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Chromium(VI)- Induced Electron Transfer in Penta-amminecobalt(III) Complexes of α-Amino Acids

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The kinetics of 2,2′-bipyridinium chromate {Cr(VI)}, oxidation of Ccbalt(III) bound and unbound α-amino acids have been studied in the presence of 1.5 M $HClO_4$ at 60°C. The rate of Cr(VI) oxidation is susceptible to polar influences. The decrease in absorbance for cobalt(III) complex at 502 nm to the extent of 25% of its initial value and the formation of CO_2 and Co(III) (25%), provide evidence for the cleavage of N—H and C—C bonds, occurring to the extent of 25% in a synchronous fashion as nearly so. The formation of glyoxylatopentaamminecobalt(III) complex (about 75%) during Cr(VI) oxidation of glycinatopentaamminecobalt(III) complex suggests cleavage of N—H and C—H bonds also to the extent of 75%.

INTRODUCTION

Amino acids are the building blocks in protein synthesis, and undergo various kinds of reactions, depending on whether the particular amino acid contains non-polar groups, polar substituents, acidic or basic substituents. The oxidation of α-amino acids by Br(V) has been studied[1] and the formation of respective aldehyde and ammonium ion has been explained with rate determining cleavage of N—H and C—H bonds. We report here in the kinetics of oxidation of cobalt(III) bound and unbound α-amino acids by 2,2′-bipyridinium chromate.

EXPERIMENTAL

2,2′-Bipyridinium chromate (BPC) was prepared by the method of Nagarajan and Gopalakrishnan[2] and the purity of the sample was determined as 99% by an iodometric procedure. Chromatographically pure samples of glycine, L-alanine, N-benzoyl alanine, N-acetyl glycine and N-benzoyl glycine (BDH) were further assayed by standard method.[3] The pentaamminecobalt(III) complexes of α-amino acids were prepared as their perchlorates following the procedure of Fan and Gould.[4]

The reactions were carried out under pseudo-first order conditions using a large excess of the Co(III) bound and unbound α-amino acids over BPC. The rates of 2,2′-bipyridinium chromate oxidation of cobalt(III) bound and unbound ligands were determined by an iodometric procedure periodically.

Co(II) was estimated after the completion of reaction in the presence of excess of BPC, by diluting 10-fold with conc. HCl, allowing evolution of chlorine to cease and then measuring the absorbance of the Co(II) chloro complex at 692 nm ($\varepsilon = 560$ dm^3 mol^{-1} cm^{-1}).[5] Optical density measurements with blank solution containing BPC were made to apply suitable corrections. It was found that the amount of Co(II) formed was around 26%.

The stoichiometric studies for the BPC oxidation of cobalt(III) bound and unbound α-amino acids were carried out under the condition of BPC ≫ [substrate]. The amount of unreacted Cr(VI) was estimated iodometrically. Due blank correction for the thermal decomposition/disproportionation for Cr(VI) under the same conditions were applied. In the case of Co(III) bound α-amino acids Δ[BPC] : Δ[Co(III)] was 0.58 : 1.0 and the amount of Co(II) formed was about 25% and the other product of the reaction was glyoxylatopentaamminecobalt(III).

RESULTS AND DISCUSSION

Table-1 summarises the kinetic data for the 2,2′-bipyridinium chromate oxidation of Co(III) bound α-amino acids at 1.5 M $HClO_4$ at 60°C. Reaction exhibits overall second order kinetics first order in each reactant. BPC oxidation of α-amino acid (Table-2) is susceptible to electronic influence. The introduction of —CH_2 group at the α position of glycine increases the rate. But acylation or benzoylation of α-amino acids reduces the rate of BPC oxidation of these compounds whereas the reduction in the rate of BPC oxidation of N-benzoyl alanine is only about 2 times compared to L-alanine, suggesting that the initial attack by Cr(VI) is probably at the amino nitrogen rather than at the α-carbon atom. The addition of salts such as $MnSO_4$ and Ce(III) did not have any influence on the rate of these reactions. It seems possible that any effects due to the addition of salts, the concentration range studied may be compensated by the ionic strength of the media.

The formation of Co(II) is nearly 25% of $[Co(III)]_{initial}$ in the BPC oxidation of glycinatopentaamminecobalt(III) suggests that the cleavage of C—C and N—H bond is occurring in a synchronous manner with electron transfer to cobalt(III) and Cr(VI) in a slow step. As this forms only 25% of the total reaction, the reaction is also accompanied by the formation of glyoxylatopentaamminecobalt(III) complex (75%) wherein there are only N—H and C—H cleavages. The above observations are also in agreement with the observed decrease in the absorbance at 502 nm for the glycinatopentaamminecobalt(III) complex, which is only about 25%.

TABLE-1

KINETIC DATA FOR THE RECACTION OF 2,2′-BIPYRIDINIUM CHROMATE OXIDATION OF COMPLEXES $[(NH_3)_5Co(III)\text{-}L]^{2+}$

$[HClO_4]$ = 1.5 M Temp. = 60 ± 0.2 °C

Compound	10^2 [Compound] M	10^3 [BPC] M	$10^5\ k_1 s^{-1}$	$10^3\ k_2\ mol^{-1}\ dm^3\ s^{-1}$
Glycinato	3.00	1.00	14.96	4.9
	4.00	1.00	18.43	4.6
	5.00	1.00	24.42	4.8
	6.00	1.00	28.39	4.7
	7.00	1.00	34.23	4.8
	3.00	2.00	15.03	—
	3.00	3.00	14.87	—

Compound	10^2 [Compound] M	10^3 [BPC] M	$10^5 k_1 s^{-1}$	$10^3 k_2$ mol^{-1} dm^3 s^{-1}
N-acetylglycinato	3.00	1.00	1.93	0.64
	4.00	1.00	2.61	0.65
	5.00	1.00	3.18	0.63
	3.00	2.00	1.96	—
	3.00	3.00	1.97	—
N-Benzoylglycinato	3.00	1.00	1.73	0.58
	4.00	1.00	2.36	0.59
	5.00	1.00	2.92	0.58
	3.00	2.00	1.68	—
	3.00	3.00	1.74	—
α-alanato	3.00	1.00	18.70	6.2
	4.00	1.00	25.99	6.4
	5.00	1.00	31.83	6.3
	6.00	1.00	38.41	6.4
	7.00	1.00	44.80	6.4
	3.00	2.00	18.91	—
	3.00	3.00	18.66	—
N-benzoyl alanato	3.00	1.00	2.21	0.73
	4.00	1.00	2.84	0.71
	5.00	1.00	3.69	0.73
	3.00	2.00	2.19	—
	3.00	3.00	2.30	—

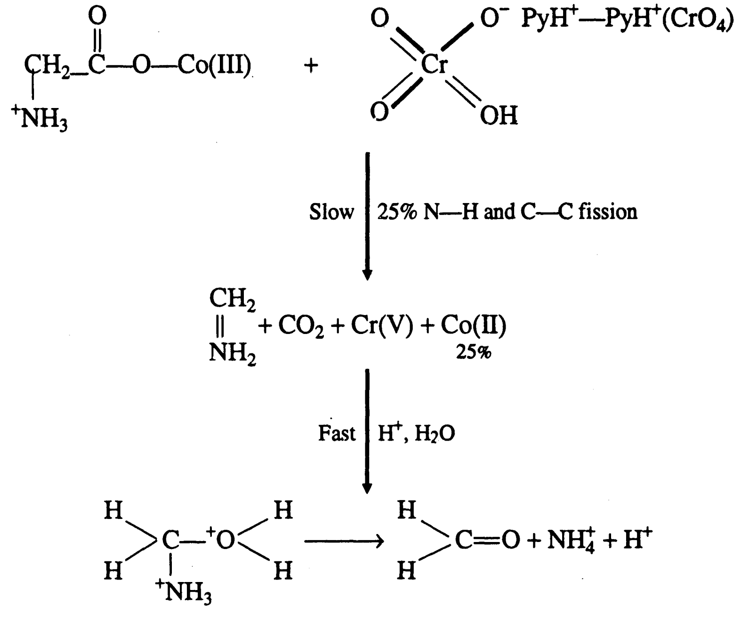
TABLE-2
SPECIFIC RATES FOR PBC OXIDATION OF α-AMINO ACIDS

$[HClO_4] = 1.5$ M; Temp. = 60 ± 0.2°C

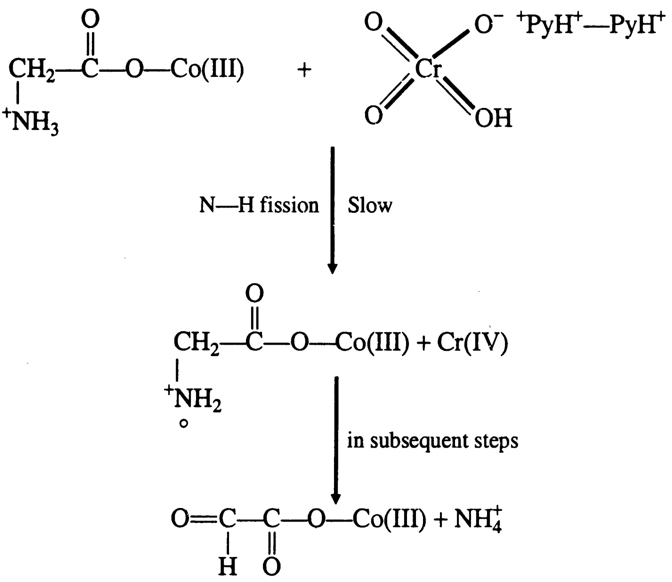
Compound	10^2 [Compound] M	10^3 [BPC] M	$10^5 k_1 s^{-1}$	$10^3 k_2$ mol^{-1} dm^3 s^{-1}
Glycinato	3.00	1.00	2.98	9.9
	4.00	1.00	3.95	9.9
	5.00	1.00	4.90	9.8
	6.00	1.00	5.92	9.8
	7.00	1.00	6.93	9.9
	3.00	2.00	2.74	—
	3.00	3.00	3.01	—
N-acetylglycinato	3.00	1.00	2.35	7.9
	4.00	1.00	3.15	7.9
	5.00	1.00	3.90	7.8
	3.00	2.00	2.40	—
	3.00	3.00	2.39	—

Compound	10^2 [Compound] M	10^3 [BPC] M	$10^5 k_1 s^{-1}$	$10^3 k_2$ mol^{-1} dm^3 s^{-1}
N-Benzoylglycinato	3.00	1.00	2.10	7.0
	4.00	1.00	2.80	7.0
	5.00	1.00	3.55	7.1
	3.00	2.00	1.99	—
	3.00	3.00	2.02	—
α-alanato	3.00	1.00	5.83	19.0
	4.00	1.00	7.66	19.0
	5.00	1.00	9.99	19.0
	6.00	1.00	12.00	20.0
	7.00	1.00	13.30	19.0
	3.00	2.00	5.79	—
	3.00	3.00	5.60	—
N-benzoyl alanato	3.00	1.00	2.69	8.9
	4.00	1.00	3.44	8.6
	5.00	1.00	4.44	8.8
	3.00	2.00	2.65	—
	3.00	3.00	2.60	—

To account for the above observations the following reaction mechanisms (Schemes I and II) have been proposed.



Scheme-1



Scheme-2

According to Scheme 1, BPC oxidises N—H centre and induces the formation of radical which in Synchronous steps undergoes C—C bond cleavage yielding cobalt(II). According to Scheme-II first it forms a nitrogen radical and then it gives glyoxylatopentaammine cobalt(III) C—H cleavage to the extent of 75%.

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