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Role of Surfactants in Oxidation of Pentaamminecobalt(III) Complexes of a-Amino Acids by Perdisulphuric Acid: A Kinetic Study

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Abstract: The oxidation of pentaamminecobalt(III) complexes of α -Amino acids by Perdisulphuric acid(PDS) in surfactants medium yielding nearly 100% of carbonyl compounds and 100% Co(II) are ultimate products. In this reaction the rate of oxidation shows first order kinetics each in [cobalt(III)] and [PDS]. The unbound α -Amino acids yield about 100% of carbonyl compound in presence of surfactants. The decrease in UV- Visible absorbance at λ = 502nm for Co(III) complex corresponds to nearly 100% of the initial absorbance. The synchronous C-C bond fission and electron transfer of Co(III) centre. The rate of oxidation of Co(III) complexes of both unbound and bound α -Amino acids are enhanced more in the presence of cationic micelle Cetyltrimethylammoniumbromide(CTAB) when compared to the anionic micelle of Sodiumlaurylsulphate (NaLS) and non-ionic micelle of TRITON-X 100. The 1.00 mole of cobalt(III) complexes of α -amino acids reacts with nearly 0.5 mole of PDS, Similarly 1.00 mole of α -amino acids reacts with nearly 1.00 mole of PDS.

Keywords: Perdisulphuric acid(PDS); α-Amino acids; Sodiumlaurylsulphate(NaLS); Cetyltrimethylammoniumbromide(CTAB); TRITON-X 100.

Introduction

Electron transfer is the process by which an electron moves from one atom or molecule to another atom or molecule. Electron transfer is a mechanistic description of the thermodynamic concept of redox, where in the oxidation states of both reaction partners change. Redox reactions between metal ion centers involving transfer of electron from reductant to oxidant have been studied in details in past and also reviewed by several groups of workers^{1,2}. Among oxidation and reduction reactions, oxidation is the most commonly studied reaction. An interesting fact is that many oxidation reactions are accompanied by the release of energy such released energy is the source of work in biological systems including human system. Hence, the knowledge of oxidative pathways may be of great help in understanding processes in nature and synthetic situations.

The Kinetics studies^{3,4} employing Perdisulphuric acid(PDS) is an efficient reagent for oxidation of primary and secondary alcohols to carbonyl compounds. PDS is an oxidant which is non-hygroscopic, non-photosensitive, colourless solid which is freely soluble in water, acetic acid, N,N-dimethyl formamide etc. The little work has been done on PDS as oxidant in surfactant medium. This interest is based on the realization that many biochemical processes proceed in a micro heterogeneous system which contains an aqueous and a lipophilic moiety⁵.

The extent of PDS oxidation of Pentaamminecobalt(III) complexes of α -Amino acids with NaLS, CTAB and TRITON-X 100 surfactants as important to study the rate of decomposition of the complexes. Since surfactant catalysis is an area of tremendous interest due to its occurrence in reaction important to biochemical, biotechnology, and industrial processes. The micelles used in the present work are NaLS, CTAB and TRITON-X 100^{6,7}. The rate of the reaction is increased by the addition of surfactants NaLS, CTAB and TRITON-X 100. A plot of specific rate constant versus surfactants concentration is sigmoidal in shape the catalytic effect is more in CTAB than NaLS and TRITON-X 100. The PDS attacks the -NH₂ or -NH center in the slow step of the reaction leading to the formation of a radical -NH or - N-.

Experimental

Preparation of Pentaamminecobalt(III) complexes of α-amino acids⁸

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 400mg of finely ground carbonato-pentaamminecobalt(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, generally precipitation an additional portion of the desired complex. N-Acetyl and N-Benzoyl glycine were prepared by following the procedure of Vogel⁹. The (NH₃)₅Co(III) complexes of Glycine, Alanine, Isoleucine, N-Acetyl and N-Benzoyl glycine were prepared as their Perchlorates by the method of Fan¹⁰.

Kinetic method^{11,12}

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 flask were standardized by usual procedure. The α -amino acids(A.R) employed as ligands were purchased from Sigma-Aldrich and used as such. The chemicals were purchased from BDH(UK), and SD Fine chemicals (INDIA), E.MERCK (INDIA).

Rate measurements^{13,14}

The rate measurements were carried out on $29 \pm 0.2^{\circ}$ C in100% aqueous medium for α -amino acids. The Temperature was controlled by electrically operated thermostat. The total volume of reaction mixture in the spectrophotometric cell was kept as 2.5ml in each kinetic run. But the rate measurement was carried out at room temperature($29 \pm 0.2^{\circ}$ C) in 100% aqueous medium for α -amino acids. The concentration of and α -amino acids was varied in the range [0.5- 2.5] x 10² mol dm⁻³ at fixed concentrations of other reaction ingredients. A plot of initial rate versus [α -amino acids] and [Surfactants] yielded a straight line passing through the origin confirming first order dependence. The concentration of NaLS, CTAB and TRITON-X 100 was varied in the range of [1 x10⁻³, 10 x 10⁻³, 1 x 10⁻⁴, 5 x 10⁻³, 5 x 10⁻⁴] mol dm⁻³.

Stoichiometric Studies^{15,16}

The stiochiometric studies for the PDS oxidation of pentaamminecobalt(III) complexes of α -amino acids and unbound ligand in the presence of micelles were carried out at 29 ± 0.2 °C. It was observed that the cobalt(II) formation was negligibly small. After nine half lives when the reaction was nearing completion, the concentration of unreacted PDS was determined both iodometrically and spectrophotometrically from the change in absorbance measured at 350 nm. Δ [PDS] was calculated after applying the due blank corrections for decomposition of PDS and aquation of Co(III) complex of α -amino acids in the presence of micelles. Similar calculation about Δ [PDS] was made for the unbound ligand also. The stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. From the decrease in the absorbance measured for the Co(III) complex, the amount of Co(III) reduced was calculated. The stoichiometric results indicate that for one mole of cobalt(III) complex, about 0.5 mole of PDS is consumed, whereas with the unbound ligands for 1 mole of α -amino acids about 1.0 mole of PDS is consumed (Table-1).

10 ³ [Compound] mol dm ⁻³	10 ² [PDS] _{initial} mol dm ⁻³	10 ² [PDS] _{final} mol dm ⁻³	$\Delta 10^{3} [PDS]$ mol dm ⁻³	[Compound]: Δ [PDS]
Glycine				
1.0	1.0	0.89	1.10	1.00:1.10
2.0	2.0	1.80	2.00	1.00 : 1.00
Alanine				
1.0	1.0	0.91	1.00	1.00 : 1.00
2.0	2.0	1.81	1.90	1.00 : 0.95
Isoleucine				
1.0	1.0	0.88	1.20	1.00 : 1.20
2.0	2.0	1.78	2.20	1.00 : 1.07
N-acetylglycine				
1.0	1.0	0.90	1.00	1.00 : 1.00
2.0	2.0	1.82	1.80	1.00:0.97
N-benzoylglycine				
1.0	1.0	0.89	1.10	1.00 : 1.10
2.0	2.0	1.79	2.10	1.00 : 1.05

Table 1: Stoichiometric data for PDS oxidation of α -amino acids in the presence of surfactants at 29 ± 0.2°C.

 $[H_2SO_4] = 0.25 \text{ mol dm}^{-3}$; $[Surfactants] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$; $[PDS] = 0.08 \text{ mol dm}^{-3}$.

Results and Discussion

Dependence of Rate on a-Amino Acidsi Micellar Medium

The rate of Perdisulphuric acid oxidation of α -amino acids depends on PDS concentration and graph of logarithm of concentration versus time are linear from the slopes of the graphs, the specific rates are calculated agree with those obtained from integrated rate equation, suggesting first order dependence of [PDS] (Table-2) (Figure-1). This is further substantiated from the studies of changing the concentration of PDS from [0.5 to 2.5] X 10² mol dm⁻³ at a fixed concentration in surfactants medium (Table-3) (Figure-2,3,4).

TABLE - 2

[PMS]	=	0.08 mol dm ⁻³
$[H_2SO_4]$	=	0.25 mol dm ⁻³
Temperature	=	$29 \pm 0.2^{\circ}\mathrm{C}$
[Glycine]	=	1.0 mol dm^{-3}
[NaLS]	=	$1.00 \text{ x } 10^{-3} \text{ mol dm}^{-3}$

Time (s)	log(a-x) mol dm ⁻³		
420	0.6627	1.984	
1128	0.602	1.978	
1800	0.544	1.980	
2400	0.491	1.989	
3120	0.431	1.971	
3900	0.371	1.989	
4620	0.311	1.982	
5172	0.245	1.975	
6090	0.172	1.977	
7230	0.099	1.974	



Fig - 1 First order dependence plot

Table 3: First order rate constants for PDS oxidation of α -amino acids in surfactants medium at 29 ± 0.2°C.

10^{2} [α -amino acids] mol dm ⁻³	$10^4 k_1 (s^{-1})$ NaLS	10 ⁴ k _{cal.} NaLS	$10^4 k_1(s^{-1})$ CTAB	10 ⁴ k _{cal.} CTAB	$10^4 k_1 (s^{-1})$	10 ⁴ k _{cal.} TRITON
ucius] mor um	1.0010	114110	onin	CIIID	maron	maron
Glycine						
0.5	0.974	0.998	1.088	1.236	0.991	0.986
1.5	2.881	2.923	3.054	3.396	2.973	2.991
2.5	4.929	4.821	5.001	5.226	4.955	5.084
Alanine						
0.5	0.896	0.923	0.956	0.942	0.920	0.891
1.5	2.647	2.726	2.848	2.938	2.761	2.632
2.5	4.401	4.498	4.751	4.882	4.638	4.592
Isoleucine						
0.5	1.233	1.380	1.400	1.500	1.310	1.402
1.5	3.680	3.726	4.254	4.402	3.931	3.894
2.5	6.241	6.344	7.005	7.193	6.558	6.636
N-acetylglycine						
0.5	2.101	2.304	2.348	2.666	2.231	2.318
1.5	6.094	6.294	6.965	6.985	6.693	6.593
2.5	10.192	10.345	11.598	11.987	11.150	11.238
N-						
benzoylglycine	2.665	2.998	2.984	3.045	2.831	2.789
0.5	7.778	7.993	8.760	8.999	8.403	8.038
1.5	12.604	12.904	14.585	14.895	13.913	14.036
2.5						

 $[PDS] = 0.08 \text{ mol } dm^{-3}; [H_2SO_4] = 0.25 \text{ mol } dm^{-3}; [Micelles] = 1.00 \times 10^{-3} \text{ mol } dm^{-3}.$

The rate of the reaction for PDS oxidation of unbound α -amino acids insurfactants mediums are arranged in the following increasing order.

Alanine < Glycine < Isoleucine < N-acetylglycine < N-benzoylglycine



Similar trends are followed in the PDS oxidation of Co(III) complex also.

Fig-2 Dependence of rate on [α-amino acid] in NaLS



Fig-3 Dependence of rate on [α-amino acid] in CTAB



Fig-4 Dependence of rate on [α-amino acid] in TRITON-X 100

Conclusion

The kinetic analysis of one electron transfer route seems to be available for PDS with cobalt(III) bound and unbound complexes of α -amino acids in surfactants medium, PDS oxidizes cobalt(III) bound and unbound α -amino acids through free radical. It explains the synchronous C-C bond fission and electron transfer to cobalt(III) centre. The oxidation of above complexes increases with increase in surfactant concentration an increase in the rate is observed. The added CTAB enhances the rate of oxidation of a reaction much more than NaLS & TRITON-X 100. The 1 mole of Co(III) complexes of α -amino acids Consumes 0.5 mole of PDS, whereas 1 mole of unbound α -amino acids consumes 1.0 mole of PDS.

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