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Kinetic study on induced electron transfer reaction of pentaamine cobalt (III) complexes of α-amino acids by 2, 2'- bipyridinium bromo chromate (BPBC) in the presence of surfactant medium

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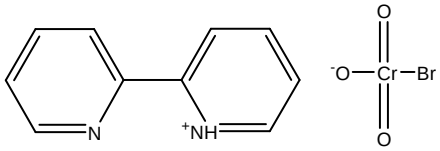
ABSTRACT

The kinetics mechanistic studied of BPBC with Cobalt (III) bound and unbound complexes of α-amino acid in micellar medium at 300 K in 50% acetic acid – 50 % water. In this reaction the rate of oxidation shows pseudo first order kinetics each in Cobalt (III) and BPBC. It rules out the synchronous C-C bond fission and N-H bond fission. With increasing micelles concentration an increase in the rate is observed. Oxidation of Cobalt (III) complexes increases with increase in temperature. The added CTAB enhances the rate of oxidation of a reaction much more than NaLS. The kinetic and stoichiometric results have been accounted by a suitable mechanism.

Key words: α –amino acids, 2, 2'–bipyridinium Bromochromate, Sodium lauryl sulphate, Cetyl trimethyl ammonium bromide, TRITON-X 100.

INTRODUCTION

Studies on the chemistry of the electron transfer reaction of cobalt (III) complexes have received a sustained high level of attention from the scientific community for decades, due to their relevance in various redox processes in biological systems, and act as a promising agent for antitumor[1], anthelmintic[2], antiparasitic[3], antibiotivs[4] and antimicrobial activities[5].Chromium (VI) reagents have been widely used in organic chemistry for the oxidation of primary and secondary alcohols to carbonyl compounds.Pyridine chromium trioxide complexes and pyridinium bromo chromate have been especially useful reagents for the mild oxidation of primary alcohols to aldehydes. There are, however, some significant difficulties associated with the reagents. For instance, chromium containing by-products often contaminate the desired products, requiring time consuming purifications. A novel compound 2, 2'-bipyridinium chlorochromate, 2, 2'-bipyridinium bromo chromate has been discovered which is useful as an oxidizing agent. The compound is especially useful as an oxidizing agent in reactions which require relatively mild oxidizing conditions, such as the conversion of primary or secondary alcohols to carbonyl compounds**.** Evolution60 thermo spectrophotometer has been utilize to study the oxidation of α-amino acids and their Cobalt (III) Complexes using Pyridinium dichromate[8] as an oxidant in the presence of surfactant. Surfactants are often used in the formulations of pesticides and herbicides[9]. They have also found a wide range of applications because of their unique solution properties such as detergency, solubilisation, and surface wetting capabilities in diverse areas such as chemical as well as biochemical research[10]. Surface active materials are major building blocks of many physical, chemical, anti-biological systems. They have been introduced into several commercial products such as antiseptic agents in cosmetics and as germicides[11], and have also found a wide range of applications in diverse areas such as mining, petroleum, and pharmaceutical industries.2,2'- bipyridinium Bromochromate ($CrO_2BrOby PyH$) BPBC structure given below



MATERIALS AND METHODS

Preparation of 2, 2'-bipyridinium Bromochromate: 2, 2´-Bipyridine (A.R. Qualigens, India), HBr, chromium trioxide from (SD Fine chemicals. India 95%) Preparation of BPBC to 16.75 ml of 6 M hydrobromic acid (0.11mole) is added 10.0 g. (0.11 mole) of chromium trioxide rapidly while stirring. After dissolution of the chromium trioxide is complete, 15.6 g. (0.1 mole) of 2, 2'-bipyridine is added in portions while stirring vigorously. A yellow slurry results which is stirred for 1 hour at room temperature. The slurry is then collected on a sintered glass funnel and washed with two 15 ml portions of cold distilled water. The resulting solid yellow filter cake is dried for 3 hours in vacuum at room temperature. The resulting product is 2, 2'-bipyridinium bromochromate, its purity was checked by an iodometric method and is obtained in a typical yield of 26.8 g. which is 92% of the theoretical yield.

Preparation of Cobalt (III) complexes carbonato Pentaamminecobalt (III) nitrate: A solution of 300 gm of Cobalt (III) nitrate hexahydrate (1.03mol) in 500 ml of water was thoroughly mixed with a solution of 450 gm of ammonium carbonate (4.68mol) in 450 ml of water and 750 ml of conc.aqueous ammonia (sp.gr.0.90, 28% NH_3).A stream of air bubbled slowly through the mixture for 24 hours. After the mixture has been cooled in ice-salt bath overnight, the product was collected on filter, washed with not more than 50 ml of ice-cold water, followed by alcohol and ether and dried at 50°C [yield 180gm (64%)]. This crude material was purified by re-crystallization from water. The 180 g of solid was dissolved with stirring in 550 ml of water at 90°C. The solution was filtered and the filtrate was cooled in ice-bath. The crystals were collected, washed with 50 ml of ice-cold water, followed by alcohol and ether and dried at 50°C.

Pentaamminecobalt (III) complexes of α-amino acids: 10 mmol of the acid and 5 mmol of LiOH or NaOH were added to 20 ml of absolute methanol and to the mixture was added 400 mg of finely round carbonatopentaammine cobalt (III) nitrate. The mixture was refluxed for 2 h with frequent shaking. The preparation was cooled. to under ice and 1ml of conc. $HClO_4$ was added after which the preparation was kept at 0°C for an additional 30 min.The precipitate, if any was filtered off and washed with ether. The mother liquor was shaken with 150ml of ether-Acetyl and N-Benzoyl glycine were prepared by following the procedure of Vogel[12].The $(NH_3)_5Co$ (III) complexes Glycine, Alanine, Isoleucine, N-Acetyl and N -Benzoyl glycine were prepared as their perchlorates by the method of Fan and gould[13]. The surfactants used in the present work are sodium lauryl sulphate[8] (NaLS) and cetyl trimethylammonium bromide[9] (CTAB). The surfactants are purified by adopting earlier procedure[14, 15,]

Kinetic measurement

Kinetic measurements of the oxidation of cobalt (III) complexes of alpha-amino acids and unbound ligands were carried out under pseudo first order conditions in 50% acetic acid 50% water at 27 ± 2°C by following the concentration of BPCC at 365 nm with the help of an UV visible spectrophotometer. The total volume of reaction mixture in the spectrophotometric cell was kept as 2.5 ml in each kinetic run all the solutions for the experiments were maintained at the specified temperature in an electrically operated thermo stated bath. Perchloric acid was used as the source of H^+ ions and ionic strength was maintained by $NaClO_4$.

Stoichiometry and product analysis

Stoichiometric studies for the oxidation of pentaammine cobalt (III) complexes of alpha-amino acids and unbound ligands by BPBC were carried out with the oxidant in excess. The $[H^+]$ and ionic strength were maintained as such in the corresponding rate measurements. After ten half-lives when the reaction was nearing 80% completion the concentration of unreacted BPBC was determined spectrophotometrically. The difference in the concentration of the oxidant [BPBC] was measured and then the stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. The amount of cobalt (III) reduced was also calculated from the decrease in the absorbance measured for the Co (III) complex (Table 1). The rate measurements were carried out on 27± 0.2℃ in 100% aqueous medium. The total volume of reaction mixture in the spectrophotometric cell was kept as 2.5ml in each kinetic run. The temperature was controlled by an electrical operated thermostat. It was provided with sufficient thermal lagging, suitable heaters, stirrer and proper cooling arrangements for continuous work. The kinetics of 2, 2-bipyridinium bromo chromate oxidation of alpha amino acid such as Glycine, Alanine,Isoleucine,N-acetyl and N-benzoyl glycine have been studied in 0.1 mol dm^{-3} in miceller medium at 27 ± 0.2°C.The concentration of alpha amino acids was varied in the range (0.5-2.5 x 10^{-2} mol dm^{-3}) at fixed concentration of reaction ingredients. The

plots of log [absorbance] initial versus time were linear indicating a first order dependence of reaction rate on initial α –amino acid. The analytical work gross estimation of BPBC all the rate constants are calculated using total Cr (VI) determined. The reaction are carried out under pseudo first order condition with BPBC in excess with performed in a spectrophotometer. The pseudo-first order rate constants were calculated using integrated rate equations:

$k = 2.303/t \log [a/a-x]$

Where initial concentration of oxidant and (a-x) concentration of oxidant at time t are expressed in sec^{-1}.

RESULTS AND DISCUSSION

The kinetic data for the BPBC oxidation of free α-amino acids with $HClO_4$ in presence of anionic and cationic micelles at 27 ± 0.2℃ (Table-1).The rate of the reaction time increases the absorbance increases linearly (Table-3).The figure -1 shows the time versus log(absorbance) get a straight line $r \geq 0.998$. The reaction exhibits total second order dependence on [Cobalt (II)] as well as [α-amino acids]. Based on the oxidation of BPBC with α-amino acids, the following rate law has been deduced.

Stoichiometric analysis showed that the following overall reaction

$H_3NCH_2COOH + O_2CrBrO^-bPyH^+ + H^+ \rightarrow CH_2 = O + NH_4^+ + CO_2$

The rate equation for this reaction could be deduced as

Rate= k [α-amino acids] [BPBC]

Table.1 Stoichiometric Data for BPBC oxidation of Co (III) unbound α –Amino acids in presence of TRITON at 27 ± 0.2 ºC

10^2[Compound] mol dm^{-3}	$10^2[BPBC]_{Initial}$ mol dm^{-3}	$10^2[BPBC]_{Final}$ mol dm^{-3}	$\Delta 10^2$[BPBC] mol dm^{-3}	[Compound]: Δ[BPBC]
Alanine				
1.0	10.0	9.31	0.69	1.00:0.69
2.0	10.0	8.66	1.34	1.00:0.67
3.0	20.0	17.96	2.04	1.00:0.68
Glycine				
1.0	10.0	9.44	0.66	1.00 : 0.66
2.0	10.0	8.66	1.34	1.00 : 0.67
3.0	20.0	18.05	1.95	1.00 : 0.65
Isoleucine				
1.0	10.0	9.36	0.64	1.00 : 0.64
2.0	10.0	8.74	1.26	1.00 : 0.63
3.0	20.0	18.08	1.92	1.00 : 0.64
N-actylglycine				
1.0	10.0	9.33	0.67	1.00 : 0.67
2.0	10.0	8.70	1.30	1.00 : 0.65
3.0	20.0	18.11	1.89	1.00 : 0.63
N-benzoylglycine				
1.0	10.0	9.37	0.63	1.00 : 0.63
2.0	10.0	8.68	1.32	1.00 : 0.66
3.0	20.0	18.05	1.95	1.00 : 0.65

$[HClO_4]$ = $1.00x10^{-1}$ mol dm^{-3} [TRITON] = $1.00x10^{-2}$ mol dm^{-3} Temperature = 27 ±0.2ºC

The concentration of the substrates,Co(III) complexes of glycolato, alaninato, isoleucinato, N-Acetyl glycinato and N-benzoyl glycinato were varied in the range of 0.5 x 10^{-2} to 2.5 x 10^{-2} mol dm^{-3} at 27±0.2ºC and keeping all other reactant concentrations were constant and the rates were measured (Table-4) The rate constants were calculated by the integrated rate equation. The rate of oxidation increased progressively with increasing the concentration of cobalt (III) complexes of α-amino acids.The rate of the α-amino acids such as N-benzoyl glycine much more than other α-amino acids. The reaction proposes that BPBC oxidizes N-H centre of the cobalt (III) bound α - amino acids at a rate comparable to that of the unbound ligand and there is 99 % reduction at the cobalt (III) centre The kinetic data for the oxidation of the pentaamminecobalt (III) complexes by BPBC in presence of Perchloric acid catalyst and maintained temperature 27±0.2^0C is given in the Table 4. BPBC undergoes a one electron change and the overall reaction between BPBC and the complexes could be written as:

$[NH_3CH_2COO - Co^{III}] + O_2CrBrO^-bPyH^+ \rightarrow H_2C = O + NH_4^+ + Co^{II} + CO_2$

The rate equation for the oxidation could be deduced as:

Rate = k [Co^{III} – Complex] [BPBC]

Table.2 Stoichiometric Data for BPBC oxidation of Co (III) bound α –Amino acids in presence of Triton-X 100 at 27 ± 0.2 ºC

10^2[Compound] mol dm^{-3}	$10^2[BPBC]_{Initial}$ mol dm^{-3}	$10^2[BPBC]_{Final}$ mol dm^{-3}	$\Delta 10^2$[BPBC] mol dm^{-3}	[Compound]: Δ [BPBC]
Co^{III} Alaninato				
1.0	10.0	9.62	0.38	1.00 : 0.38
2.0	10.0	9.30	0.70	1.00 : 0.35
3.0	20.0	18.92	1.08	1.00 : 0.36
Co^{III} Glycinato				
1.0	10.0	9.64	0.36	1.00 : 0.36
2.0	10.0	9.36	0.68	1.00 : 0.34
3.0	20.0	18.05	1.05	1.00 : 0.35
Co^{III} Isoleucinato				
1.0	10.0	9.66	0.37	1.00 : 0.37
2.0	10.0	9.32	0.70	1.00 : 0.35
3.0	20.0	18.98	1.02	1.00 : 0.34
Co^{III} N-acetylglycinato				
1.0	10.0	9.65	0.35	1.00 : 0.35
2.0	10.0	9.28	0.72	1.00 : 0.36
3.0	20.0	18.95	1.05	1.00 : 0.35
Co^{III} N-Benzoylglycinato				
1.0	10.0	9.66	0.34	1.00 : 0.34
2.0	10.0	9.34	0.66	1.00 : 0.33
3.0	20.0	19.04	0.96	1.00 : 0.32

$[HClO_4]$ = $1.00x10^{-1}$ *mol* dm^{-3} [TRITON] = $1.00x10^{-2}$ *mol* dm^{-3} Temperature = 27 ± 0.2ºC

Table.3 Rate data on the oxidation α-amino acids by BPBC at 27±0.2^{0}C

Time(s)	Log(Absorbance)	$10^4 k_1$ (s^{-1})
0	-0.18776	0.00
304	-0.21538	2.093
608	-0.24109	2.020
907	-0.27246	2.151
1204	-0.2993	2.134
1508	-0.32422	2.084
1810	-0.35067	2.073
2106	-0.38405	2.147
2405	-0.41005	2.129
2709	-0.43771	2.125
3009	-0.46597	2.129

[BPBC] = 10^{-3}*mol* dm^{-3}
$[HClO_4]$ = 0.1 *mol* dm^{-3}
Temp = 27 ± 0.2°C
[Substrate] = 1.00 $x10^{-2}$ *mol* dm^{-3}
[NaLS] = $1.00x10^{-2}$ *mol* dm^{-3}

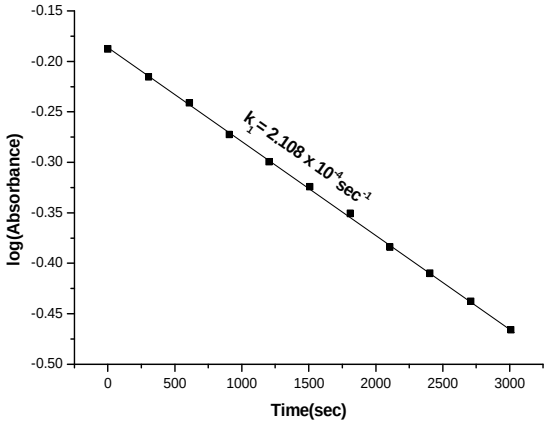


Fig.1. First Order Dependence Plot

Table.4 Rate data on the oxidation α-amino acids unbound BPBC with and without micelles at 27±0.2^{0}C

10^2[α-amino acids] mol dm^{-3}	$10^4k_1(s^{-1})$	NaLS$10^4k_1s^{-1}$	TRITON$10^4k_1s^{-1}$	CTAB $10^4k_1s^{-1}$
Alanine				
0.5	0.688	0.802	1.041	1.193
1.0	1.374	1.603	2.083	2.384
1.5	2.067	2.408	3.128	3.572
2.0	2.758	3.218	4.164	4.770
2.5	3.440	4.020	5.128	5.973
Glycine				
0.5	0.781	1.052	1.205	1.438
1.0	1.566	2.103	2.405	2.874
1.5	2.345	3.158	3.611	4.314
2.0	3.136	4.212	4.812	5.746
2.5	3.918	5.268	6.023	7.198
Isoleucine				
0.5	0.907	1.257	1.457	1.684
1.0	1.815	2.515	2.915	3.365
1.5	2.724	3.771	4.374	5.051
2.0	3.638	5.034	5.838	6.738
2.5	4.543	6.290	7.293	8.410
N-acetyl glycine				
0.5	1.124	1.452	1.713	1.888
1.0	2.245	2.902	3.424	3.776
1.5	3.374	4.359	5.142	5.667
2.0	4.492	5.814	6.846	7.548
2.5	5.618	7.273	8.573	9.433
N-benzoyl glycine				
0.5	1.324	1.857	1.956	2.164
1.0	2.649	3.717	3.915	4.327
1.5	3.971	5.573	5.874	6.489
2.0	5.286	7.434	7.836	8.648
2.5	6.620	9.298	9.793	10.813

[BPBC]=10^{-3}*moldm*$^{-3}$ [$HClO_4$] = 0.1*moldm*$^{-3}$ [Micelles] =1.00x10^{-3}*moldm*$^{-3}$
Substrate = 0.5 to 2.5 x 10^{-2} *mol dm*$^{-3}$ Temperature = 27 ± 0.2^{0}C

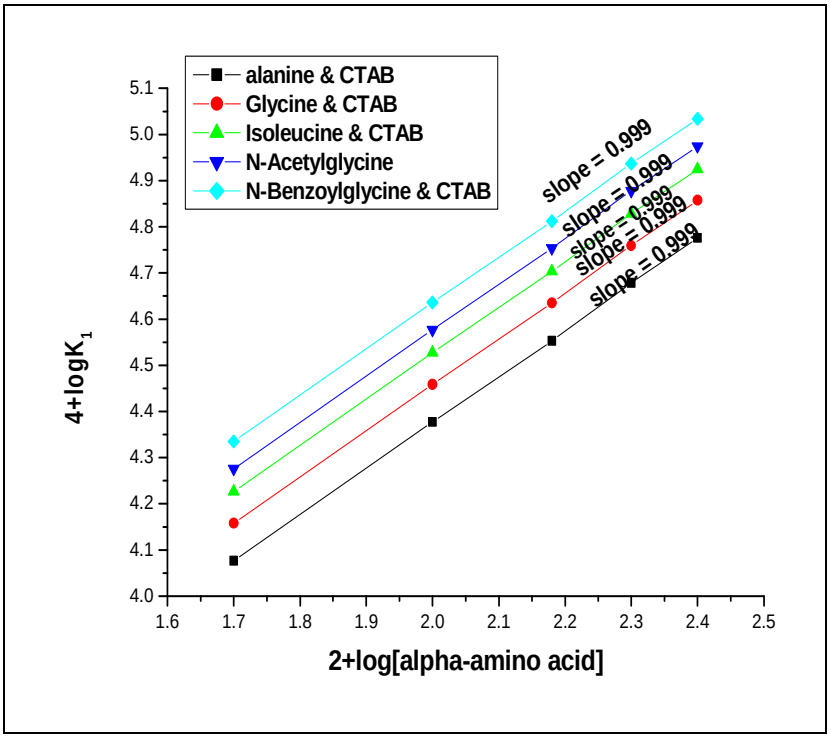


Figure .3. Dependence of rate on α-amino acids with CTAB

Table.4 Kinetic data for the oxidation of Pentaammine Cobalt(III) Complexes of α-amino acids by BPBC with varying Co(III) of α-amino acid concentrations

$10^2[(NH_3)_5Co^{(III)}\text{-}L]$ mol dm^{-3}	$10^4k_1(s^{-1})$	NaLS $10^4k_1s^{-1}$	TRITON $10^4k_1s^{-1}$	CTAB $10^4k_1s^{-1}$
Alaninato				
0.5	0.837	1.156	1.407	1.608
1.0	1.676	2.315	2.816	3.214
1.5	2.150	3.476	4.223	4.826
2.0	3.350	4.632	5.634	6.430
2.5	4.195	5.788	7.045	8.045
Glycinato				
0.5	0.957	1.308	1.652	1.856
1.0	1.916	2.617	3.305	3.716
1.5	2.877	3.923	4.955	5.571
2.0	3.834	5.236	6.612	7.432
2.5	4.788	6.533	8.270	9.295
Isoleucinato				
0.5	1.158	1.560	1.908	2.107
1.0	2.317	3.124	3.816	4.218
1.5	3.473	4.688	5.721	6.326
2.0	4.636	6.254	7.632	8.432
2.5	5.798	7.815	9.543	10.538
N-acetylglycinato				
0.5	1.377	1.806	2.163	2.258
1.0	2.754	3.614	4.324	4.517
1.5	4.137	5.426	6.489	6.777
2.0	5.502	7.230	8.654	9.026
2.5	6.890	9.045	10.820	11.288
N-benzoylglycinato				
0.5	1.584	2.112	2.267	2.471
1.0	3.164	4.225	4.536	4.944
1.5	4.752	6.342	6.806	7.421
2.0	6.330	8.454	9.070	9.892
2.5	7.908	10.565	11.330	12.363

[BPBC] = 10^{-3}moldm^{-3} [$HClO_4$] = 0.1moldm^{-3} [Micelles] =1.00x10^{-3}moldm^{-3} Substrate = 0.5 to 2.5 x 10^{-2} mol dm^{-3} Temperature = 27 ±0.2^{0}C

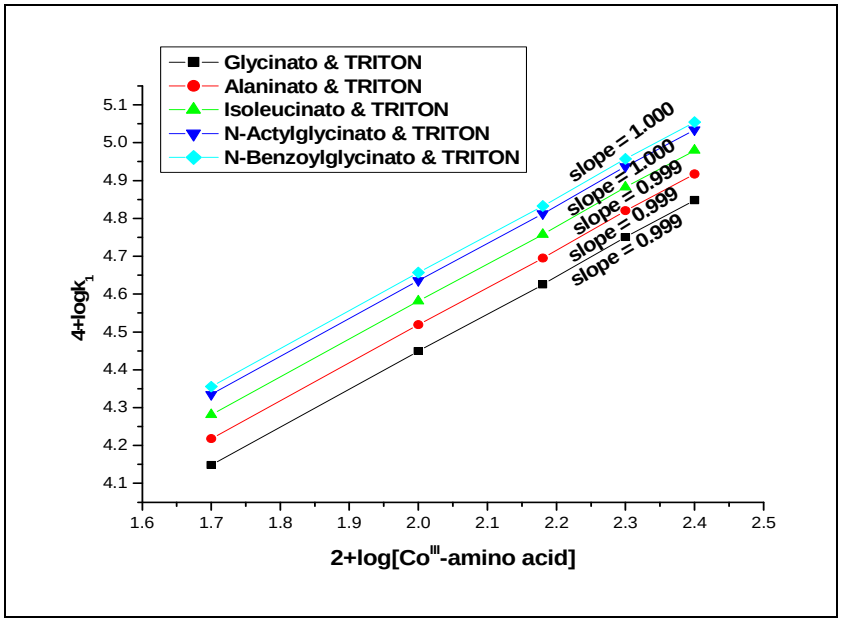


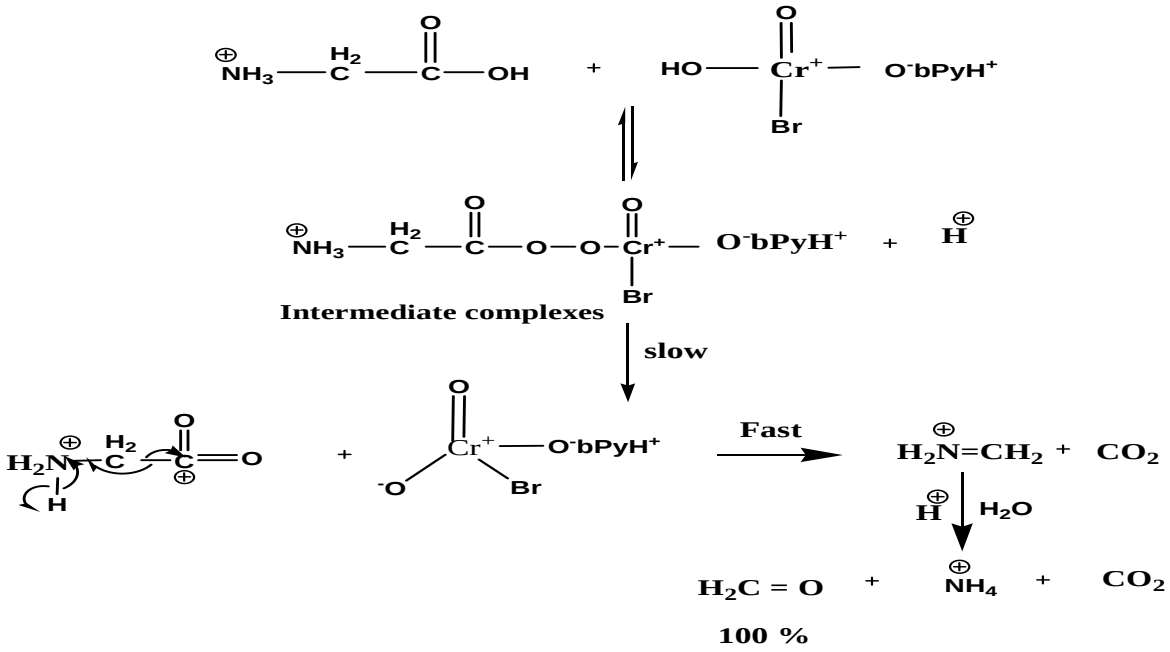
Fig. 3. Rate dependence on the cobalt (III) complexes with TRITON

MECHANISM

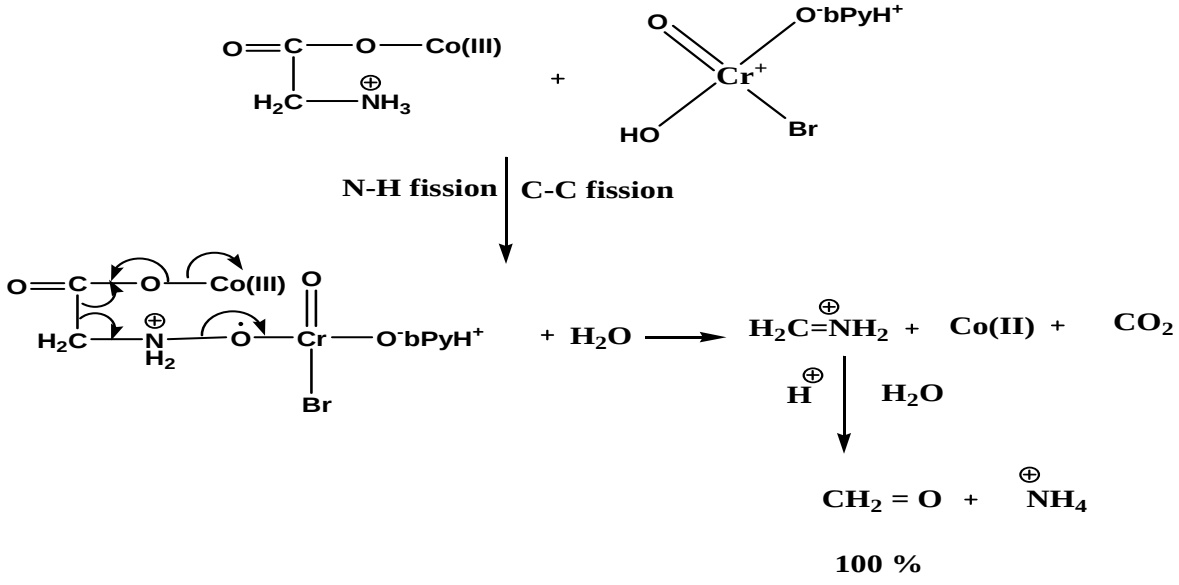
The reaction between BPBC oxidation of Co (III) complexes of α-amino acids exhibits total second order kinetics first order with respect to each reactant. Scheme-1 the electron transfer possibly occurs within the intermediates complexes. The BPBC attacks the $–NH_2$ or NH centre in the slow step of the reaction leading to the formation of a radical NH or N. proposes that Cr (IV) oxidizes NH centre and induces the formation of a radical which in a synchronous step undergoes carbon – carbon bond fission.Scheme-2 the rate of reaction carries with first power of AcOH concentration. Decrease in absorbance at 502 nm corresponds to the reduction of Co (III) bound complex. The ligation of carboxylic acid of α-amino acids by Co (III) changes the order with respect to Co (III) complex to

unity. No possibility of binuclear complex formation between BPBC and Co (III) complexes is seen. One electron transfer to BPBC acetate may occur by an outer-sphere path in the slow step As One electron transfer to BPBC acetate may occur by an outer-sphere path in the slow step. The formation of binuclear complex with high association constant K between BPBC acetate and α-amino acids is possibly due to the ligation of BPBC acetate to free carbonyl end. (Absent in Co (III) complex).

Scheme: 1



Scheme: 2



CONCLUSION

Oxidation of pentaamminecobalt (III) complexes of both bound and unbound ligands in micellar medium has been studied.Thus, the kinetics of one electron transfer route seems to be available for with BPBC- Cobalt (III) bound and unbound complexes of α-amino acids in micellar medium, BPBC oxidizes Cobalt(III) bound and unbound α- amino acids through free radical. Mechanism explains the synchronous C-C bond fission and electron transfer to Cobalt (III) centre.Oxidation of above complexes increases with increase of concentration.With increase in micellar concentration, an increase in the rate is observed.The added CTAB enhances the rate of oxidation of a reaction much more than NaLS.1 mole of Co (III) complexes of α-amino acids consumes 0.5 mole of BPBC whereas 1 mole of unbound α-amino acids consumes 1.0 mole of BPBC.

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