Thermal Studies of Some Metal Porphins

S.D. Gokakakar and A.V. Salkar

Department of Chemistry Goa University-Goa 403 206

Abstract

Tetraphenyl Porphin (TPP) and M-TPP (Where M= Co, Ni& Zn). were synthesized and characterized by UV-Visible spectroscopy. Thermal studies were carried out using DTA-TG techniques in synthetic air from room temperature to 700°C. This analysis revealed that these compounds have thermal stabilities upto 400°C. Further residues of these compounds obtained after heating upto 700°C, have shown the presence of metal oxides and decomposed products.

Introduction

Porphyrins are important class of components which find applications in the industries as enzyme models, photosensitizers, photocatalysts medicinal preparations, semiconductors and even as blood substitutes [1]. Further, they find important applications in photodynamic theraphy (PDT), Light emitting diodes (LED) and solar energy storage. [2]. In the present investigation the synthesis of metal free and metalloporphines were undertaken and were characterized by UV-Visible spectroscopy. Thermal behaviour of these compounds were studied employing DTA-TG techniques.

Experimental

Synthesis of tetraphenyl porphine (TPP) [3] was done by condensation reaction of equimolar mixture of pyrrole and benzaldehyde in propionic acid as a solvent at refluxing temperature for 30 minutes. The reaction temperature was brought to room temperature followed by cooling with ice, filtered and washed with hot methanol. The resulting TPP was further purified using a column of silica gel and $CHCl_3$ as an eluting agent.

The metalloporphins of Co^{2+}, Ni^{2+}, and Zn^{2+}, were synthezised [4] by dissolving TPP in dimethyl formamide (DMF) and refluxing this solution with stoichiometric amounts of corresponding metal salts. The reaction mixture is brought to room temperature followed by cooling with ice. Then sufficient amount of distilled water was added and allowed to cool in ice- bath. It was filtered, vacuum dried and chromatographed for purification on silica gel column followed by recrystallization. The above synthesized produced were characterized by UV-Visible 'SHIMADZU' spectrophotometer. Thermal studies of these compounds were done on DTA-TG 'NETZSCH' thermal analyzer from room temperature to 700°C in synthetic air.

Results and Discussion

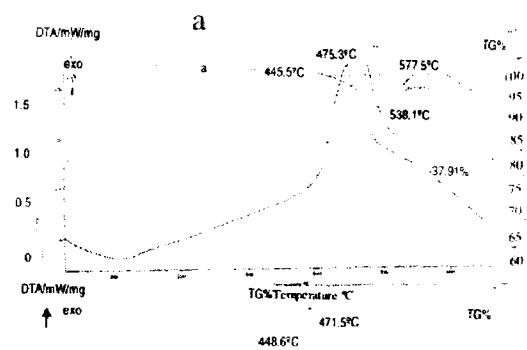
TPP, Co-TPP, Ni –TPP and Zn-TPP were characterized using UV-Visible spectrophotometer. The corresponding λ_{max} values are shown in Table 1.

Table 1: Visible absorption maxima

Sr. No	Compound	λ_{max} (nm)
1	TPP	416
2	Co-TPP	409
3	Ni-TPP	414.5
4	Zn-TPP	418.5

These values are in good agreement with the reported values.

Figs. 1 and 2 show the thermal behaviour of the compounds in DTA-TG thermograms. These measurements reveal that all these compounds are thermally stable upto 400°C. TPP shows two broad stages. First decomposition is from around 450°C to 475°C and second from 538°C to 578°C along with the weight loss. In case of Co-TPP the first decomposition is at 448.6°C and last decomposition is at 532.1°C respectively accompanied by the weight loss. Ni-TPP gave first decomposition at 446.6°C and last decomposition at 563.6°C also with weight loss. Zn-TPP gave first decomposition at 479.8°C and last at 624.1°C accompanied by the weight loss at these temperatures



E-Mail: Sal_arun@rediffmail.Com.

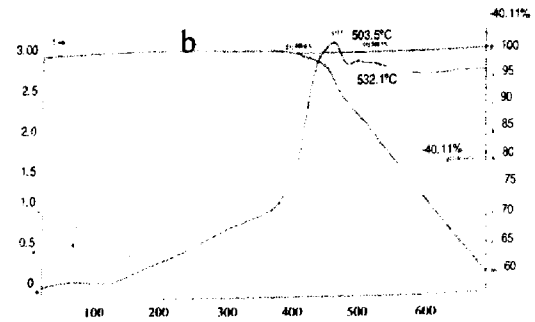


Fig. 1: DTA-TG Thermograms of (a) TPP and (b) Co-TPP.

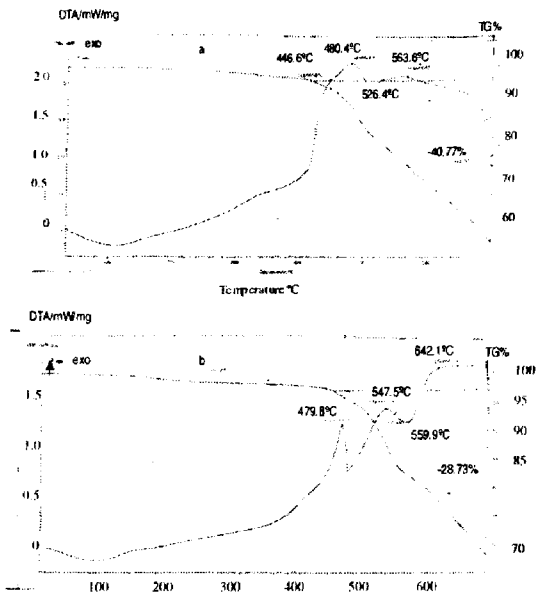


Fig. 2: DTA-TG Thermograms of (a) Ni-TPP and (b) Zn-TPP.

It is observed from above facts that the thermal stability of Co-TPP and Ni-TPP has marginally lowered whereas in the case of Zn-TPP it is marginally increased in comparison with thermal stability of TPP. Thus, the thermal stability of above compounds decreases in the following order.

Zn-TPP > TPP > Co-TPP > Ni-TPP

This may be justified on the basis of nature of metal and its oxidation state, electronic configuration and the nature of linkage in between metal – nitrogens of TPP.

The residues after thermal studies of the corresponding metalloporphines were qualitatively analyzed for respective metals. This has shown a positive test for a respective metal in the residue of M-TPP.

On the basis of above observations, it may be expected that during the process of heating, NH_x, hydrocarbon gases and other gaseous products may be evolved. The metal may be present as its metal–oxide along with some decomposed products of TPP residue. Further analysis of residue is in progress.

References

1. B.D. Berezin, "Coordination compounds of Porphyrins and Phthalocyanines" John Wiley and Sons Ltd. (1981)
2. J.C.P. Grancho, M.M. Pereira, M. da G. Miguel, A.M. R. Gonsalves and H.D. Burrows. Photochem. Photobiol., 75 (2002) 249.
3. A.D. Adler, F.R. Longo and J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, J. Org. Chem., 32 (1967) 476.
4. A.D. Adler, F. R. Longo, F. Kampas and J.Kim. J. Inorg. Nucl. Chem., 32 (1970) 2443.

Dr.AV.Salker, M.Sc (Mumbai Univ.), Ph.D (IIT, Mumbai, 1986) is Reader in chemistry Department, Goa university, Goa. He did his post-doctoral work at university of Karlsruhe, Germany and is a visiting scientist at Kyungpook National University, South Korea. His scientific interest are material sciences, thermal studies, catalysis and gas sensors.

Shri S.D.Gokakakar is M.Sc in chemistry from Karnatak university and is working as a faculty member in chemistry department of PESRSN college of Arts & Science. He is pursuing Faculty Improvement Programme under UGC at Goa University, Goa.