Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der ChemicaSinica, 2016, 7(1): 1-8

Der Chemica Sinica
Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Kinetic study of oxidation of pentaammine cobalt (III) complexes of α-amino acids by quinoxalinium bromo chromate in micellar

S. Chandrasekaran and K. Subramani

PG and Research Department of Chemistry, Islamiah College, Vaniyambadi, Vellore, TN, India

---

ABSTRACT

The kinetics of oxidation of QxBC unavailable with Cobalt (III) complexes of α-amino acids and free α-amino acids in acetic acid-water 50% (v/v) medium in the presence of Micellar. QxBC oxidize Pentaammine Cobalt (III) complexes of α-amino acids and free α-amino acids. The reaction was followed by observing the decrease in the absorbance at 365nm for Cr (VI) in spectrophotometer. The increase in the rate is observed to increase in the concentration of the Surfactant. The added CTAB enhances the rate of oxidation of reaction much more than TRITON-X 100 and NaLS. As well as added TRITON enhances the rate of oxidation of reaction much more than NaLS.

Keywords- Pentaammine Co(III)complexes, Sodium lauryl sulfate, Cetyltrimethylammoniumbromide,α-Amino acids Quinoxaliniumbromochromate(QxBC)

INTRODUCTION

In chemistry, the electron transfer reactions 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], antibiotics [4] and antimicrobial activities [5].

Surfactants are often used in the formulations of pesticides and herbicides [6]. They have also found a wide range of applications because of their unique solution properties such as detergency, solubilization, and surface wetting capabilities in diverse areas such as chemical as well as biochemical research[7]. 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 [8] and have also found a wide range of applications in diverse areas such as mining, petroleum, and pharmaceutical industries. It has been observed that several redox reactions in micellar media were influenced by the hydrophobic and electrostatic forces and, for a given set of reactions, the observed rate depends on the extent of association between the reactants and micellar aggregates[9-12].

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds. The kinetics and mechanism of oxidation of α-amino acids by various oxidants have been reported. A number of new chromium(VI) containing compounds like pyrazinium chlorochromate [13], benzyl trimethyl ammonium chloro chromate[14],triethylammonium chloro chromate[15], morpholinium chloro chromate[16-17], 4-(dimethylamino)pyridinium chlorochromate[18], quinolinium fluoro chromate[19], quilnolinium bromo chromate[20], quilnolinium dichromate[21],tributyl ammonium chloro chromate[22], tripropylammonium fluorochromate[23] and isoquinolinium bromo chromate[24] have been used to study the kinetics and mechanism of various organic compounds. A variety of compounds containing chromium (VI) have proved to be versatile reagents

capable of oxidizing almost every oxidiasable functional group[25]. However, the kinetics of oxidation of α-amino acid by QxBC, a Cr(VI) reagent has not yet been studied. This prompted us to undertake the present investigation. The present work reports the kinetics of oxidation of α-amino acid by QxBC and evaluates the rate constants. Mechanistic aspects are also discussed. The Literature survey reveals that no report is available on the kinetics of oxidation of α-amino acid by QxBC. In this article, the kinetics and mechanism of oxidation of α-amino acid by QxBC is reported.

MATERIALS AND METHODS

Materials

Glycine, Alanine, Isoluecine, N-Acetyl Glycine, N-Benzoyl Glycine (99%, s.d. fine), CrO_3 (99%, Merck, India), Hydrobromic acid (47%,Merck, India) $HClO_4$ were used as supplied and their stock solutions were prepared in double distilled (first time from alkaline $KMnO_4$), Deionized and CO_2 free water. Acetic acid was purified by standard method and the fraction distilling at 118^0C was collected. Quinoxalinium Bromochromate has been prepared [26]. QxBC is a mustard yellow, non-hygroscopic, but moderately light-sensitive solid which should be protected from light during preparation and storage. The purity of QxBC was checked by the iodometric method.

Preparation of quinoxalinium bromochromate

A solution of chromium trioxide (20 g; 0.2 mol) in water(25 mL) was cooled to 0°C and to this 47% aqueous hydrobromic acid (23.5 mL; 0.2 mol) was slowly added with vigorous stirring. To this resulting solution quinoxaline (27 g; 0.2 mol) was added and then cooled for 2h. The resulting mustard yellow solid was collected on a sintered glass funnel and washed with ether, kept under suction until moderately dry, and placed under vacuum pump pressure until a dry powder, mp: 108-110 °C, Yield 83 % (52 g).

Preparation of Carbonatopentaamminecobalt (III) nitrate

Carbonato pentaamminecobalt (III) nitrate was prepared by dissolving 58 g of powdered ammonium carbonate in 60 mL of water and 100 mL of aqueous ammonia, adding a solution of 30 g of cobalt (II) nitrate. hexahydrate in 40 mL of water and then bubbling air very slowly through the mixture (20 bubbles/min.) for 20 days. The solution was cooled to 0°C and 600 mL of methanol was added slowly with stirring. The preparation was kept at 0ºC for 3 days, and the precipitated carbonato nitrate was filtered off. This was purified by dissolving in twice its weight of water, adding LiCl (1 g of LiCl / 2 g of complex),filtering and then slowly adding an equal volume of methanol. The solution was kept 0ºC for 10 hrs and the crystalline complex was filtered off and dried in a vacuum[27].

Preparation of Pentaaminecobalt (III) complexes of α-amino acids

10 mmol of the selected α-amino acid and 5 mmol of NaOH were added to 20 mL of absolute methanol, and to the mixture was added 400 mg of finely ground carbonatopentaamminecobalt (III) nitrate. The mixture was refluxed for 2 hr. with frequent shaking. The preparation was cooled to under ice, and 1 mL of conc. HClO4 was added, after which the preparation was kept at 0ºC for an additional 30 min. The precipitate, if any was filtered off and washed with ether. The mother liquor was shaken with 150 mL of ether, generally precipitation an additional portion of the desired complex.

Kinetic measurements

All kinetic measurements were carried out An Evolution 60 Thermo spectrophotometer fitted with recording and thermostating arrangement was used to follow the rate of the reaction [28]. The progress of the reaction was followed at 365 nm by monitoring the decreases of Cr(IV) in free α-amino acids and 502nm by monitoring the changes in absorbance of remaining Co(III) in complexes. The required [α-amino acids], [$HClO_4$], and [QxBC] were premixed in a reaction vessel, thermostated in an oil bath, and QxBC solution (thermally equilibrated at 323K) was then added prior to the absorbance measurements. Under pseudo-first-order conditions of α-amino acid, the plots of log *A versus* time (*A* is absorbance intensity) were linear up to 80% completion of the reaction with an average of linear regression coefficients, $r \geq 0.996$.

Stoichiometric analysis

Kinetic measurements of the oxidation of cobalt(III) complexes of α-amino acids and unbound ligands were carried out under pseudo first order conditions in 50% acetic acid at 323K. The stiochiometric studies for the oxidation of pentaamminecobalt (III) complexes of α- amino acids and unbound ligands by QxBC were carried out with the oxidant in excess. After nine half lives when the reaction was nearing completion, the concentration of unreacted was determined spectrophotometrically. The stoichiometry was calculated from the ratio between reacting [oxidant] and [substrate] from the decrease in the absorbance measured for the cobalt (III) complex, the amount of cobalt (III) reduced was calculated. This value was then compared to the amount of cobalt (II), and carbonyl compounds (Table 1).

Product Analysis

Co (II) was estimated after the completion of reaction, by diluting the reaction mixture 10 – fold with concentrated HCl, allowing the evolution of chlorine to cease, and then measuring the absorbance at 692 nm [29]. The amount of Co (II) estimated to nearly 40% of [Co (II)]$_{initial}$. After 48h, the product was extracted with ether and analyzed iodoimetrically for the amount of HCHO formed in the case of the [glycinato] and [N – acetyl glycinato]Cobalt (III) complexes, the dimeric Co (III) complex, and unbound glycine. The yield of HCHO in all these cases is nearly 60% [Co (III)]$_{initial}$ [30]. After neutralization of the reaction mixture with sodium bicarbonate, the pH of the aqueous layer was adjusted to about 6.5 and the aqueous layer was separated by filtration in the case of both free ligands and corresponding complexes. On evaporation of water under reduced pressure, the product separated and the percentage yield was calculated. Though the yield of glyoxalic acid was nearly quantitative, the estimation of glyoxalic acid complex was less nearly quantitative. In both the cases the IR spectra of the product agreed with that of authentic samples of glyoxalic acid or the [glyoxalato] cobalt (III) complex[31].

Table - 1 Stoichiometric data for the oxidation of α-amino acids and their pentaammine cobalt (III) complexes by Quinoxalinium BromoChromate in the presence of CTAB

[HClO$_4$]=0.1mol dm^{-3}; Temperature= 323K ; [CTAB]=1.0x10^{-2} mol dm $^{-3}$

10^2 [Compound] mol dm $^{-3}$	10^2 QxBC]Initial mol dm^{-3}	10^2 [QxBC]Final mol dm^{-3}	$\Delta 10^2$ [QxBC] mol dm^{-3}	[Compound]: Δ[QxBC]
Alanine				
1.0	10.0	9.34	0.66	1.00:0.66
2.0	10.0	8.72	1.28	1.00:0.64
3.0	20.0	18.14	1.86	1.00:0.62
Glycine				
1.0	10.0	9.36	0.64	1.00:0.64
2.0	10.0	8.76	1.24	1.00:0.62
3.0	20.0	18.16	1.84	1.00:0.62
Isoluecine				
1.0	10.0	9.36	0.64	1.00:0.64
2.0	10.0	8.68	1.32	1.00:0.66
3.0	20.0	18.02	1.98	1.00:0.64
N-acetylglycine				
1.0	10.0	9.35	0.65	1.00:0.65
2.0	10.0	9.68	1.32	1.00:0.66
3.0	20.0	18.08	1.92	1.00:0.64
N-Benzoylglycine				
1.0	10.0	9.37	0.63	1.00:0.63
2.0	10.0	8.72	1.28	1.00:0.64
3.0	20.0	18.11	1.89	1.00:0.63

RESULTS AND DISCUSSION

Dependence of rate on α-amino acids in micellar

The rate of oxidation of the reaction by QxBC had been followed under pseudo first order condition by keeping excess of α-amino acids concentration than the reagent. The rate constants were calculated by the integrated rate equation. The graph of the logarithm of Absorbance versus time linear and the rate constants calculated from the slope of the graph agreed with the experimental value. which shows a first order dependence plot on α-amino acid (Table – 2, Figure 1). The concentration of the substrates, glycine, alanine, isoleucine, N-Acetyl glycine and N-benzoyl glycine were varied in the range of 0.5 x 10^{-2} to 2.5 x 10^{-2} mol dm^{-3} at 323K (Table – 3) and keeping all other reactant concentrations were constant and the rates were measured. The rate constants were calculated by the integrated rate equation. The rate of oxidation increased progressively with increasing the concentration of α-amino acids. The plot of log k_1 *versus* log [α-amino acids] with CTAB gave the slope of 0.998 (Figure 2). Under pseudo-first-order conditions, the plot of 1/*k1* versus 1/[α-amino acids] were linear with a negligible intercept indicating that the intermediate formed in a slow step got consumed in a subsequent fast step.

Dependence of rate on Co(III) bound α-amino acids in micellar

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 323K and keeping all other reactant concentrations were constant and the rates were measured(Table - 3).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 plot of log k_1 *versus* log [α-amino acids] with CTAB gave the slope of 0.998(Figure 3). Under pseudo-first-order conditions, the plot of 1/*k1* versus 1/[α-amino acids] were linear with a negligible intercept indicating that the intermediate formed in a slow step got consumed in a subsequent fast step.

Table - 2 Kinetic data for the oxidation of α-amino acids by QxBC
[QxBC]=10^{-3}mol dm^{-3}: [$HClO_4$]=0.1 mol dm^{-3}: [Glycine]=1.00 $x10^{-2}$ mol dm^{-3}: [NaLS]=1.00$x10^{-2}$ mol dm^{-3}

Time(S)	log(Abs)	$10^4k_1(S^{-1})$
0	-0.195	0
311	-0.234	2.899
607	-0.269	2.809
907	-0.305	2.799
1205	-0.342	2.806
1509	-0.379	2.803
1808	-0.415	2.794
2110	-0.451	2.792
2411	-0.495	2.862
2707	-0.523	2.788
3006	-0.562	2.812

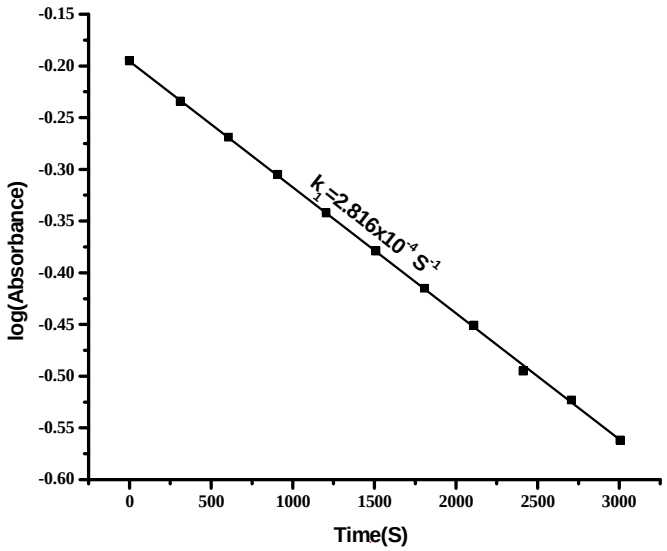


Fig. 1 Dependence of first order plot

Dependence of rate on Perchloric acid

Perchloric acid has been used as a source of H+ in the reaction medium. The concentration of perchloric acid was varied in the range 0.06 to 0.14 mol dm^{-3} keeping all other reactant concentration as constant at 323K as well as Cobalt(III) complexes and the rates were measured. The acid catalyzed nature of this oxidation is confirmed by an increase in the rate with the addition of perchloric acid. The plot of log *k1* versus log [H+] is a straight line with a slope of 0.999.

Depedence of rate on Micelles

The concentration of micelles, sodium laryl sulfate, cetyltrimethylammoniumbromide and Triton X 100 were varied in the range of $1.0x10^{-4}$ to $1.0x\ 10^{-2}$ mol dm^{-3} at 323K as well as Cobalt(III) complexes and keeping all other reactant concentrations as constant and the rates were measured. The rate of oxidation increased with increasing the concentration of micelles. When formation of micelles on the substrates the rate of reaction was observed constantly. A plot of specific rate constant versus micellar concentration is sigmoidal in shape both free ligand and cobalt (III) complexes. The rate of the reaction is increased by the addition of NaLS, CTAB and TRITON. The catalytic effect is more in CTAB than TRITON and NaLS.

Table – 3 Kinetic data for the oxidation of free α-amino acids and Co(III) Complexes of α-amino acids by QxBC with varying α-amino acid concentrations

[QxBC] =10^{-3}mol dm^{-3}; [$HClO_4$]=0.1 mol dm^{-3}; [Micelles]=1.00 x10^{-3} moldm^{-3}: Temperature=323K

10^2 [α-aminoacids] /[Co(III) amino acids] mol dm^{-3}	NaLS	CTAB	TRITON	NaLS	CTAB	TRITON
	10^4k_1 (s^{-1})	10^4k_1 (s^{-1})	10^4k_1 (s^{-1})	10^4k_1 (s^{-1})	10^4k_1 (s^{-1})	10^4k_1 (s^{-1})
Alanine				Alaninato		
0.5	1.109	1.575	1.383	1.183	1.644	1.422
1.0	2.211	3.149	2.778	2.349	3.268	2.861
1.5	3.398	4.734	4.103	3.549	4.890	4.284
2.0	4.478	6.330	5.500	4.700	6.540	5.754
2.5	5.600	7.843	6.920	5.970	8.160	7.225
Glycine				Glycinato		
0.5	1.415	1.910	1.823	1.482	1.982	1.878
1.0	2.816	3.821	3.688	2.958	3.956	3.765
1.5	4.298	5.768	5.496	4.376	5.964	5.610
2.0	5.660	7.640	7.340	5.980	7.888	7.490
2.5	7.065	9.735	8.375	7.415	9.968	9.390
Isoluecine				Isoluecinato		
0.5	1.533	2.312	1.935	1.574	2.373	1.987
1.0	3.041	4.614	3.891	3.165	4.776	3.980
1.5	4.616	7.011	5.801	4.761	7.133	5.919
2.0	6.108	9.360	7.730	6.376	9.354	7.954
2.5	7.650	11.625	9.613	7.845	11.626	9.820
N-Acetylglycine				N-Acetylglycinato		
0.5	1.928	2.655	2.115	1.961	2.750	2.199
1.0	3.844	5.308	4.214	3.916	5.488	4.265
1.5	5.775	7.991	6.265	5.876	8.247	6.491
2.0	7.736	10.630	8.574	7.860	11.002	8.756
2.5	9.615	13.300	10.675	9.818	13.675	10.913
N-Benzoylglycine				N-Benzoylglycinato		
0.5	2.394	3.235	2.859	2.428	3.300	2.925
1.0	4.777	6.481	5.706	4.867	6.598	5.849
1.5	7.118	9.669	8.565	7.284	9.909	8.795
2.0	9.466	12.912	11.446	9.720	13.220	11.744
2.5	11.913	16.100	14.263	12.218	16.520	14.638

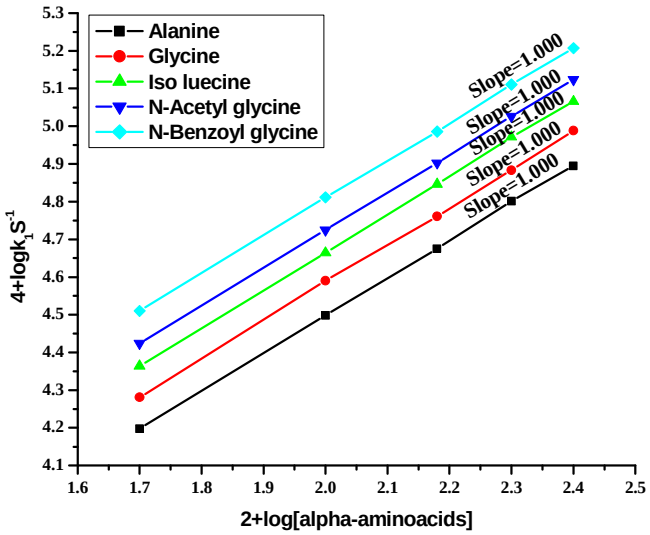


Fig. 2 Dependence of rate on α-Hydroxy acids with CTAB

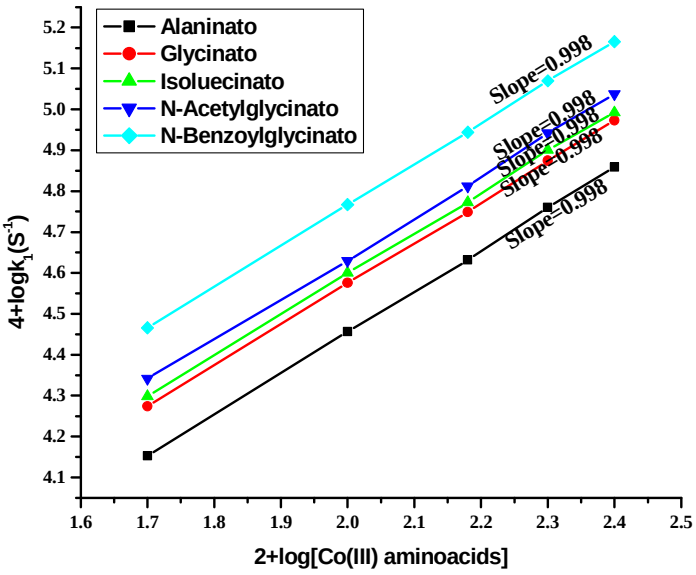
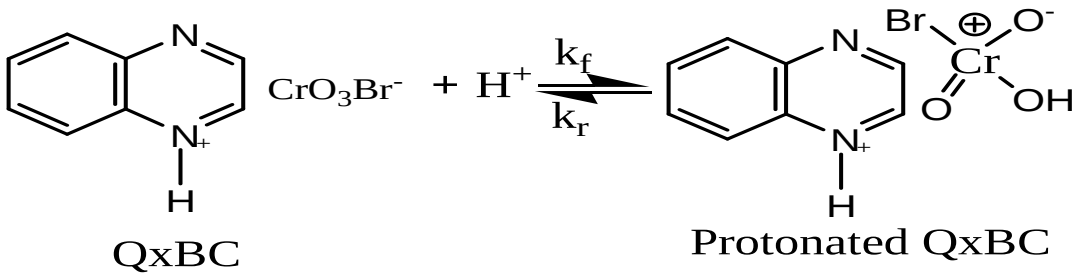
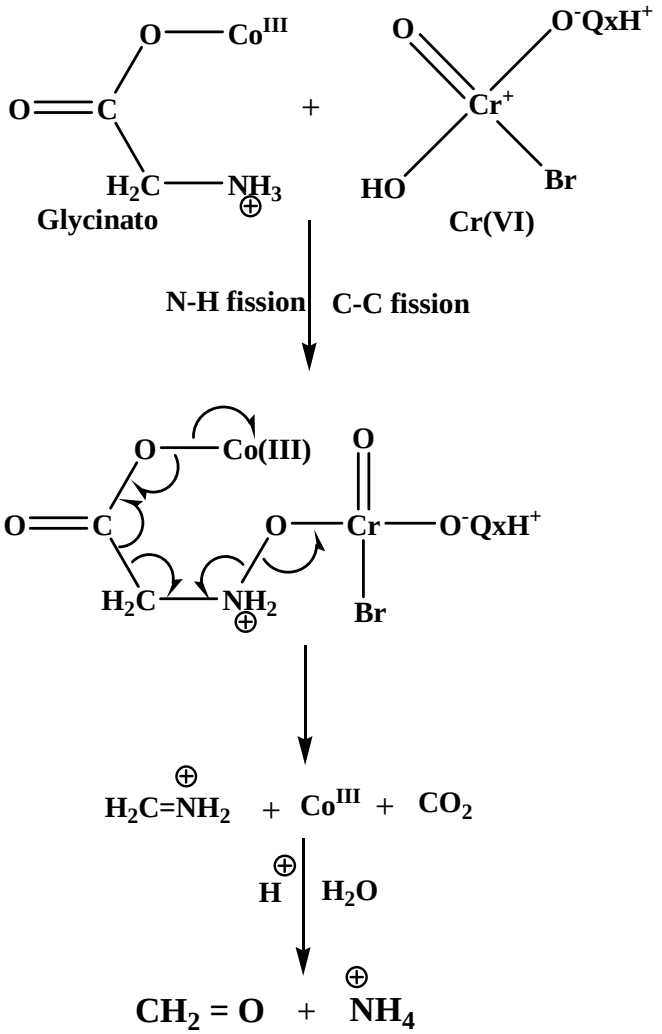


Fig 3 Dependence of rate on Co(III) complexes of α-aminoacids with CTAB

Mechanism

There is 100% decrease in absorbance of 502 nm corresponding to the reduction of Co (III) center. The rate of Cr (VI) oxidation of unbound α-aminoacids are different suggesting the ligation of carboxlicacid increases the rate of induced electron transfer. There is a possibility of binuclear complex formation between Cr (VI) and Co (III) complex. In the presence of any such precursor complex formation, the initial act of one electron transfer to Cr (VI) may occur by inner sphere path in the slow step. This suggests that Cr(IV) attacks the – NH_2 or –NH centre in the slow step of the reaction, leading to the formation of a radical – . NH or – . N. The reduction in the specific rate of Cr (IV) oxidation of Co (III) complexes of N – Acetyl and N – Benzoyl glycine compared to that of unbound ligands, points to the significant electronic influence of the acyl group and also the electrostatic influence of the Co(III) center on the seat of attack Viz, the NH group. Such an electrostatic influence due to ligation of α- amino acids to the Co (III) center seems to be absent as the amino nitrogen is protonated both in the complex and in the unbound ligand,exerting possibly the same electrostatic influence at the set of attack. In the first step flurochromate gets protaonated. The protonated flurochromate brings out the decarboxylation of amino acid followed by deamination resulting in the formation of aldehyde and Cr (IV).A suitable Mechanism is proposed for glycinato and similar trends were observed all other α-amino acids and Co(III) complexes of amino acids.





Scheme-1 Mechanism of oxidation of Cobalt(III) Complexes of α-amino acids by QxBC

CONCLUSION

In all these reactions, ultimately reductions at cobalt (III) center have been achieved due to the generation of a radical at the bound ligand by the one equivalent oxidant. But the percentage of cobalt (III) formed differed from reaction to reaction due to the partitioning of the reaction paths. Such as induced electron transfer reaction has been attempted presently with free α-amino acids and pentaamminecobalt (III) complexes of α-aminocids.The induced electron transfer in cobalt (III) complexes, the intermediate radical formed dissociated in a nearly synchronous manner with carbon-carbon bond cleavage only to the extent of 100% and suggesting 100% C-C cleavage. The added CTAB enhances the rate of oxidation of a reaction much more than Triton and NaLS. Similar trends have been observed in alaninato, Isoluecinato,N-acetyl glycinato and N-benzoylglycinato cobalt (III) complexes.

Acknowledgement
Authors are thanks to the Management of Vaniyambadi Muslim Educational Society and PG & Research Department of Chemistry, Islamiah College Vaniyambadi for providing the necessary facilities for the successful completion of this research work.

REFERENCES

[1] Osinsky S, Levitin I, Bubnovskaya L, Sigan A, Ganusevich I, Kovelskaya A, Valkovaskaya N, Campanella L, Ward-man P, *Exp. Oncol.*,**2004**, 26,140
[2] Behm C. A, Creaser I, Daszkiewicz B, Geue R.J, Sargeson A.M, Walker G.W *J. Chem.Soc., Chem. Commun.*,**1993**,24,1844
[3] Behm C.A, Boreham P.F.L, Creaser I, Daszkiewicz B, Maddalena D.J, Sargeson A.M,Snowdown M, *Aust. J. Chem.*,**1995**,48,1009

[4] Ghirlanda G, Scrimin P, Tecillam P, Offoletti A.T, *Langmuir.*,**1998**,14,1646
[5] Srinivasan S, Annaraj J, Attappan P.R, *J. Inorg. Biochem.*,**2005**,99, 876
[6] Scramm L.L, Stasiuk E N, Marangoni D.G, *Annu. Rep. Prog. Chem. Sect.*,**2003**,3,99
[7] Rosen M.J, *Surfactants and Interfacial Phenomenon, 3rd Edn. Wiley, New Jersey*, **2004**, 569
[8] Tadros T.F, *Applied Surfactants, 1st Edn., Wiley-VCH, Germany*,**2005**, 48, pp589
[9] Majumdar T, Mahapatra A, *Colloids Surf. A.*,**2005**, 302, 360
[10] De La Vega R, Tejeda P.P,Corbejo P.L, Sanchez F,*Langmuir.*, **2004**,20, pp1558
[11] Corneio P.L, Perez P, Garcia F, De La Vega R, Sanchez F, *J. Am. Chem. Soc.*,**2002**,124, 5154
[12] Cornejo P.L, Hernandez M, Tejeda P.P, Perez F, Gotor R. P, Sanchez F, *J. Phys. ChemB.*,**2005**,109, 1703
[13] Sekar K.G, Prabaharan A,*Transition Met.Chem.*,**2008**, 33, 393
[14] Mansoor S.S, Shafi S.S, *Int. J. Chem.Tech. Res.*,**2009**, 1,1206
[15] Sharma P.K, Swami P, Yajurvedi D, Mishra P, *Int. J. Chem. Kinet*.,**2010,** 42, 50
[16] Sharma P.K, Malinin N, Baghmar M, *Int.J. Chem. Kinet.*,**2009**, 41, 65
[17] Sharma V, Choudhary, Agarwal S**,** *Indian J. Chem.Sec b.*, **2009**,48A,362
[18] Rajarajan G, Jayachandramani N, Manivarman S, Jayabharathi J, Thanikachalam V, *Transition Met. Chem*., **2008**,33, 393
[19] Banerji K.K, Dave I,Sharma V,*J.Indian Chem. Soc*.,**2002**,79,347
[20] Hiran B.L, Nalawaya N, Jain A, *J. IndianChem. Soc.* **2002**,79, 587
[21] Anandaratchagan K, Md.Nawaz B, Subramani K, *Acta Chim.Pharm.Indica.*,**2011**,1,44
[22] Mansoor S.S, Shafi S.S, *React. Kinet.Mech. Catal.*,**2010**,100,1, 21
[23] Mansoor S.S, Shafi S.S,*J. Mol. Liq.*,**2010**, 155, 85
[24] Vibhute A.Y, Patwari S.B, Khansole S.V,Vibhute Y.B, *Chin Chem. Lett.*,**2009** 20,256
[25] Wiberg K.B,*Oxidations in Organic Chemistry*, Academic Press, NewYork,**1965**
[26] Nebahat Degirmenbsi, Beytiye ozgun, *G.U.Journal of Science*,2006,19,9
[27] Udayavani S, Subramani K**,** *Acta Chim. Pharm. Indica:***2012**, 2,213
[28] Mohammed Nawaz B, Subramani K, Mansur Ahmed,*J.Chem.Bio.phy.sci.Sec.A.*,**2011,** 1,204
[29] Gould E.S, Taube H, *J. Am. Chem. Soc.*,**1964**,86,pp1318
[30] Mann F.G, Saunders H.C, *Practical Organic Chemistry, Longman Group, London.*,**1960**,pp455
[31] Thaminum Ansari A, Subramani K, *Int.J. ChemTech Res.*,**2009**,1,139