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Br(V)-Induced Electron Transfer in Pentaamminecobalt(III) Complexes of α-Amino Acids

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Br(V) induced electron transfer in pentaamminecobalt(III) complexes of α-amino acids yielding 30 % of CO_2, 30 % of Co(II) and 70 % of glyoxalato complex are ultimate products. The decrease in absorbance at 502 nm for Co(III) complex corresponds to nearly 40 % of the initial absorbance. Though the stoichiometry of Br(V) to unbound ligand is 1.0:0.6, the ratio of Br(V) to cobalt(III) complex is 1:0.3 accounting for about 40 % reduction at the cobalt(III) centre.The kinetic and stoichiometric results have been accounted by a suitable mechanism involving radical cation intermediate.

Key Words: Pentaamminecobalt(III) complexes, Induced electron transfer reaction, Complex formation, Triol.

INTRODUCTION

Mechanism of oxidative decarboxylation of α-amino acids[1-5] is of considerable interest. Since, it is one of the important biochemical processes of electron transfer in pentaaminecobalt(III) complexes of α-amino acids[6], however, some inconsistencies and incomplete work exist. The extent of Br(V) oxidation of pentaaminecobalt(III) complexes of α-amino acids as a diagnostic tool to find out the fraction proceeding by synchronous cleavages of N-H and C-C bonds.

EXPERIMENTAL

Ammonium cerium(IV) nitrate, (BDH, AnalaR grade) (anal. calculated for $(NH_4)_2Ce(NO_3)_6$:Ce 25.5 found (ignition of CeO_2) Ce, 25.5) and α-amino acids employed as ligands Aldrich) were used as obtained.

N-Acetyl and N-benzoyl glycine and N-benzoyl alanine were prepared by following the procedure of Vogel[7]. The $(NH_3)_5Co(III)$ complexes of glycine, α-alanine, N-acetyl and N-benzoyl glycine and N-benzoyl alanine were prepared as their perchlorates by the method of Fan[8]. The *tris*(*m*-hydroxo) complex $(NH_3)_3Co(OH)_3(Co(NH_3)_3(ClO_4)_3$ (triol) has been prepared by the procedure of Srinivasan *et al.*[9] and Siebert[10].

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The reaction between Br(V) and Co(III) complexes was carried out at 30 ± 0.2 ºC in a thermostated bath. The concentrations of unreacted Br(V) were determined both iodometrically and spectrophotometrically at 400 nm. The disappearance of Co(III) was followed spectrophotometrically by following the decrease in absorbance at 502 nm [for the monomeric Co(III) complex] and at 520 nm [for the dimeric Co(III) complex)]. The specific rates estimated from the optical density measurements agree with the values from the volumetric procedure with in ± 5 % curiously, the change in absorbance observed at 502 or 520 nm for the Co(III) complexes of glycine corresponds to very nearly 20 % of the initial concentration of Co(III), while the change in optical density at 400 nm for Br(V) corresponds to 30 % of $[Co(III)]_{initial}$.

Co(II) was estimated after the completion of reaction, by diluting the reaction mixture 10-fold with conc. HCl, allowing evolution of chlorine to cease and then measuring the absorbance at 692 nm (Ç = 560)[11]. The amount of Co(II) estimated in all these cases corresponds to nearly 30 % of $[Co(II)]_{initial}$.

After 48 h, the product was extracted with ether and analyzed iodometrically for the amount of HCHO formed in the case of the [glycinato] and [N-acetylglycinato]cobalt(III) complexes, the dimeric Co(III) complex and unbound glycine. The yield of HCHO in all these cases is nearly 30 % $[Co(III)]_{initial}$[12] (Table-4).

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 filteration 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 cases, the IR spectra of the product agreed with IR spectra of authentic samples of glyoxalic acid or [glyoxalato]cobalt(III) complex.

RESULTS AND DISCUSSION

Table-1 summarizes the kinetic data for the Br(V) oxidation of free α-amino acids with 1 N H_2SO_4 at 30 ± 0.2 ºC. Though the reaction exhibits first-order dependance on Br(V), kinetic saturation has been observed with respect to substrate concentration, suggesting a complex formation between Br(V) and α-amino acids.

Assuming 1:1 complex involving Br(V) and α-amino acids the following rate law has been deduced for this reaction.

TABLE-1
FIRST ORDER RATE CONSTANTS FOR Br(V) OXIDATION OF α-AMINO ACIDS AT 30 ± 0.2 ºC

Substrate (unbound)	α-Amino acids (mol dm^{-3})	10^5k_1 (s^{-1})	$10^5k_{calculated}$
a) Glycine	0.1	5.93	5.19
	0.2	6.20	6.19
	0.3	6.51	6.71
	0.4	6.81	6.70
	0.5	7.51	7.01
b) L-Alanine	0.1	4.34	4.43
	0.2	5.36	5.68
	0.3	6.37	6.29
	0.4	6.68	6.62
	0.5	6.89	6.84
c) L-Isoleucine	0.1	4.32	4.46
	0.2	6.14	6.13
	0.3	7.00	7.02
	0.4	7.51	7.54
	0.5	7.83	7.90
d) N-Acetyl glycine	0.1	40.38	41.33
	0.2	42.45	46.09
	0.3	46.27	47.92
	0.4	49.01	45.68
	0.5	49.75	49.50
e) N-Benzoyl glycine	0.1	26.57	27.94
	0.2	31.89	31.45
	0.3	32.54	32.82
	0.4	33.46	33.56
	0.5	34.10	34.01

$KBrO_3$ - 0.2 M, H_2SO_4 1 N, Mercuric acetate – 1 g, Temp. 30 ± 0.2 ºC

$$\frac{\text{rate}}{\text{Br(V)}} = k_{obs} = \frac{k_{limit}[\alpha-\text{amino acid}]}{K^{-1}+[\alpha-\text{amino acid}]}$$

where k_{limit} is the limiting specific rate observed at higher [α-amino acid]/[Br(V)] ratios and K is the formation constant for the Br(V) α-amino acid complex.

Hence, from the plot of $1/k_{obs}$ *vs.* 1/[α-amino acid] the slope and intercept can be evaluated.

Table-2 lists the formation constants for Br(V) Co(III) complexes of α-amino acid along with the limiting specific rates.

TABLE-2
FIRST ORDER RATE CONSTANTS FOR Br(V) OXIDATION OF Co(III) COMPLEXES OF α-AMINO ACIDS AT 30 ± 0.2 °C

Substrate (bound)	α-Amino acids (mol dm^{-3})	10^5 k_1 (s^{-1})	10^4 $k_{calculated}$
a) Glycine	0.1	2.61	2.47
	0.2	3.64	3.60
	0.3	4.30	4.24
	0.4	4.70	4.65
	0.5	4.80	4.95
b) L-Alanine	0.1	2.74	2.58
	0.2	3.02	3.94
	0.3	4.10	4.78
	0.4	5.56	5.35
	0.5	5.95	5.76
c) L-Isoleucine	0.1	3.94	3.33
	0.2	4.85	4.54
	0.3	5.94	5.17
	0.4	5.86	5.55
	0.5	6.23	5.81
d) N-Acetyl glycine	0.1	22.10	21.27
	0.2	25.21	27.02
	0.3	29.42	29.69
	0.4	32.20	31.24
	0.5	34.34	32.25
e) N-Benzoyl glycine	0.1	16.01	13.25
	0.2	18.10	18.64
	0.3	21.20	21.53
	0.4	23.20	23.35
	0.5	24.50	24.59

$KBrO_3$ - 0.2 M, H_2SO_4 - 1 N, Mercuric acetate - 1 g, Temp. - 30 ± 0.2 °C

Such complex formation seems to be absent when the carboxyl group linked up by Co(III) and the reaction between Br(V) and Co(III) complexes of α-amino acids exhibit uncomplicated second order kinetics.

From a comparison of the specific rates for Br(V) oxidation of the respective Co(III) complexes and the dimeric cobalt(III) glycine complex (Table-3), one can infer that the oxidation rates of α-amino acids are not significantly affected by complex formation. This may be because the point of attack lies away from the Co(III) centre so that its electrostatic influence is less felt. There is, however a considerable change in the specific rate of Br(V) oxidation of the dimeric Co^{3+} glycine complex as the two Co(III)

TABLE-3

Br(V) OXIDATION OF Co(III) COMPLEXES OF α-AMINO ACIDS

Substrate (bound)	10^4 k_{limit}** (s^{-1})	K* (m^{-1})	Correlation coefficient (γ)
Glycine	6.66	6.00	0.99
L-Alanine	7.14	4.51	0.97
L-Isoleucine	8.33	8.75	0.98
N-Acetyl glycine	37.03	13.5	0.97
N-Benzoyl glycine	31.25	7.39	0.99

*Formation constant, K for Br(V)- α-amino acid complexes were calculated as the ratio of intercept or slope from the plot of $1/k_{obs}$ *vs.* 1/[α-amino acids] at 1 N H_2SO_4 30 ± 0.2 ºC with mercuric acetate.

**The limiting specific rates were calculated from the intercept of the $1/k_{obs}$ *vs.* 1/[α-amino acids] at 1 N H_2SO_4

centres can exert greater electrostatic influence over the reacting centre. This suggests that Br(V) 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 Br(V) oxidation of Co(III) complexes of N-acetyl and N-benzoyl glycine and N-benzoyl alanine, compared to that of unbound ligands, points to significant electronic influence of the acyl group and also the electrostatic influence of the Co(III) centre at the seat of attack *viz.*, the NH group. Such electrostatic influence due to coordination of α-amino acids to the Co(III) centre (in the monomer only) 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.

The stoichiometric results indicate that for one mole of cobalt(III) complex, about 0.3 mole of Br(V) is consumed, whereas with the unbound ligands for one mole of α-amino acid about 0.4 mole of Br(V) is consumed (Table-4). The stoichiometric results coupled with kinetic data and product analysis, can be accounted by the following reaction schemes.

Scheme-I proposes that Br(V) oxidizes NH center and induces the formation of a radical which in a synchronous step undergoes carbon-carbon bond fission, yielding Co(II). As the amount of HCHO or Co(II) formed is only 30 % of $[Co(III)]_{initial}$, the above reaction probably contribute only 30 % of the total reaction.

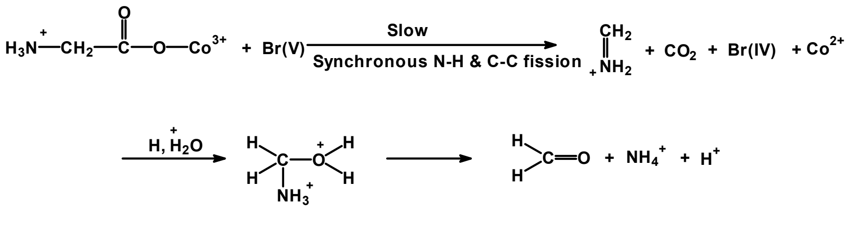
Scheme-II envisages the formation of nitrogen radical that reacts with Br(V) in subsequent steps, yielding ultimately the Co(III) complex of glyoxalic acid. This probably forms the rest of the reaction (about 80 %). In this case the amount of Br(V) consumed by one mole of Co(III) should be around 0.4 mol, which is in agreement with the observed stoichiometric

TABLE-4
STOICHIOMETRIC DATA FOR Br(V) OXIDATION OF Co(III) COMPLEXES OF α-AMINO ACIDS AND CORRESPONDING Co(III) COMPLEXES AT 30 ± 0.2 °C WITH MERCURIC ACETATE

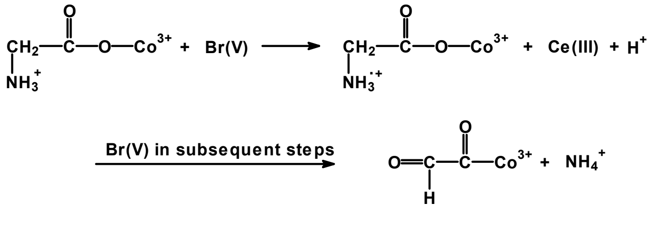
Substrate	$Compd._{initial}$ M	$[Br(V)]_{initial}$	D[Br(V): $D[Co(III)]_{initial}$	[Co(II)] mM (%)	[HCHO]** mM (%)	Glyoxalic acid mM (%)
Glycine	0.010	0.050	0.40:1	-	3.0(30)	6.9(69)
N-acetyl glycine	0.010	0.050	0.38:1	-	3.1(31)	7.1(71)
α-Alanine						
$(NH_3)_5Co^{3+}$- L^{2+}	0.010	0.050	0.38:1	-	-	-
L=Glycine	0.010	0.049	0.28:1	3.2(32)	3.0(30)	-
L=Glycine	0.020	0.100	0.29:1	5.5(27)	5.4(27)	-
L=N-Acetyl glycine	0.010	0.050	0.28:1	3.0(30)	3.1(31)	-
L= α-Alanine	0.010	0.050	0.30:1	3.1(31)	-	-
L= α-Alanine	0.020	0.100	0.30:1	5.8(29)	-	-
Co_2^{3+}(gly)*	0.010	0.050	-	-	3.3(33)	-

*Formation constant, K for Br(V)- α-amino acid complexes were calculated as the ratio of intercept or slope from the plot of $1/k_{obs}$ *vs.* 1/[α-amino acids] at 1 N H_2SO_4 30 ± 0.2 °C with mercuric acetate.

**The limiting specific rates were calculated from the intercept of the $1/k_{obs}$ *vs.* 1/[α-amino acids] at 1 N H_2SO_4.



Scheme-I



Scheme-II

results. In the case of unbound glycine and N-acetyl glycine, the consumption of Br(V) is around 0.4 mol, the yield of HCHO is about 30 % and that of glyoxalic acid is about 70 %. In the case of the Co(III) glycinato complex, the other product is the Co(III) glyoxalato compex.

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