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OXIDATION OF PENTAAMMINE COBALT (III) COMPLEXES OF α-AMINO ACIDS BY MANGANESE (IV) HETEROPOLYANION IN THE PRESENCE OF SURFACTANTS

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ABSTRACT

Manganese (IV) heteropolyanion oxidation of pentaamminecobalt (III) complexes of α-amino acids micellar medium yielding nearly 100% Co (II), and about 100% carbonyl compounds are ultimate products. The decrease in UV-visible absorbance at λ = 502 nm for Co (III) complex corresponds to nearly 100% of the initial absorbance. The unbound amino acids yield about 100% of carbonyl compound in presence of micelles. The kinetic and stoichiometric results have been accounted by a suitable mechanism.

Key words: Pentaamminecobalt (III) complexes, Induced electron transferreaction, Miscelles, Sodiumlaurylsulphate, Cetyltrimethylammoniumbromide.

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].

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].

In the course of studies on the effects of metallosurfactants on chemical reactions, catalytic effects were observed above a critical micelle concentration (CMC). Such systems offered the possibility to investigate the effects of the local reactant concentrations in the micellar subphase, as well as the local

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microenvironment, on the reactivity[13-17]. Cobalt (III) complexes, by virtue of their abundance and diversity, have played a fundamental role in our understanding of the structural, spectroscopic, and electrochemical properties of coordination compounds. We have been interested in the synthesis and micelle-forming properties of cobalt (III) complexes containing lipophilic ligands for a long time[18-19].

EXPERIMENTAL

Preparation of cobalt (III) complexes carbonatopentaamminecobalt (III)-nitrate

Carbonatopentaamminecobalt (III) nitrate was prepared by dissolving 58 g of powdered ammonium carbonate in 60 mL of water and 100 mL of concentration 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° and 600 mL of methanol was added slowly with stirring. The preparation was kept at 0° 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 0° for 10 h and the crystalline complex was filtered off and dried in vacuum.

Pentaaminecobalt (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 ground carbonatopentaamminecobalt (III) nitrate. The mixture was refluxed for 2 h with frequent shaking. The preparation was cooled to under ice, and 1 mL of conc. $HClO_4$ was added, after which the preparation was kept at 0° 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.

Preparation of $[Mn^{IV}Mo_9O_{32}]^{6-}$

An aqueous solution of manganese sulphate containing the oxidant sodium peroxydisulphate was added to the solution of ammonium hepta molybdate. The resulting mixture was boiled for five minutes with constant stirring, quickly filtered and cooled. The orange red crystals were recrystalised from hot water.

Analytical and physical method

Molybdenum was estimated gravimetrically as oxinate. Manganese was estimated spectrophotometrically. The d^3 configuration of manganese in $[Mn^{IV}Mo_9O_{32}]^{6-}$ was verified by back titration with $KMnO_4$.

Kinetic method

All the glass apparatus were made of pyrex glass and stoppers were well ground. The loss of solvent, tested in standard flask and in reaction bottles, was found to be negligible. Burettes, pipettes and standard flasks were standardized by usual produce.

Rate measurement

For the HPA oxidant of Co (III) complexes of α-amino acids and unbound ligands, the rate of measurements were made at 28°C in 100% aqueous medium. The standard solution prepared and required amount solutions were pipette out into a 1 cm cell. The total volume of the reaction mixture in the spectrophotometer cell was kept as 2.5 mL in each kinetic run. A UV-Visible spectrophotometer was used to follow the rate of the reaction.

Rates of these unbound ligand and Co (III) bound complexes were calculated from the observed

decrease in absorbance at 350 nm. For all the kinetic experiments, conversion were followed at least for four half-lives and specific rates from successive half-lives agreed with + or 7% and the average values did not differ from a plot of logarithmic change in concentration vs time calculated using integrated rate equation.

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

Where 'a' is initial concentration of oxidant and (a-x) concentration of oxidant at time t, are expressed in sec^{-1}. The values reported are averages of least two runs.

RESULTS AND DISCUSSION

The kinetic data for the Mn (IV) heteropolyanion oxidation of free α-amino acids with 1N H_2SO_4 at 30°C in micellar medium.The reaction exhibits second order dependence on [cobalt (II)] as well as [α-amino acids].

Stiocheometric studies

The stiochiometric studies for the HPA oxidation of pentaamminecobalt (III) complexes of α- amino acids and unbound ligands in the presence of sulphuric acid were carried out with oxidant in excess. The $[H^+]$ and ionic strength were maintained as in the corresponding rate measurements. The temperature was maintained at 30°C. After nine half lives when the reaction was nearing completion, the concentration of unreacted HPA was determined both iodometrically and spectrophotometically from the change in absorbance measured at 350 nm. [HPA] was calculated after applying due blank correction for decomposition of HPA and aquation of cobalt (III) complexes of α-amino acids in the presence of sulphuric acid. The stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate] from the decrease in the absorbance measured for the cobalt (III) complexe, the amount of cobalt (III) reduced was calculated. This value was then compared to the amount of cobalt (II), and carbonyl compound.

Table 1: Stochiometric data in the HPA oxidation of Co (III) bound α-amino acids (glycine, alanine, valine, N-acetyl glycine and N-benzoyl glycine)

$10^2[Co^{III}L]_{initial}$ moldm^{-3}	$10^2[HPA]_{initial}$ moldm^{-3}	$10^2[HPA]_{final}$ moldm^{-3}	Δ[[HPA]/Co(III)$_{initial}$ moldm^{-3}	10^3[Co (II)]Mm (%) moldm^{-3}
Glycine				
1.0	10.0	8.9	1.1	1.0
1.0	5.0	4.0	1.0	1.1
Alanine				
1.0	10.0	8.8	1.2	0.98
1.0	5.0	3.9	1.1	1.0
Valine				
1.0	10.0	9.0	1.0	1.1
1.0	5.0	4.1	1.2	1.1
N-acetyl glycine				
1.0	10.0	9.1	1.0	1.1
1.0	5.0	4.2	1.0	1.0
N-benzoyl glycine				
1.0	10.0	9.8	1.2	1.0
2.0	5.0	4.4	0.96	1.1

Table 2: Stochiometric data in the HPA reaction with unbound α- amino acids

10^2[Ligand] moldm^{-3}	10^2[HPA]$_{initial}$ moldm^{-3}	10^2[HPA]$_{final}$ moldm^{-3}	Δ[[HPA]/[Ligand]$_{initial}$ moldm^{-3}
Glycine			
1.0	5.0	3.2	1.8
1.0	10.0	8.8	1.2
Alanine			
1.0	10.0	8.9	1.1
1.0	20.0	9.0	1.0
Valine			
1.0	5.0	4.0	1.0
1.0	10.0	8.7	1.3
N-acetyl glycine			
1.0	5.0	4.5	1.2
1.0	10.0	9.1	1.1
N-benzoyl glycine			
1.0	5.0	4.9	1.0
1.0	10.0	9.5	1.2

Table 3: First order rate constant for HPA oxidation of cobalt (III) complexes of α-amino acids in NaLS at 30 ± 0.2°C

Substrate (unbound)	10^3[α-amino acids] mol dm^{-3}	10^5 k_1 sec^{-1}	10^4 $k_{calculated}$
Glycinato	10.0	2.8	3.0
	20.0	3.0	3.1
	30.0	3.2	3.4
	40.0	3.4	3.5
	50.0	3.7	3.9
Alaninato	10.0	2.0	2.1
	20.0	2.3	2.4
	30.0	2.5	2.6
	40.0	2.7	2.8
	50.0	3.0	3.2
Valinato	10.0	4.7	4.9
	20.0	4.9	5.1
	30.0	5.0	5.2
	40.0	5.2	5.4
	50.0	5.4	5.6

Cont…

Substrate (unbound)	10^3[α-amino acids] mol dm^{-3}	10^5 k_1 sec^{-1}	10^4 $k_{calculated}$
N-acetyl Glycinato	10.0	5.0	5.2
	20.0	5.2	5.3
	30.0	5.4	5.5
	40.0	5.6	5.7
	50.0	5.8	6.0
N-benzoyl Glycinato	10.0	6.1	6.3
	20.0	6.3	6.5
	30.0	6.4	6.7
	40.0	6.6	6.9
	50.0	6.8	7.0
Mn (IV) -1M, H_2SO_4 – 1N, NaLS – 0.01M, Temp 30 ± 0.2°C			

Table 4: First order rate constant for HPA oxidation of Co (III) complexes of α-amino acids in CTAB at 30 ± 0.2°C

Substrate (bound)	10^3[α-amino acids] mol dm^{-3}	10^5 k_1 sec^{-1}	10^4 $k_{calculated}$
Glycinato	10.0	4.8	4.5
	20.0	9.9	8.9
	30.0	14.7	14.1
	40.0	20.1	19.8
	50.0	24.5	23.6
Alaninato	10.0	5.2	4.9
	20.0	8.9	7.9
	30.0	11.8	11.5
	40.0	15.3	15.0
	50.0	19.9	19.1
Valinato	10.0	7.7	7.5
	20.0	9.5	9.4
	30.0	13.8	13.7
	40.0	18.9	18.8
	50.0	21.3	21.1
N-acetyl glycinato	10.0	9.9	9.5
	20.0	13.8	13.7
	30.0	16.5	16.4
	40.0	20.8	20.7
	50.0	24.7	24.6
N-benzoyl glycinato	10.0	11.5	11.3
	20.0	15.9	15.7
	30.0	19.5	19.3
	40.0	23.3	23.0
	50.0	27.4	27.1
Mn (IV) -1M, H_2SO_4 – 1N, CTAB – 0.01M, Temp 30 ± 0.2°C			

Dependence of rate on HPA concentration in micellar bound α-amino acids ligand

The rate of oxidation of glycinato, alaninato, valinato N-acetyl glycinato and N-benzoyl glycinato cobalt (III) complexes depends on HPA concentration.

Table 5: **First order values for HPA of cobalt (III) bound Ligand. $[(NH_3)_5 Co^{III} – L]^2 = 2.5 \times 10^{-3}$M, H_2SO_4 = 1M, [NaLS] = [CTAB] = 2 x 10^{-2} M, Temp. = 28 ± 0.2°C**

10^{-4} X [Micelles]	10^2x k_1 lit.mol^{-1}sec^{-1}	
	NaLS	CTAB
2	4.85	7.53
4	9.84	14.25
6	13.52	19.52
8	18.96	29.71
10	26.55	33.85
12	29.37	37.86
14	31.20	40.56
16	32.78	41.52

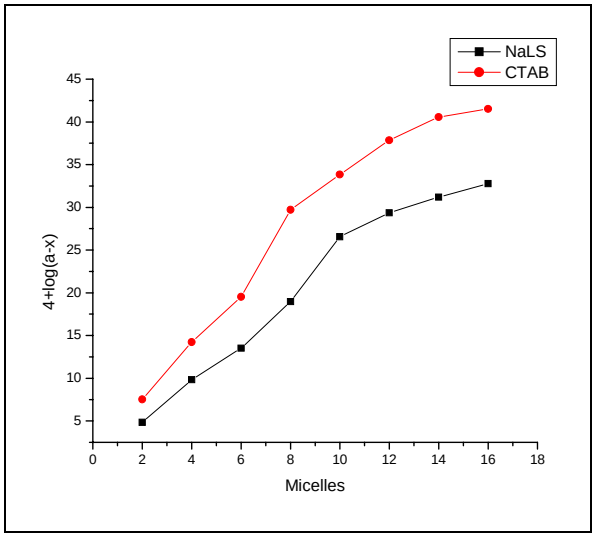
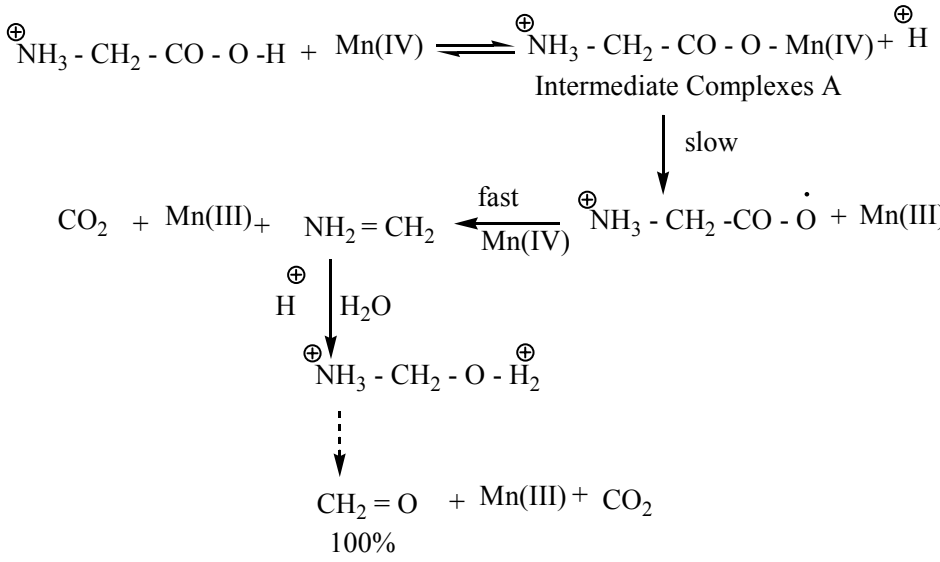


Fig. 1: First order dependence plots

Mechanism

The rate of Mn (IV) induced electron transfer in pentaamminecobalt (III) complexes of α-amino acids depends on the first power of concentration of cobalt (III) and the first power of concentration of Mn (IV). There is 100% decrease in absorbance of 502 nm corresponding on the reduction of Co (III) centre. The rate of Mn (IV) oxidation of unbound α-aminoacids are different suggesting the ligation of carboxlic acid increases the rate of induced electron transfer. The ligand of carboxlic acids (α-amino acids) by Co (III) centre, the order with the respect to Co (III) complexes is unity, probably. There is a possibilities of binuclear complex formation between Mn (IV) and Co (III) complex. In the presence of any such precursor complex formation, initial act of one electron transfer to Mn (IV) may occur by inner sphere path in the slow step.



CONCLUSION

Mn (IV) and pentaamminecobalt (III) complexes with bound ligands featuring conjucated fragments. In all these reactions, ultimately reduction at cobalt (III) centre has been achived 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 attemoted presently with HPA 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 extant of 100% and suggesting 100% C-C cleavage. The added CTAB enhances the rate of oxidation of a reaction much more than NaLS. Similar trends has been observed in glycinato, alaninato, valinato, N-acetyl glycinato and N-benzoyl glycinato cobalt (III) complexes.

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