Phenyliodoso Acetate Oxidation of Cobalt(III) Bound and Unbound α-Amino Acids

C. ANBUSELVAN and K.R. SANKARAN*
Department of Chemistry, Annamalai University, Annamalainagar-608 002, India

The kinetics of phenyliodoso acetate (PIA) oxidation of cobalt(III) bound and unbound α-amino acids have been studied in aq. acetic acid in the presence of 1.00 M HClO$_4$ at 50°C. The reaction exhibits total second order kinetics, first order in each reactant. The rate of PIA oxidation is susceptible to polar influences. The introduction of substituents at the α-carbon atom in amino acids increase rate marginally while introduction of substituents at the amino nitrogen retard the rate considerably evidencing an initial attack by PIA at amino nitrogen. The formation of glyoxylato-pentaamminecobalt(III) complex during the PIA oxidation of glycinato-pentaamminecobalt(III) complex suggests cleavage of N—H and C—H bonds.

INTRODUCTION

The oxidation of α-amino acids by cobalt(III) in aq. perchloric acid yielded ammonia and the corresponding aldehyde with C—C cleavage occurring in a slow step and N—H bond cleavage in a fast step.[1] But in the ceric sulphate oxidation of α-amino acid[2], the formation of ammonia and respective aldehyde has been explained through the formation of carboxylate radical and the cleavage of N—H and C—C bonds seems to occur in a fast step. From the yield of Co(II) and other cleavage products in the Ce(IV) oxidation of pentaamminecobalt(III) complexes of α-amino acids[3] a synchronous cleavage of N—H and C—C bonds is assumed to constitute at least 20% of total reaction. Potassium bromate oxidation of α-amino acids has been studied[4] and the formation of respective aldehyde and ammonium ion has been explained with rate-determining cleavage of N—H and C—H bonds. In the present work, we report the oxidation of Co(III) bound and unbound α-amino acids by phenyliodoso acetate (PIA).

EXPERIMENTAL

α-Amino acids used were of AnalaR grade (BDH) and were used as such after checking physical constants. Pentaamminecobalt(III) complexes of α-amino acids were prepared by the method of Fan and Gould.[5] Phenyliodoso acetate was prepared by the method of Baeseken and Schneider[6], the purity of its solution was checked by an iodometric procedure. The rate of PIA oxidation of cobalt(III) bound and unbound α-amino acids was followed by estimatiing unreacted PIA iodometrically to starch end point. Cobalt(II), one of the expected product of PIA oxidation of glycinatopentaamminecobalt(III) complex, was estimated after about nine half-lives, by diluting the reaction mixture ten times with conc. HCl, allowing the evolution of chlorine to cease and then measuring the absorbance of chloro complex of cobalt(II) at 692 nm ($\varepsilon = 560$ dm^3 mol^{-1} cm^{-1})[7]. Almost zero absorbance noted at 692 nm suggested that the yield of cobalt(II) was negligibly small. This shows that there is no C—C cleavage.

RESULTS AND DISCUSSION

The kinetic data for PIA oxidation of cobalt(III) bound and unbound α-amino acids are included in Tables 1 and 2. The reaction exhibits over all second order kinetics first order in each reactant. PIA oxidation of α-amino acids is susceptible

TABLE-1

KINETIC DATA ON PIA OXIDATION OF α-AMINO ACIDS

[HClO₄] = 1.0 M   AcOH = 50% (v/v)   Temp. = 50°C

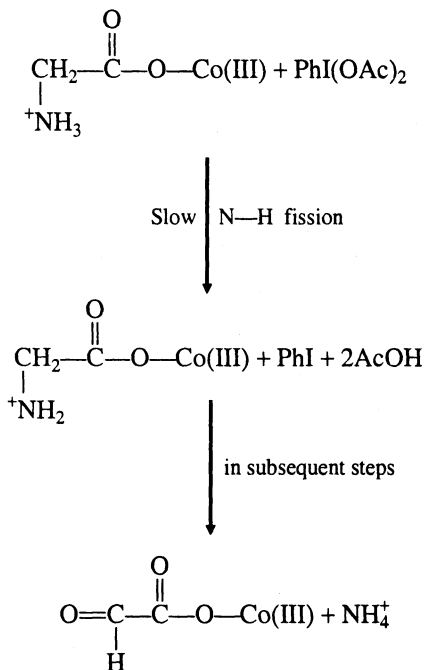| Compound	[Compound] $\times 10^2$ M	[PIA] 10^3 M	$k_1 \times 10^5$ s^{-1}
Glycine	3.00	1.00	4.04
	4.00	1.00	5.32
	5.00	1.00	6.71
	6.00	1.00	8.14
	7.00	1.00	9.42
	4.00	2.00	5.34
	4.00	3.00	5.52
	4.00	4.00	5.57
	4.00	5.00	5.08
N-Acetyl glycine	3.00	1.00	2.33
	4.00	1.00	3.15
	5.00	1.00	3.95
	6.00	1.00	4.72
	7.00	1.00	5.47
N-Benzoyl glycine	3.00	1.00	1.14
	4.00	1.00	1.51
	5.00	1.00	1.95
	6.00	1.00	2.25
α-Alanine	3.00	1.00	8.68
	4.00	1.00	10.80
	5.00	1.00	14.40
	6.00	1.00	16.70
	7.00	1.00	19.50
N-Benzoyl alanine	3.00	1.00	1.82
	4.00	1.00	2.40
	5.00	1.00	2.99

to electronic influence. Introduction of —CH_2 group at the α-position of glycine increases the rate. But acylation or benzoylation of glycine reduces the rate of PIA oxidation of these compounds at least by fivefold whereas the reduction in the rate of PIA oxidation of N-benzoylalanine more than ten times compared to alanine, suggesting that the intial attack by PIA is probably at the amino nitrogen rather than at the α-carbon atom.

TABLE-2
KINETIC DATA FOR OXIDATION OF COBALT(III)
BOUND α-AMINO ACIDS BY PIA

AcOH = 50% (v/v)	[HClO$_4$] = 1.00 M	Temp. = 50°C	
Compound	10^2 [Cobalt(III)-L] M	10^3 [PIA] M	10^4 k_1 s^{-1}
Glycine	3.00	1.00	1.590
	4.00	1.00	2.120
	5.00	1.00	2.650
	6.00	1.00	3.160
	7.00	1.00	3.780
N-Acetyl glycine	3.00	1.00	0.208
	4.00	1.00	0.285
	5.00	1.00	0.325
N-Benzoyl glycine	3.00	1.00	0.099
	4.00	1.00	0.147
	5.00	1.00	0.170
α-Alaninato	3.00	1.00	3.470
	4.00	1.00	4.570
	5.00	1.00	5.780
	6.00	1.00	6.930
N-Benzoyl alanine	3.00	1.00	0.166
	4.00	1.00	0.220
	5.00	1.00	0.280

As for the specific rates of PIA oxidation, cobalt(III) bound glycine will react faster than the unbound ligand. In the cobalt(III) complex, though, the metal ion exerts electrostatic influence on the neighbouring α-carbon atom. This is suggestive of an initial attack by PIA, in the rate determining step, at a position in glycine away from cobalt(III), possibly on the amino nitrogen. The formation of glyoxylato-pentaamminecobalt(III) complex shows that there is only N—H and C—H cleavage.

To account for the above observations, the following reaction mechanism has been proposed

$$\underset{\underset{^+NH_3}{\overset{|}{}}}{CH_2}-\overset{\overset{O}{\|}}{C}-O-Co(III) + PhI(OAc)_2$$

Slow | N—H fission

$$\underset{\underset{^+NH_2}{\overset{|}{}}}{CH_2}-\overset{\overset{O}{\|}}{C}-O-Co(III) + PhI + 2AcOH$$

in subsequent steps

$$\underset{\underset{H}{\overset{|}{}}}{O{=}C}-\overset{\overset{O}{\|}}{C}-O-Co(III) + NH_4^+$$

Glycinatopentaamminecobalt(III) will react with PIA to form nitrogen radical that reacts with variable iodine species at higher oxidation states to yield ultimately glyoxylatopentaamminecobalt(III) by C—H cleavage. Thus the present work on PIA oxidation of unbound and cobalt(III) bound glycines suggests an initial attack by PIA on the amino nitrogen resulting in a two electron transfer yielding C—N and α-C—H bound cleavage products. The formation of a radical as intermediate is also evidenced by initiation of acrylonitrile polymerisation.

REFERENCES

1. R.A. Sheikh and W.A. Waters, *J. Chem. Soc. (B)*, 988 (1970).
2. M. Adinarayana, B. Sethuram and T. Navaneetha Rao, *J. Indian Chem. Soc.*, **53**, 530 (1976)
3. K. Subramani and V.S. Srinivasan. *Inorg. Chem.*, **24**, 235 (1985).
4. S. Anandan, P.S. Subramanian and R. Gopalan, *Indian. J. Chem.*, **24A**, 308 (1985).
5. F.R. Fan and E.S. Gould, *Inorg. Chem.*, **13**, 2639 (1974).
6. J. Boesken and G.C.C.C. Schneider, *J. Prakt. Chem.*, **131**, 285 (1931).
7. E.S. Gould and N. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).