C-2: Thermal studies of some sulphonated metalloporphyrins with di and trivalent metals

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Abstract: A precursor of aqueous porphyrins i. e. a free-base tetra sodium meso-tetra (p-sulphonatophenyl) porphyrin ($TPPS_4$) and its corresponding metalloporphyrins ($MTPPS_4$), where M = Ag, Mn and Fe were synthesized and characterized by UV-Visible spectroscopy, Infra red spectroscopy and ^{1}H NMR spectroscopy. Thermal studies of above compounds were carried out using TG-DSC analyzer in synthetic air from room temperature to 800 °C. This analysis revealed that these compounds have thermal stabilities up to 400 °C. Further, qualitative analysis of the residues has shown the presence of metal oxides, Na_2SO_4 and coal respectively.

1.Introduction

Last three decades have seen the tremendous growth and development of water-soluble and water-insoluble base-free porphyrins and their respective metalloporphyrins. It is also an evidenced fact that, they are promising catalysts or photocatalysts for degradation of textile dyes and lignin in the paper and pulp processes. Monomeric, dimeric and oligomeric lignin model compounds were extensively degraded by metalloporphyrins both in water and in organic solvents. It was also seen that manganese porphyrins are more selective than iron porphyrins [1, 2]. Metalloporphyrins are also widely and extensively used in the models and mimics of enzymes like catalase, paroxidases, P-450 cytochromes or transmembrane electron transport agents [3,4,5]. As a class of molecule, they possess distinctive, reversible oxidation and reduction chemistry that potentiates use as wires, switches, transistors, junctions, and photodiodes [6]. Further, as materials, they find applications in nanostructures as films, crystals, tubes, wires, nanoparticle spheres etc. [7, 8, 9].

2.Experimental

The free-base $TPPS_4$ was synthesized by suitable method [10] and further it was subjected to purification by dry column chromatography using basic alumina as stationary phase. The mobile phase was comprised of gradient solution of water, methanol and acetone in the ratio of 7:2:1 [11]. During elution only purple fraction because of $TPPS_4$ was collected and other fractions were rejected.

The metalloporphyrins of $TPPS_4$ such as $AgTPPS_4$ was obtained by independently devised method whereas $MnTPPS_4Cl$ and $FeTPPS_4Cl$ were obtained by [12] prescribed method.

The purification of all these metalloporphyrins were carried out as is used for $TPPS_4$. The fractions due to dication and excess of metal salts were rejected and the fractions corresponding to respective metalloporphyrins were checked using spectrophotometer and selected.

The above synthesized porphyrins were characterized by UV-Visible spectroscopy, IR spectroscopy and 1H NMR spectroscopy. The thermal studies of these compounds were carried out in synthetic air using NETZSCH-Geratbau Gmbh thermal analyzer (STA 409PC) from room temperature to 800° C.

3. Results and discussions

UV-Visible spectroscopy was used as a characterization tool for $TPPS_4$, $AgTPPS_4$, $MnTPPS_4Cl$ and $FeTPPS_4Cl$, where soret bands and Q-bands were recorded for all of these compounds and compared with the literature values [13,14]. Similarly, IR spectroscopy and ^1H NMR spectroscopy were used and the above synthesized compounds were confirmed [13,10].

It is observed that, all DSC curves (Fig 4) are showing broad-endotherm which indicates loss of water of crystallization. Further, based on percent loss of water within the specified range of temperatures, the number of molecules of water of crystallization was confirmed as $5H_2O$ for $TPPS_4$ and $10H_2O$ for $AgTPPS_4$, $9H_2O$ for $MnTPPS_4Cl$ and $11H_2O$ for $FeTPPS_4Cl$ respectively (Table 1). It was also found out that all the above mentioned porphyrins are deliquescent in nature.

TG-DSC curve of $TPPS_4$ as shown in Fig. 1 reveals that the loss in mass is 34% excluding 7.7% due to water molecules and three exotherms at 362 °C, 468 °C, and 605 °C. This indicates that, this compound decomposes in three stages. The qualitative analysis of the residue was done which showed the presence of Na^+ and SO_4^{2-} ions in $TPPS_4$ and corresponding metal oxides and Na+ and SO_4^{2-} for remaining metalloporphyrins. . This throws light on the fact that SO_3^{2-} present in the structure of the molecule is oxidized to SO_4^{2-} and therefore, positive tests for presence of respective metals and Na_2SO_4 are obtained [13].

TG-DSC curve of $AgTPPS_4$ shows 57.2% loss and 13.84% loss in mass due to water molecules. For this curve, four decomposition temperatures 390 °C, 450 °C, 548 °C and 585 °C were obtained respectively. In $MnTPPS_4Cl$, TG-curve shows 52.5% mass loss whereas 13.53% mass loss is seen for water molecules which are shown in Fig. 2. The respective decomposition temperatures are 331 °C, 438 °C, 525 °C and 590 °C which confirm the compound has four stages of decomposition. Fig. 3 shows TG-DSC curve for $FeTPPS_4Cl$, where, mass loss is 52.5% and 15.5% loss due to water molecules. Here, decomposition of the compound is seen in six stages at 429 °C, 514 °C, 569 °C, 598 °C, 642 °C and 732 °C respectively. The qualitative analysis of all the residues has shown the presence of metal oxides, Na_2SO_4 and coal. The thermal stabilities of these porphyrins is established on the basis of their first decomposition temperature as shown in Fig. 4 as well as tabulated from onset temperatures of TG curves (Table 2) and is given by $FeTPPS_4Cl > AgTPPS_4 > TPPS_4 > MnTPPS_4Cl$. Thus it explains that thermal stability of a respective porphyrin is a characteristic property of the respective metal from the transition series. From above results, it can be confirmed that, none of the above porphyrin shows complete loss in mass because of the formation of metal oxide, Na_2SO_4 and coal.

4.Conclusions

The percent loss of water was used to calculate the number of molecules of water of crystallization in $TPPS_4$, $AgTPPS_4$, $MnTPPS_4Cl$, and $FeTPPS_4Cl$ as 5, 10, 9 and 11 respectively.

The metalloporphyrin $AgTPPS_4$ has least thermal stability whereas $MnTPPS_4Cl$ has maximum thermal stability. This can be attributed to the nature of the respective transition metal from the transition series. The qualitative analysis of $TPPS_4$ has shown presence of Na_2SO_4 and coal whereas in metalloporphyrins in addition to these, metal oxides were detected. In $MnTPPS_4Cl$ and $FeTPPS_4Cl$ gradual decrease in the mass loss is due to the loss of axial ligand Cl. It is also observed that first decomposition temperature of a respective porphyrin depends upon the strength of metal nitrogen bond of the porphyrin ring as well as metal-Cl axial bond and in case of base-free prphyrin it depends upon the strength between nitrogen and pyrrole protons.

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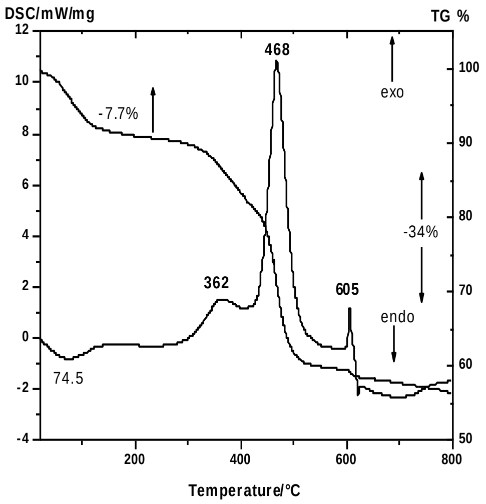

Fig.1 TG/DSC curve for $TPPS_4$

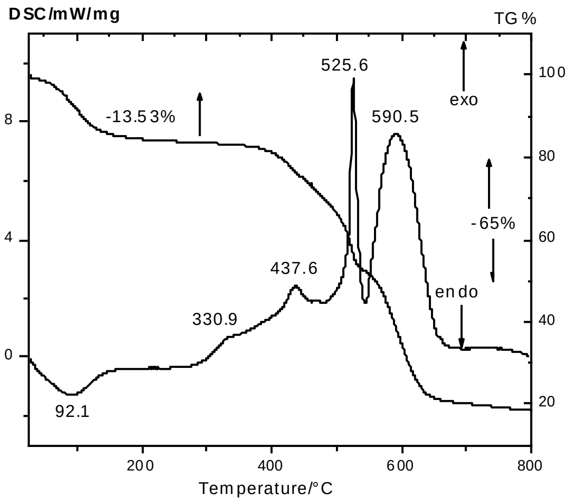

Fig.2 TG/DSC curve for $MnTPPS_4Cl$

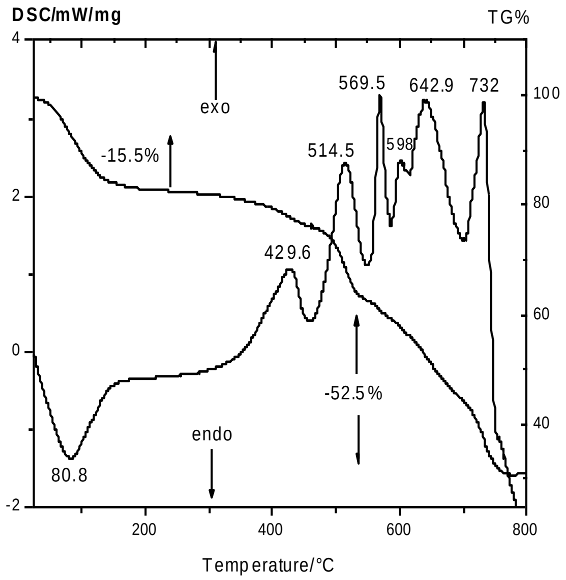

Fig.3 TG/DSC curve for $FeTPPS_4Cl$

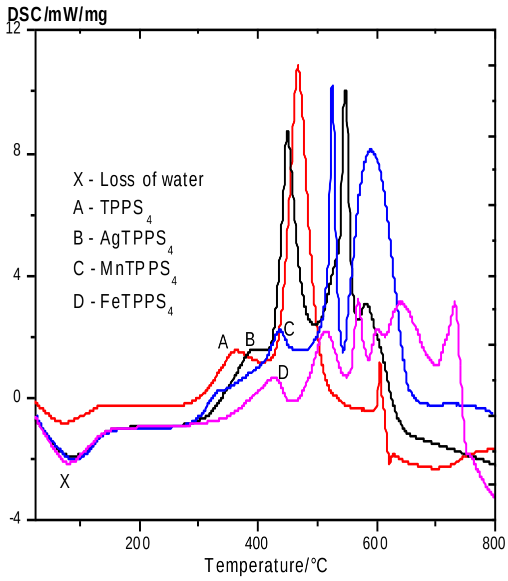

Fig. 4 First decomposition temperatures of porphyrins

Table1 . Compound, mass loss (%) , respective no of water molecules and first decomposition onset temperatures for porphyrins

Compound	Temperature range (°C)	Mass loss (%)	No. of water molecules	First decomposition onset temperature (°C)
$TPPS_4$	50-100	7.7	5	362
$AgTPPS_4$	50-125	13.8	10	390
$MnTPPS_4Cl$	50-125	13.5	9	438
$FeTPPS_4Cl$	50-100	15.5	11	430