Thermal studies of free base and metalloporphyrins

S.D. Gokakakar[1] and P.K. Ajikumar[2], A.K. Tyagi[2] and A.V. Salker[1]*
[1] Dept. of Chemistry, Goa University, Goa – 403206, India.
[2] Mater. Sci. Div., IGCAR, Kalpakam, India.
***e-mail: sal_arun@rediffmail.com**

Abstract

Tetraphenyl porphyrin (TPP) and Metalloporphyrins (MTPP) were synthesized, where M = Cu and Fe. These compounds were characterized by UV-Visible spectrophotometry, FTIR spectrophotometry, and ^{1}Hmr spectroscopy. Thermal studies of these porphyrins were carried out using TG-DSC analyzer in synthetic air from room temperature to 800° C. The residue was then analyzed qualitatively, which shows presence of respective metals. Further, FeTPPCl was subjected to TG-EGA-MS analysis for the detailed information of evolved gases at corresponding temperatures.

Introduction

Much of the current research activities in porphyrins deals with the synthetic analogues to biologically important molecules. These extraordinarily interesting compounds can act as photocatalysts in redox reactions, storage and transportation of oxygen, photosynthetic energy conversions, semiconductors, fluorescent probes and sensitizers in photodynamic therapy [1-3]. The present objective of our study is focused on the thermal stabilities of base free porphyrin and metalloporphyrins. Further, this was supplemented by TG-EGA-MS study of FeTPPCl.

Experimental

TPP was synthesized by the suitable known method [4]. The equimolar quantities of AR grade pyrrole and benzaldehyde were refluxed in propionic acid for half an hour, cooled, filtered and washed with hot methanol followed by hot water. The TPP obtained was purified further by dry column chromatography using silica gel and AR grade $CHCl_3$ as a mobile phase. The recovery of pure TPP was more than 90%.

Metalloporphyrins such as CuTPP and FeTPPCl were synthesized by the standard method [5]. TPP was dissolved in refluxing dimethyl formamide (DMF), then corresponding metal salts were added more than two folds in stiochiometry and the reaction was refluxed for 10 - 15 minutes. The mixture was cooled, added cold water to it and filtered. The purification of CuTPP and FeTPPCl was done using dry column chromatography with silica gel.

The above porphyrins were characterized by UV-Visible spectrophotometry, FTIR spectroscopy and ^{1}Hmr spectroscopy. The thermal studies of these compounds were done using NETZSCH-Geratbau GmbH thermal analyzer (STA 409PC). The TG-EGA-MS study was done for FeTPPCl up to 800°C.

Results and Discussion

The porphyrins TPP, CuTPP and FeTPPCl were characterized by UV-Visible spectrophotometry. The corresponding bands in soret and Q- bands are in good agreement with the literature. FTIR spectroscopy was used to characterize the above compounds. ^{1}Hmr was also used as a characterization tool for above porphyrins.

Figures 1 and 2 show the thermal behaviour in TG-DSC thermograms of porphyrins TPP and FeTPPCl respectively. The measurements reveal that all these compounds are thermally stable upto 400°C. TPP shows four stages of decomposition. First decomposition of TPP takes place at 432°C, second at 472°C, third at 545°C and last at 718°C respectively. The decomposition temperatures of FeTPPCl shows 397°C, 439°C, 481°C and 562°C in four stages respectively. In base free TPP, the weight loss is nearly complete whereas in metalloporphyrins like CuTPP and FeTPPCl the weight loss was nearly 85%. This fact discloses that after metallation of porphyrins , metals are remaining in the residual form as metal oxides and therefore complete weight loss is not seen. Qualitative analysis of the residues of CuTPP and FeTPPCl has shown the presence of respective metals. With regards to the thermal stabilities of the above porphyrins, it is seen that they decrease in the following order, CuTPP > TPP > FeTPPCl. The reasoning for this may be attributed to the fact that, TPP a free base porphyrin possesses a rectangular geometry with D_{2h} symmetry whereas in CuTPP porphyrin ring becomes square with D_{4h} symmetry. Therefore decomposition temperatue of CuTPP is higher than

TPP. In FeTPPCl, chlorine is an axial ligand attached to central Fe, which possesses square pyramidal geometry.

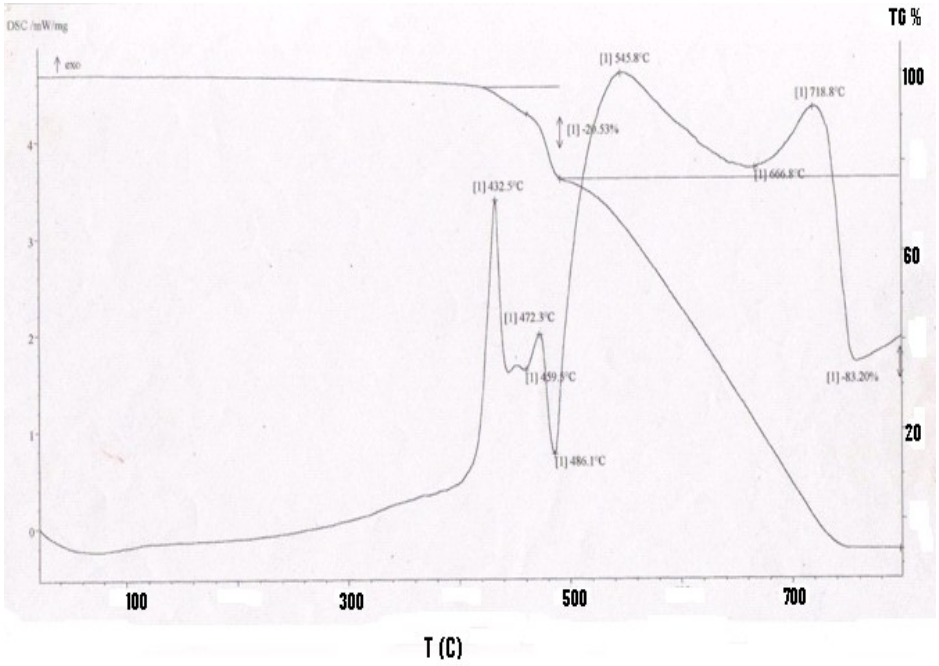

Fig. 1 TG/DSC of porphyrin TPP

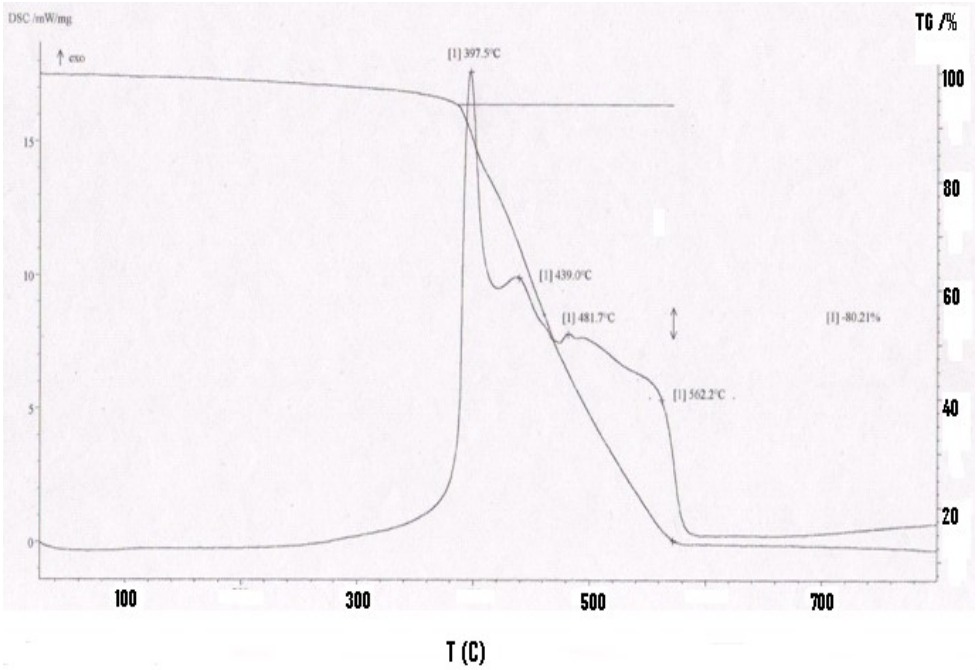

Fig. 2 TG/DSC of FeTPPCl

Figure 3 shows TG-EGA-MS results of FeTPPCl. According to the information available from the figure is that there is evolution of Hydrogen, CH_2, Nitrogen and minutely HCl gases respectively at different temperatures. This throws light on the fact that there is a rupture of porphyrin ring with hydrocarbons and imino groups followed by axial ligand Cl at different temperatures. In the beginning slight loss in weight may be reasoned out for loss of CH_2 species.

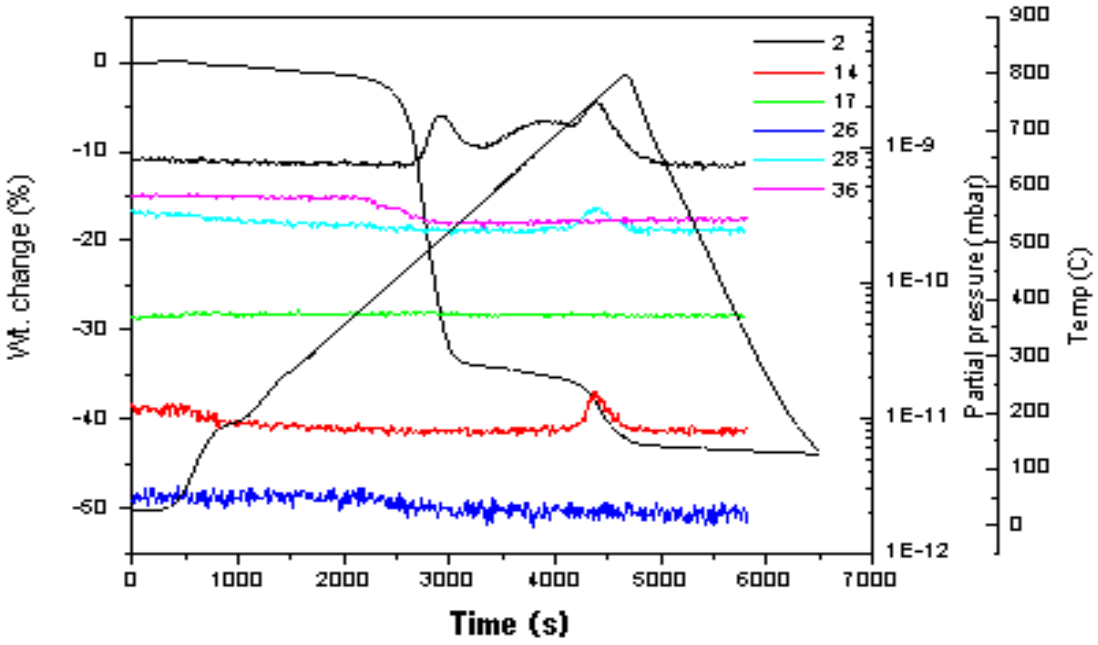

Fig. 3 TG-EGA-MS results of FeTPPCl

The TG/DSC studies did not show any meting of these compounds but observed the decomposition beyond 350 ºC giving various gaseous products. These porphyrins have good thermal stability up to 400 ºC unlike many metal organic compounds.

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