Pyrolysis studies of Metal Chelates of Pr and Nd metals with p-chlorobenzaldehydethiosemicarzone

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Abstract

Co-ordination compounds gaining ground due to its wide spectrum covering petroleum chemistry, bio-chemistry, medicinal chemistry, analytical chemistry etc. and deserves attention.

Complex of p-chlorobenzaldehydethiosemicarzone also shows anti-bacterial and anti-carcinogenic properties etc in order to understand its chemistry its structural aspects are very important. Heat is an analytical tool and has been useful in contributing greatly to ascertaining some of the structural aspects, like thermal stability, stoichiometry of compound including metal complexes.
present study includes pyrolysis study of solution of complex Pr(III) and Nd(III) metals with p-chlorobenzaldehydethiosemicarzone.

Key Words- Pyrolysis, Co-ordination compounds

Introduction

Considerable interest in recent years has been generated in structural aspects of metal complexes of thiosemicarbazones, possessing the carcinostatic properties with the view to understand their mode of action. The field is being greatly addressed on account of its promising role in fighting the disease like cancer.

Besides exploration on the metal-thiosemicarbazones complex in solid state, their solution chemistry too deserve the attention of the researchers[1-7]. Observation on the increased activity of some drugs when administered as metal complexes by William[8],Frunst *et al*.[9] and inhibition of tumor growth with metal complex of thiosemicarbazones by Dwyer et al.[10] have further increased the interest on coordination chemistry.

Synthesis of P-chlorobenzaldehydethiosemicarbazone

Equimolar solution of thiosemicarbazide in (aquous base) was reacted with equimolar solution of p-chlorobenzaldehyde (acetone base) at room temperature with constant stirring. When the reaction was complete, dirty white ppt was filtered, washed and kept overnight in oven at 35^{o}-40^{o}C. for drying

Instruments

Elemental Analyser Model 4208, for pyrolysis study, manually operated assembly equipped with Toshmiwal furnace, duly standardized with calcium oxalate are employed.

Experiment

All the chemical used were of analytical grade, For isolation of metal complexes of Pr, Nd, three moles of p-chlorobenzaldehydethiosemicarzone(in acetone) were mixed with a mole of metal ion, the deepening of colour resulted on mixing. On mild shaking following by cooling the precipitate appeared in all cases. The precipitate was filtered, washed with ice cooled water and dried at 35^{o}-40^{o}C. The elemental analysis agreed to the accompanying composition:
$Pr.R_3.2H_2O$ and $Nd.R_3 1½H_2O$ where R = $Cl.C_6H_4.CH=N-N=CS-NH_2$.

Result and Discussion

Thermogram of metal complex of p-chlorobenzaldehydethiosemicarzone with Pr(III) : $Pr.R_3.2H_2O$ where R is an anion of chelator consists of five plateaus which successively correspond to the stable phases of $Pr.R_3.2H_2O$, $Pr.R_3$., $Pr.R_2$., Pr. 3/4R., Pr_2O_3. $Pr.R_3.2H_2O$ is stable upto 76°C. From 76°C to 96°C two water molecules were lost leaving behind anhydrous chelates: $Pr.R_3$ which could uphold its identity in the temperature range 96°-110°C. The departure, from this stable phase of R molecule began at 110°C and was complete at 252°C, resulting in other intermediate with definite composition: $Pr.R_2$ (252°C-316°C) which further raising the temperature lost 11/4R molecules from 316°C to440°C. Pr.3/4R was constant in weight upto 480°C and after which the rest of the organic molecule was sliced off upto 500°C forming Pr_2O_3 as an end product. Table 1 contains the analytical data on the decomposition progress of chelate. $Pr.R_3.2H_2O$----------→ $Pr.R_3$---------→ $Pr.R_2$-----→ Pr. 3/4R--→ Pr_2O_3

Pyrolysis curve of Nd.R3. $1^1/_2H2O$ manifested four leveled off portion demonstrating the species of definite composition within certain temperature range:

Stable Phase	Temp. range (°C)
Nd.R3. $1^1/_2H2O$	Upto 92
Nd.R3	132-160
Nd. $1^1/_2R$	320-360
Nd_2O_3	540 onwards

The slope appearing between first two plateaus corresponded to the departure of $11/2H_2O$ molecules from 92°C-132°C. In the temperature range: 160°C-320°C, 11/2R molecules of the chelator cleaved leaving behind a constant species having definite composition as represented by the third plateau. Before the formation of Nd_2O_3 540°C onwards, loss of 11/2R molecules from 360°C to540°C was observed (Table 2)

Table:1Pyrolysis Data On Progress Of Decompostion Of tris-(p-chlorobenzaldehydetiosemicarbazonato) Pr(III)2H2O

Stability/Phase (Temp. Range)°C	Loss (Temp. Range) ^0C	% Loss		% Pr_2O_3	
		Calc.	Found	Calc.	Found
Pr. R_3. $2H_2O$ (upto 76^0C)	$2H_2O$ (76-96)	04.42	04.09		
Pr. R_3. (96-100)	R (110-252)	27.64	27.72		
Pr. R_2 (252-316)	1¼R (316-440)	60.16	60.00		
Pr. ¾ R (440-480)	R	79.40	75.50		
Pr_2O_3 (560 onwards)	--	---	---	20.57	24.36

% losses are accumulated

R = Cl. C_6H_4. CH = N – N = C – NH_2
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S

Stability/Phase (Temp. Range)^{o}C	Loss (Temp. Range) ^{0}C	% Loss		% ND_2O_3	
		Calc.	Found	Calc.	Found
Nd. R_3. 1½H_2O	1½H_2O	3.17	3.15		
(upto 92)	(92-132)				
Nd. R_3.	1½R	39.93	39.00		
(132-160)	(160-320)				
Nd. 1½R	1¼R	82.10	82.84		
(320-360)	(360-540)				
Nd_2O_3	--	--	--	19.74	18.42
(540 onwards)					

% losses are accumulated

R = Cl. C_6H_4. CH = N – N = C – NH_2
|
S

Table:2 Pyrolysis Data On Progress Of Decomposition Of tris-(p-chlorobenzaldehydetiosemicarbazonato) Nd(III)11/2H2O

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