

Thermal Stabilities of Isomeric Alkaline earth Chelates of Phthiocol and Plumbagin

Mrudula P. Wadekar

Assistant Professor

Department of Chemistry

Y. M. College, Bharati vidyapeeth (Deemed to be) University, Pune, India.

ABSTRACT:

Thermal decomposition of isomeric chelates of Mg(II), Ca(II), Sr(II), Ba(II) of some hydroxy 1,4 naphthoquinones named as phthiocol and plumbagin are studied with the help of TGA and DSC. The Phthiocol (3Methyl 2hydroxy 1,4 naphthoquinone) and plumbagin (2Methyl 5hydroxy 1,4 naphthoquinone) are position isomers of each other due to different positions of hydroxyl groups on naphthoquinone. They form five and six membered hetero rings with metals as a result of chelation. The resulting chelates also exhibit ring isomerism due to difference in their ring size. Thermal properties of isomeric metal chelates of phthiocol and plumbagin are compared which are found to be distinctly different. A comparative study of the thermal patterns isomeric pairs of chelates throw light on relative number of coordinated water molecules and thermal stabilities. In general alkaline earth chelates of phthiocol are found to be thermally more stable than plumbagin. Thermal stabilities are found to be inversely proportional to atomic number of alkaline earth metals.

Key Words: Phthiocol, Plumbagin, Thermal Properties

INTRODUCTION:

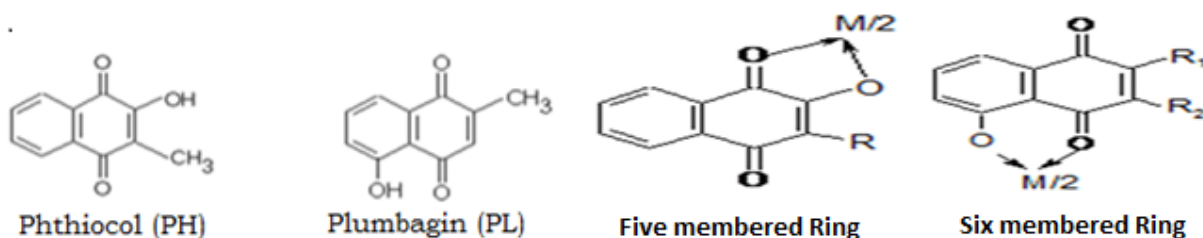


Fig-1 Phthiocol plumbagin and its isomeric metal chelates

Hydroxy derivatives of 1,4 naphthoquinone such as phthiocol and plumbagin belong to a unique group of ligands which is recognized as 'Juglones' Fig-1. These two members possess excellent coordinating properties and can form a large number of metal complexes which are conveniently called as 'Juglonates'. The metal chelates of phthiocol and plumbagin are called as metal phthiocolates and metal plumbaginates. Literature review reveals that very less studies are reported on coordination, analytical and biological characteristics of alkaline earth juglonates. We have previously reported, the some spectral and antimicrobial properties of Mg(II), Ca(II), Sr(II), Ba(II) juglonates [1-2]. The metal chelates of phthiocol result in five membered chelate ring while the metal chelates of plumbagin result in six membered ring chelates showing significantly different structural and biological properties. Fig-1. The difference in ring size results in formation of two series of isomeric metal chelates. It has been found that six membered alkaline earth juglonates are thermodynamically more stable than five membered juglonates. As a continuation of this work, we have reported a comparative study of thermal decomposition behavior of isomeric alkaline earth chelates.

MATERIAL AND METHODS:

The detailed method of synthesis of ligands and alkaline earth chelates is described in our previous communications [1-2].

Synthesis of ligands: Phthiocol is prepared from 2-methyl,4 naphthoquinone (Fluka A G Switzerland) by following method suggested by Fieser [3] while plumbagin is a commercial product obtained from HiMedia (India)

Synthesis of Chelates: The alkaline earth chelates of phthiocol and plumbagin were precipitated by mixing the corresponding metal ion solution and ligand solution in 1:2 proportion and by adjusting required pH followed by refluxing the mixture for three hours. The precipitated chelates were filtered and dried.

Thermal Analysis of Chelates:

The TG and DSC patterns of the chelates were recorded on NATZSCH simultaneous thermo analyzer STA-490 model in air atmosphere in the temperature range of RT to 1000°C. The sample used for each run was 4-5mg and the heating rate was maintained 10°C per minute.

RESULT AND DISCUSSION:

Our previous studies based on elemental analysis and IR spectroscopy indicate the chemical composition of the metal complexes is $[ML_2 \cdot 2H_2O] \cdot nH_2O$ where M is Mg(II), Ca(II), Sr(II) or Ba(II), L is ligand:phthiocol or plumbagin and n is number of lattice water associated with water. The ligands are coordinating the central metal through phenolic oxygen and hydroxyl oxygen. Fig-2. The thermal patterns of the chelates are presented in the Fig-3 and the oxidative stepwise decomposition is summarized in Table-1. The important observations from DSC curves are depicted in Table-2.

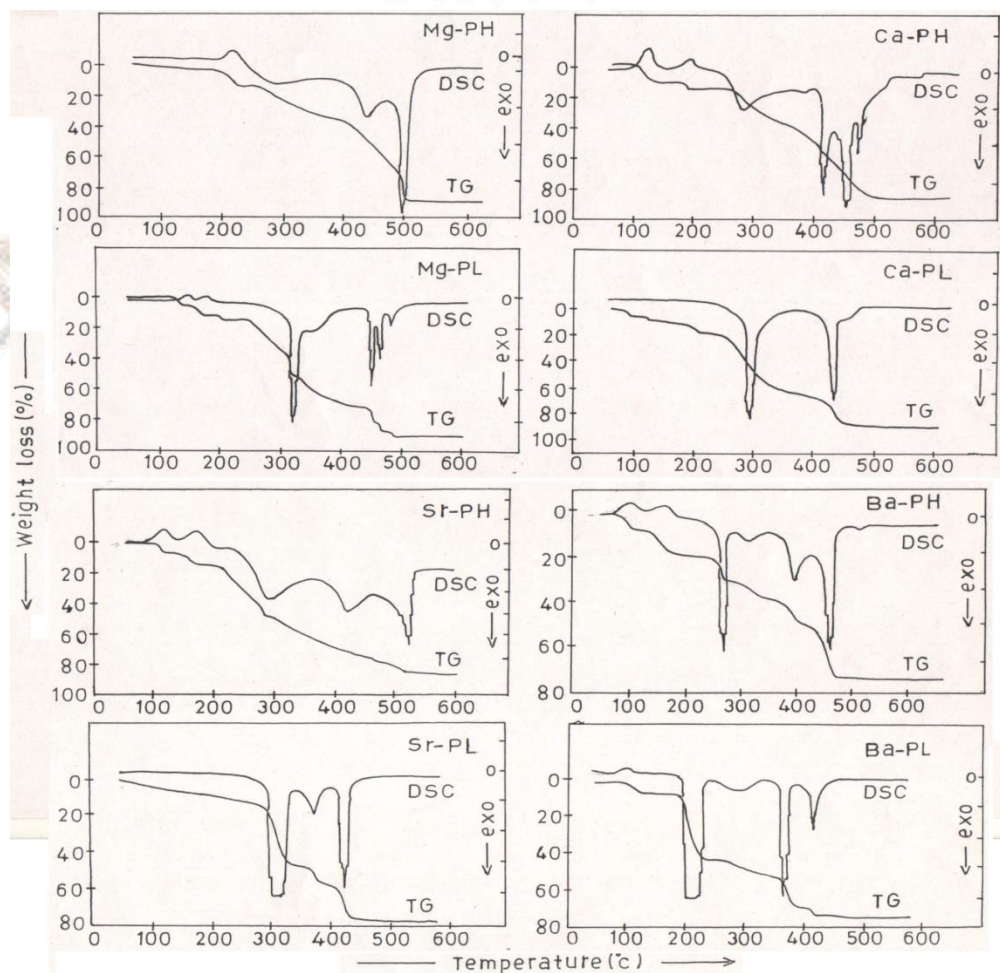


Fig-2 TGA and DSC Curves of Alkaline earth chelates of Phthiocolate and Plumbaginates

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Table-1 Stepwise Thermal Decomposition of Alkaline earth Chelates.

Chelate	Steps of Decomposition.	Temp Rang (0C)	% Wt Loss	Tentative Assignment
Mg-PH	I	208-236	8	Loss of two water molecules
	II	236-418	28	Partial oxidative decomposition of the two ligands
	III	418-512	47.20	
				% Residue= 8.35 (9.29)
Mg-PL	I	135-176	10	Loss of two water molecules
	II	176-330	42.60	Oxidative decomposition of one ligand
	III	330-482	37.40	Oxidative decomposition of remaining ligand
				% Residue= 10.00 (9.29)
Ca-PH	I	100-195	15.00	Loss of four water molecules
	II	265-407	37.50	Oxidative decomposition of one ligand
	III	407-507	24.40	Oxidative decomposition of remaining ligand
				% Residue= 11.97 (11.93)
Ca-PL	I	60-315	52.00	Loss of Three water molecules along with one ligand
	II	315-465	36.00	Oxidative decomposition of remaining ligand
				% Residue= 13.48 (11.93)
Sr-PH	I	84-169	13.14	Loss of four water molecules
	II	169-298	35.07	Oxidative decomposition of one ligand
	III	298-528	32.06	Oxidative decomposition of remaining ligand
				% Residue= 19.51 (19.41)
Sr-PL	I	60-340	45.68	Loss of two water molecules along with one ligand
	II	340-460	33.70	Oxidative decomposition of remaining ligand
				% Residue= 20.74 (21.24)
Ba-PH	I	80-177	15.80	Loss of five water molecules
	II	177-275	12.80	Oxidative decomposition of two ligand
	III	275-462	37.80	
				% Residue= 25.23 (25.48)
Ba-PL	I	78-118	3.40	Loss of one water molecule
	II	206-232	33.50	Loss of one water molecule along with Oxidative decomposition of two ligands
	III	250-425	29.80	
				% Residue= 32.41 (32.33)

Table-2 Analysis of DSC curves of Alkaline Earth Chelates

Chelate	Temp rang °C	Peak Temp °C	Reaction Type
Mg-PH	208-236 236-418 418-512	-	Endothermic Exothermic Exothermic
Mg-PL	135-176 176-330 330-482	142.0 176.0 320.0 450.3 464.3 481.0	Endothermic Endothermic Exothermic Exothermic Exothermic Exothermic
Ca-PH	100-195 265-407 407-507	127.2 193.6 283.7 415.6 452.4 474.2	Endothermic Endothermic Exothermic Exothermic Exothermic Exothermic
Ca-PL	60-315 315-465	295 434	Exothermic Exothermic
Sr-PH	84-169 169-298 298-528	120.3 168.2 294.8 425.0 524.9	Endothermic Endothermic Exothermic Exothermic Exothermic
Sr-PL	60-340 340-460	322.2 376.6 425.0	Exothermic Exothermic Exothermic
Ba-PH	80-177 177-275 275-462	105.2 168.1 270.0 317.0 399.4 453.6	Endothermic Endothermic Exothermic Exothermic Exothermic Exothermic
Ba-PL	80-118 206-232 250-425	116.0 229.1 373.8 424.7	Endothermic Exothermic Exothermic Exothermic

The nature of the TG as well as DSC curves for alkaline earth phthiocolates is remarkably different from that of the corresponding plumbaginate which suggests that the modes of decomposition of the two series are different. This difference is indicative of the difference in the packing systems of phthiocolates as compared to plumbaginate.

The decomposition temperatures show that in general the phthiocolates are thermally more stable than the plumbaginate. The initial as well as the final decomposition temperatures are lower for plumbaginate than phthiocolates (Fig-3). This shows that, in phthiocolates which involve five membered ring, intermolecular forces are stronger than those, in plumbaginate which involve six membered ring.

The initial weight loss in the temperature range (100-230 °C) is attributable to loss of lattice and coordinated water associated with the metal chelates [4].

For Mg-PH two water molecules are lost showing one endothermic peak at 220.1 °C in DSC. Its isomeric chelate Mg-PL show two endothermic peaks at 142 °C and 176 °C corresponding to sequential wt loss of two coordinated water molecules.

For Ca-PH two endothermic peaks are seen at 127.2 °C and 193.6 °C which are attributable to lattice and coordinated water molecules respectively. On the contrary for Ca-PL, loss of water molecules takes place along with the ligand showing no endotherm.

Similarly TG-DSC pattern of the Sr-PH displays two endothermic peaks at 120.3 °C and 168.2 °C corresponding to loss of two lattice and two coordinated water molecules respectively but in Sr-PL, loss of water molecules takes place along with the ligand.

The TG pattern of Ba-PH indicates loss of five water molecules in the temperature range of 80-177 °C. The first endotherm at 105 °C could be due to loss of three water molecules while the second endotherm at 168 °C could be due to two coordinated water molecules.

Therefore, in general, for all the phthiocolates, the water molecules are lost initially and then partial decomposition of the ligands takes place. In plumbagينات, for Mg(II) and Ba(II) chelates, similar trend is observed but for Ca(II) and Sr(II), loss of water molecules takes place along with the ligand.

The initial loss of water molecules in four phthiocolates and two plumbagينات referred above is clearly indicated by the endotherms in the DSC curves but such clear endotherms for loss of water molecules are not observed for the remaining two plumbagينات, due to the simultaneous loss of ligands along with water molecules. Secondly the endotherms observed for phthiocolates in the DSC curves are more prominent than in plumbagينات. Therefore it may be concluded that water molecules are more strongly bonded in plumbagينات as compared to those in phthiocolates. Further the study supports presence of two coordinated molecules in each chelates. Calculation of number of coordinated water molecules is useful to decide the coordination number six in the present metal complexes.

The exothermic peaks observed in DSC curves of the five membered metal phthiocolates and six membered plumbagينات show different stages of decomposition process which are significantly different as indicated by their peak positions and peak shapes. The endothermic peaks are resulted due to vaporization of water molecules and exothermic peaks are resulted due to decomposition of ligands.

Finally, the percent residue obtained from TG curves, left behind in the form of metal oxides, matches with percent residue calculated from theoretical calculations.

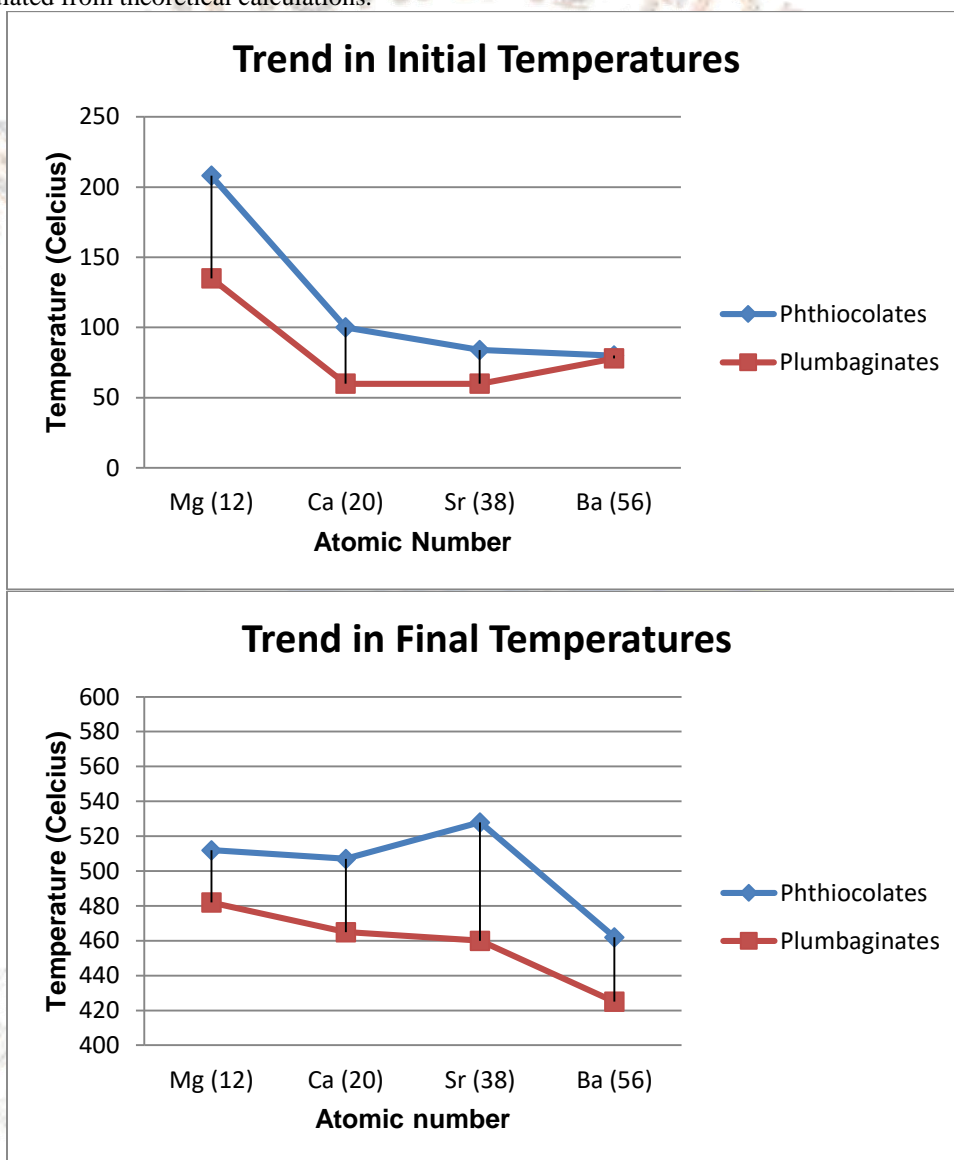


Fig-3 Trend in Initial and Final Temperatures of Alkaline earth Phthiocolates and Plumbagينات

From Mg chelates to Ba chelates, procedural and final decomposition temperatures of alkaline earth chelates under study go on decreasing (Fig-3.) This may be correlated to the bond dissociation energy of alkaline earths metals which decreases with increasing atomic number [5]. Accordingly thermal stability decreases with increasing Atomic numbers.

When thermal stability of isomeric pairs is compared, the five membered phthiocolates are observed to be thermally more stable than six membered plumbagينات, as seen from their initial and final decomposition temperatures (Fig-3). Greater thermal stability of phthiocolates is attributed to stronger intermolecular hydrogen bonding present in them [6]. On the other hand very weak intermolecular hydrogen bonding in plumbagينات results in lower thermal stability in them.

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