Thermal Studies on Chelates of 2-Hydroxy-4-Aminobenzoic Acid with Group IB and IIB Metals

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Summary: Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) have been employed in the present work to investigate thermal stability, stoichiometry and cleavage patterns of the chelates of 2-hydroxy-4-aminobenzoic acid (sodium salt) with group IB, IIB metals and Ni. The decomposition patterns revealed interesting information about bonding situations and thermodynamic values of the complexes.

Introduction

Insufficient data are available in the literature on thermal fragmentation of chelates derived from salicylates. Roston and Spirey have reported that dipotassium salicylate on heating in a closed container between 207°-240°C yields *p*-hydroxybenzoate almost quantitatively [1]. On the other hand, during the investigation on the thermal rearrangement of alkali metal salts of hydroxybenzoic acids, it was found that potassium salt of *o*- and *p*-hydroxybenzoic acids remained stable upto 180°C and no isomerisation from *o*- to *p*-isomer took place [2]. Ammonium nitrate propellants containing salts of nitrosalicylic acids as combustion catalyst have been patented. These substantially ash-free propellants, having low ignition temperature and pressure exponents, burn smoothly and are stable when stored at low temperature [3]. In this paper chelates of 2-hydroxy-4-aminobenzoic acid with group IB, IIB metals and Ni have been subjected to thermal degradation and the results are reported here.

Results and Discussion

It is obvious from the TGA data in Table-1 that the hydrated copper(II) chelate of 2-hydroxy-4-aminobenzoic acid (i) loses its lattice water between 100°-120°C [4] corresponding to a weight loss of 4.52% against theoretically required loss of 4.67 %. The differential thermal analysis (DTA) (Fig. 1) indicates that this dehydration is an endothermic process, which begins at about 100°C and becomes prominent at 100°C as reflected by an inflection at this temperature. However, the process of dehydration appears to be complete at about 120°C. The resulting dehydrated chelate remains thermally stable between 120°-200°C. An endothermic change is again observed at 210°C. The reduction in weight (37.5%) between 200°-260°C nearly matches with the cleavage of the

Table-1: TGA of some chelates of groups IB and IIB metals with 2-hydroxy-4-aminobenzoic acid

Temp. (°C) Thermal Step	% Loss Actual (Calc.)	Assignment
	$(C_7H_6O_3)_2$ Cu(H_2O)	
100-120	4.52 (4.67)	loss of lattice H_2O
120-200	—	thermal stability
200-260	37.50 (39.48)	loss of one ligand
260-310	—	no striking change
310-700	—	complete decomposition and formation of oxide
	$(C_7H_6O_3N)$ Ag(H_2O)	
165-220	6.08 (6.47)	loss of coord. H_2O
200-380	—	thermal stability
380-540	38.20 (38.85)	loss of Ag metal
>540	—	formation of oxide
	$(C_7H_6O_3N)_2$ Zn$(H_2O)_4$	
100-120	4.02 (4.44)	loss of lattice H_2O
120-180	3.94 (4.44)	loss of coord. H_2O
180-440	—	thermal stability
440-580	36.90 (37.53)	loss of one ligand
>580	—	formation of oxide
	$(C_7H_6O_3)_2$ Cd$(H_2O)_4$	
80--120	7.34 (7.37)	loss of lattice H_2O
160-180	7.23 (7.37)	loss of coord. H_2O
200-400	—	thermal stability
400-600	29.78 (31.15)	loss of one ligand
>600	—	formation of oxide
	$(C_7H_6O_3N)_2$ Hg$(H_2O)_3$	
190-210	10.16 (9.66)	loss of coord. H_2O
260-280	26.7 (27.19)	loss of one ligand
280-600	35.50 (35.96)	loss of Hg metal
>600	—	formation of oxide
	$(C_7H_6O_3N)_2$ Ni$(H_2O)_2$	
160-200	8.86 (9.23)	loss of coord. H_2O
200-260	—	thermal stability
260-300	37.82 (38.07)	loss of one ligand
300-440	14.26 (14.79)	elimination of metal
>440	—	formation of oxide

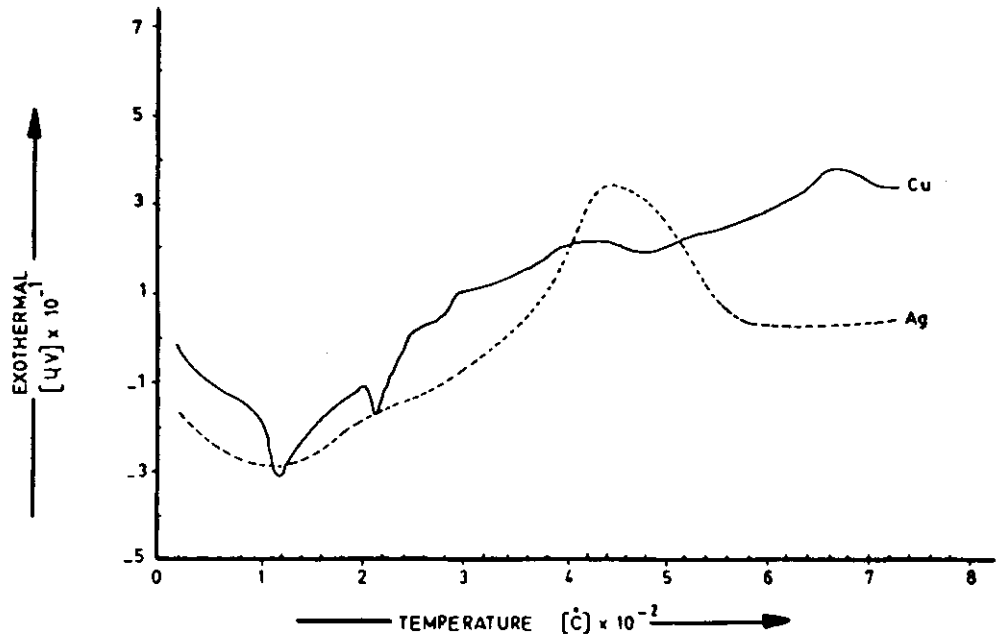

Fig.1: Differential thermal analysis of group IB metals chelates of 2-hydroxy-4-aminobenzoic acid (sodium salt).

chelate corresponding to one ligand molecule, which theoretically requires a weight loss of 39.48%. Further on no striking change is noticed between 260°-310°C. Beyond this temperature (310°-700°C) complete decomposition takes place and the metal content gradually transforms to its oxide.

It may be inferred from the TGA data in Table-1 and DTA (Fig. 1) that the silver chelate of 4-aminosalicylic acid (ii) loses coordinated water [4] between 165°-220°C. This dehydration is accompanied by a loss of 6.08% weight as against 6.47% required theoretically. The unsolvated silver chelate indicates thermal stability between 220°-380°C but with some physical changes. It, however, undergoes complete rupture between 380°-540°C and loses 38.12% weight almost corresponding to the theoretical loss of silver metal (38.85%). Thereafter, the metal converts to its oxide beyond 540°C.

It is clear from the TGA data in Table-1 and DTA (Fig. 2) that the zinc chelate of 4-aminosalicylic acid (iii) initially loses lattice water endothermally between 100°-120°C followed by loss of coordinated water between 120°-180°C indicating a loss of 4.02% and 3.94% respectively against theoretical requirement of 4.40% in each case. The resulting dehydrated chelate shows considerable thermal stability between 180°-440°C. Thereafter, the weight loss of 36.90% between 440°-580°C corresponds to the loss of one ligand against 37.53% required theoretically for this elimination. The metal transforms to its oxide beyond 580°C.

It is gathered from the TGA data in Table-1 and DTA (Fig. 2) that the cadmium chelate of the 4-aminosalicylic acid (iv) loses water molecules in two steps. The first endothermic loss of two lattice water molecules takes place between 100°-120°C followed by an another loss of two coordinated water molecules between 160°-180°C [4]. Thus, an over all experimental loss of 14.57% is observed against calculated loss of 14.74% for complete dehydration. The anhydrous chelate remains thermally stable between 200°-400°C. Thereafter, one ligand molecule gets lost between 400°-600°C; this transformation is attended with a loss of 29.78% against theoretical amount of 31.15%. Consequently, complete cleavage of the remaining segment and formation of metal oxide takes place beyond 600°C.

It is apparent from the TGA data in Table-1 and DTA (Fig. 2) that mercury chelate of 4-aminosalicylic acid (v) loses 10.16% weight

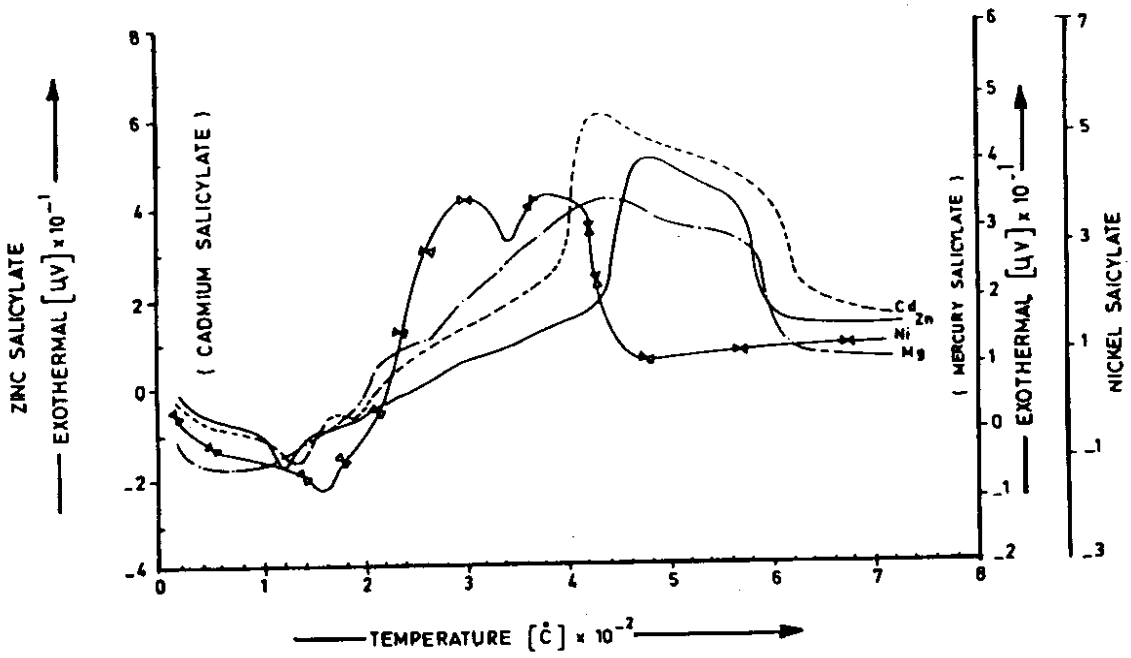

Fig.2: Differential thermal analysis of group IIB metal chelates of 2-hydroxy-4-aminobenzoic acid (sodium salt).

endothermally as against 9.66% theoretically required for the loss of three coordinated water molecules from this complex [4]. This process of desorption continues upto 210°C. The dehydrated complex loses one ligand molecule between 260°-280°C followed by the loss of mercury between 280°-600°C. These transformations indicate weight losses of 26.7% (calculated 27.19%) and 35.5% (calculated) respectively. Consequently, the oxide of the metal is obtained beyond 600°C.

It may be deduced from the TGA data collected in Table-1 and DTA (Fig. 2) that nickel chelate of 4-aminosalicylic acid (vi) loses two coordinated water molecules endothermally between 160°-200°C [4]. This dehydration process represents a weight loss of 8.86% against 9.23% theoretically required loss. The dehydrated chelates remains stable between 200°-260°C followed by loss of one ligand molecule between 260°-300°C. The latter change indicates a weight loss of 37.82% against theoretical requirement of 38.07% loss. The remnant loses metal between 300-440°C in accordance with a weight loss of 14.6% against theoretical demand of 14.79%. During this cleavage the material undergoes an other endothermic change at about 340°C. After the elimination of metal, oxide formation takes place beyond 440°C.

It may be concluded from TGA and DTA results that chelates of 4-aminosalicylic acid with group IB, IIB metals initially lose lattice water followed by the coordinated water and subsequently cleave with loss of one ligand molecule in case of bidentate products in conformity with an earlier report [1]. As the temperature increases the remaining materials undergo complete or partial rupture. Consequently, the eliminated metals transform to their respective oxides which show considerable thermal stability upto 700°C.

Experimental

The following chelates of 2-hydroxy-4-aminobenzoic acid (sodium salt) with group IB, IIB metals and Ni have been synthesised: i) $(C_7H_6O_3N)_2$ $Cu(H_2O)$, ii) $(C_7H_6O_3N)Ag$ (H_2O), iii) $(C_7H_6O_3N)_2$ $Zn(H_2O)_2$, iv) $(C_7H_6O_3N)_2$ $Cd(H_2O)_4$, v) $(C_7H_6O_3N)_2$ $Hg(H_2O)_3$ and vi) $(C_7H_6O_3N)_2$ $Ni(H_2O)_2$.

The details of their synthesis and other analyses have already been reported recently [5]. Simultaneous thermal analyser NETZSCH, Model

SAT-429, was used for their thermal studies and all the thermograms were recorded in air. In this connection each samples (60 mg) was heated upto 800°C at the rate of 1°C/min in the alumina crucible of the thermal analyser. Alumina (previously burnt at 1000°C for 30 min.) was used as the reference material.

Thermogravimetric analysis (TGA) data of the chelates of group IB, IIB metals and Ni with 2-hydroxy-4-aminobenzoic acid (sodium salt) are given in Table-1 and their differential thermal analysis (DTA) are depicted in Figs. 1 and 2 respectively.

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