completion of reaction): $[\text{L-glutamic acid}]_T = 75 \times 10^{-4}$ mol dm^{-3}, $[Cr(VI)]_T = 5 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, (a) $[PA]_T = 150 \times 10^{-4}$ mol dm^{-3}, (b) $[bpy]_T = 125 \times 10^{-4}$ mol dm^{-3}, (c) $[phen]_T = 75 \times 10^{-4}$ mol dm^{-3}, Temp = 30 °C.

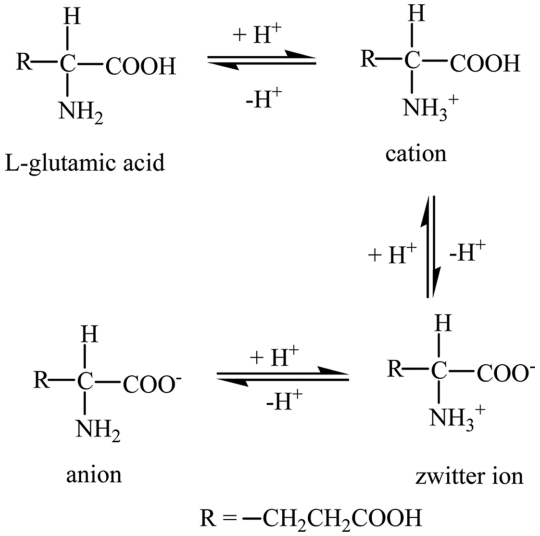
the reaction may be formulated as:

$$2Cr(VI) + 3COOHCH_2CH_2CH(NH_2)COOH + 3H_2O \rightarrow 3COOHCH_2CH_2CHO + 3CO_2 + 3NH_4^+ + 2Cr(III) + 3H^+$$

Under the kinetic condition glutamic acid is oxidized to succinic semialdehyde and estimation of the reaction products was carried by gravimetrically as 2,4-dinitrophenyl hydrazone. In a typical experimental set, 10 ml of 0.06 mol dm^{-3} Cr(VI) in 1.0 mol dm^{-3} H_2SO_4 was added to 40 ml of 0.2 mol dm^{-3} glutamic acid and the reaction was allowed to proceed to completion. Then the reaction mixture was added slowly with stirring to 60 ml of a saturated solution of 2,4-dinitrophenyl hydrazine in 2.0 mol dm^{-3} HCl. After storing for about 1 h in an ice-bath, the precipitate was collected weighed sintered glass crucible, washed with 2.0 mol dm^{-3} HCl followed by water and dried to a constant weight at 100–105 °C. The hydrazone shows the melting point 200 °C.[27] Glutamic acid is also detected by chrotographic method.[28] Nesseler's reagent and lime water test were used to detect ammonium ion and carbon dioxide respectively.[29]

RESULT AND DISCUSSION

Glutamic acid is an acidic amino acid. Again under the present experimental condition ($[H^+] = 0.5$ mol dm^{-3}) the concentration of the anion form of it is very low. The possible species may be either cation form of glutamic acid or zwitter ion and protonated Cr(VI) is assumed to be the reactive oxidant. An amino acid is known to exist in the following equilbria

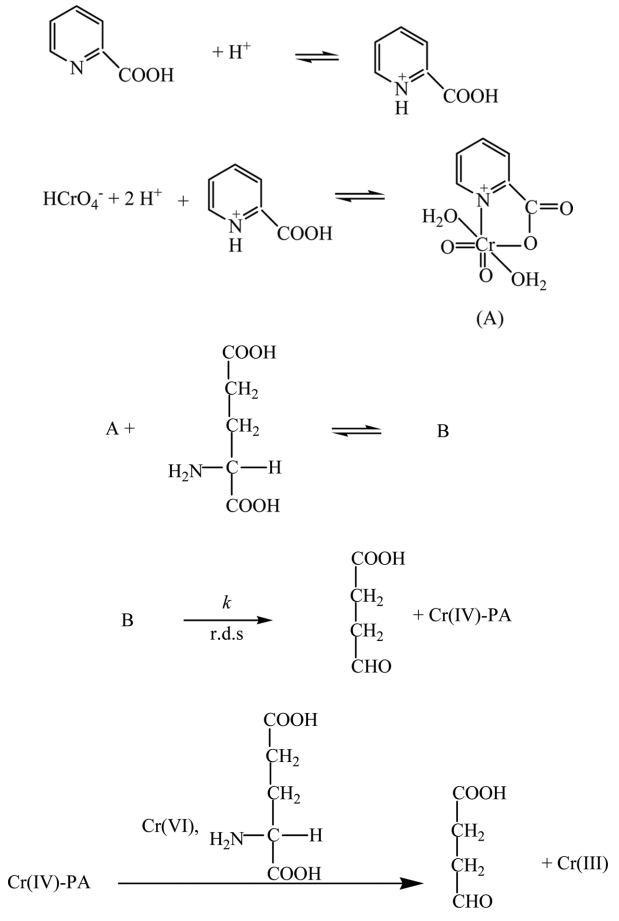


From *Table* 1 it is seen that the oxidation of glutamic acid by Cr(VI) is very sluggish. Rate is slightly increased upon the addition of the promoters (PA, bpy, phen) in aqueous media. In micellar media (SDS) the rate is comparatively greater even for unpromoted reaction also. For unpromoted reaction SDS catalyses the reaction by the usual way of micellar catalysis. But in case of the promoted reactions active oxidants like Cr(VI)-PA, Cr(VI)-bpy and Cr(VI)-phen are produced. L-glutamic acid forms ternary complex with these active oxidants (*Scheme* 1, 2, 3) This complex undergoes redox decomposition in the rate limiting step. In micellar media the rate of the promoted reaction is much greater. To observe the kinetic data in presence of micellar catalyst the applicability of the pseudo phase kinetic model proposed by Menger and Portnoy[30] must be taken into consideration. Partitioning of L-glutamic acid is equally probable in both types of surfactants (*Fig*. 10). But the portioning of H^+ is maximum in SDS medium due to electrostatic interaction. All the active oxidants are positively charged species so they are attracted towards the negative head groups of anionic surfactant SDS. The probability of collision of the substrate with the active oxidant molecules is greater in anionic SDS micelle. SDS will allow Cr(VI)-bpy into her core compare to Cr(VI)-PA and Cr(VI)-phen considering electrostatic and steric factor (*Fig*. 11).[31] For this reason combination of bpy and SDS produce maximum rate enhancement.

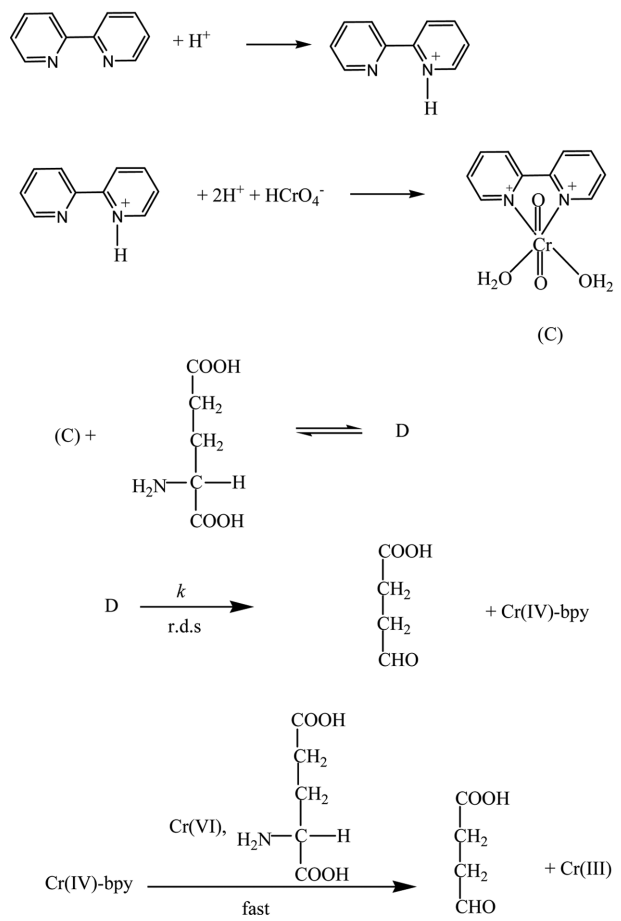
***Table* 1.** k_{obs} and half life of the reaction in absence and presence of promoters and non functional micellar catalyst

Promoter [mol dm^{-3}]		Micellar catalysat [mol dm^{-3}]		$10^4 \times k_{obs}$ (sec^{-1})	$t_{1/2}$ (h)
None		None		0.029	66.38
PA	0.015	None		0.0341	56.45
bpy	0.0125	None		0.0383	50.26
phen	0.0075	None		0.0548	35.13
None		SDS	0.04	0.225	8.56
PA	0.015	TX-100	0.03	6.83	0.28
PA	0.015	SDS	0.04	2.67	0.72
Phen	0.0075	TX-100	0.03	7.91	0.24
Phen	0.0075	SDS	0.04	7.15	0.27
bpy	0.0125	TX-100	0.03	12	0.16
bpy	0.0125	SDS	0.03	160.42	0.012

$[Cr(VI)]_T = 5 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4]_T = 0.5$ mol dm^{-3}, [L-glutamic acid] $= 75 \times 10^{-4}$ mol dm^{-3}, Temp. = 30 °C.



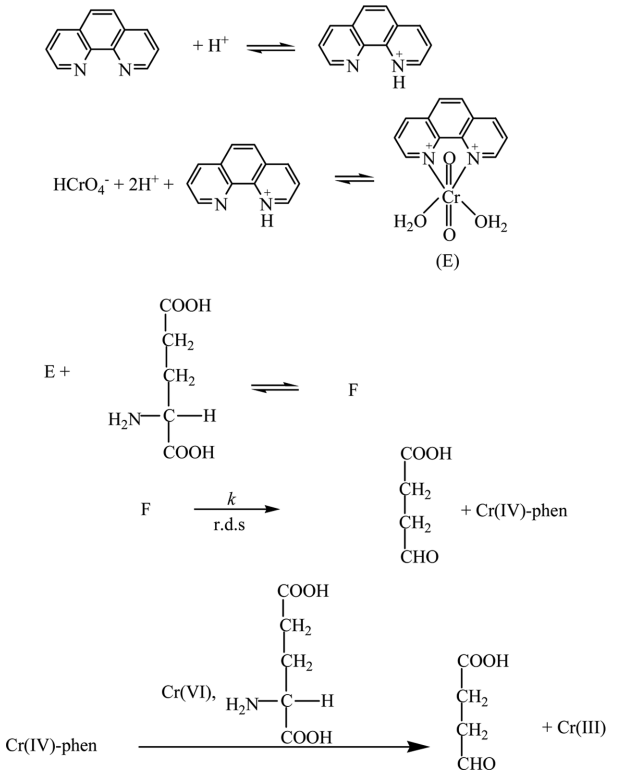
***Scheme* 1.** Steps for PA promoted Cr(VI) oxidation of L-glutamic acid in aqueous acid media.



***Scheme* 2.** Steps for bpy promoted Cr(VI) oxidation of L-glutamic acid in aqueous acid media.

MECHANISM AND INTERPRETATION

In the promoted reaction path of glutamic acid oxidation by Cr(VI) the formation of the Cr(III)-promoter complexes characterized by UV spectrophotometer indicates that the ligands (PA, bipy and phen) used here undergo complexation with the highest oxidation states of chromium, i.e. Cr(VI) (labile, t_{2g}^0, e_g^0). Based on this explanation, it is believed that the Cr(VI)-promoter complexes



***Scheme* 3.** Steps for phen promoted Cr(VI) oxidation of L-glutamic acid in aqueous acid media.

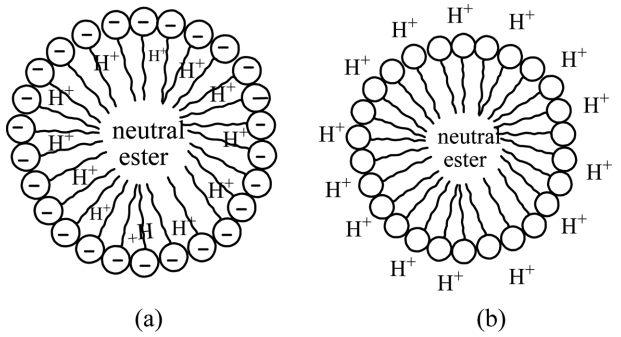


***Figure* 10.** Schematic representation of partitioning of neutral ester and proton in (a) Anionic surfactant (b) Neutral surfactant.

produced in the pre-equilibrium step are the active oxidants (mentioned as AO^+ in *Scheme* 1, 2 and 3). The observed rate is zero order with respect to hydrogen ion in PA promoted path. On the other hand the rate is first order with respect to hydrogen ion in bipy and phen promoted path respectively. The mechanism of the promoted reaction path for the three different promoters is shown below:

At the initial step all the promoters (PA, bpy, phen) are protonated under the experimental condition. These protonated species then combines with chromate ion to form the active oxidant A for PA (*Scheme* 1), C for bpy (*Scheme* 2), E for phen (*Scheme* 3) respectively. The active oxidants then form intermediate complexes B (in PA promoted path), D (in bpy promoted path), E (in phen promoted path) with the substrate glutamic acid for each of the promoted reaction path. This complex gives the final product succinic semi aldehyde and Cr(IV) in the rate determining step. Cr(IV) is converted to Cr(III) through different possible routes.[32,33]

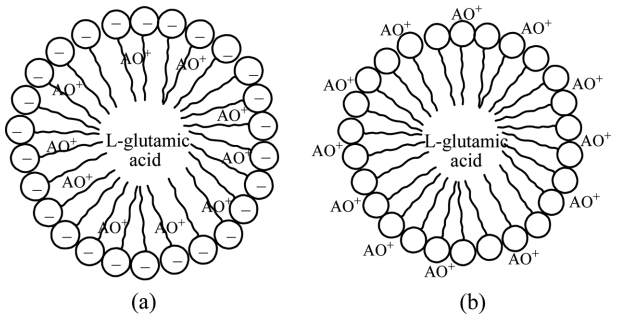


***Figure* 11.** Schematic representation of partitioning of substrate and active oxidant [AO^+= Cr(VI)-Promoter complex] in (a) Anionic surfactant (b) Neutral surfactant.

CONCLUSION

From the kinetic observation for the micellar effect on the oxidation of L-glutamic acid to succinic semialdehyde in presence of promoter it is found that the very sluggish oxidation of this amino acid can be performed within very short period of time by the use of the combination of bpy and SDS.

Acknowledgments. Thanks to CSIR, New Delhi for providing financial helps in the form of project (K. Mukherjee). And the publication cost of this paper was supported by the Korean Chemical Society. And the publication cost of this paper was supported by the Korean Chemical Society.

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