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ABSORPTION SPECTRA, PHOTOBLEACHING EFFECTS AND STABILITY CONSTANT OF BIS(PYRIDYL)MAGNESIUMTETRABENZOPORPHIN

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ABSTRACT. An investigation of the general chemical properties of bis-pyridylmagnesiumtetrabenzoporphin, $MgTBP(Py)_2$, in the solid state and in solution was attempted. This study is mainly on the determination of absorption spectra in various solvents, photobleaching effect, stability constant and thermodynamic parameters of $MgTBP(Py)_2$.

INTRODUCTION

There has been continuing interest in the chemistry of porphyrin type molecules. The presence of bispyridylmagnesiumtetrabenzoporphin, $MgTBP(Py)_2$, in interstellar space has been reported (1). It was observed that under laboratory conditions many of the spectral lines of $MgTBP(Py)_2$ coincided with those of certain interstellar diffuse bands. The function of porphyrin like species in photosynthesis (chlorophyll), animal respiration (hemoglobin and myoglobin), electron transfer (cytochromes), and in certain vitamins (vitamin B_{12}) has attracted particular attention for their importance on earth. Manganese porphyrin chelates occur in the oxygen evolution step in photosynthesis (2). A novel cosmochemical synthesis of porphyrins are known (3).

The effect of light on the metal-axial ligand bond in metalloporphyrins has been investigated on metalloporphyrins and related compounds of transition metal such as iron, cobalt, and ruthenium by steady-light photolysis (4-9), in connection with the mechanism of ligand binding in vitamin B_{12} or heme group compounds. It has also been documented that the transition metal-carbon bond in macrocycles is subject to homolysis by light, accompained by the change in valence of the central metal (10-12).

As a result of limited information available on the properties of bispyridylmagnesiumtetrabenzoporphin with particular reference to absorption spectra, photobleaching effects and stability constant, we report in this paper the general chemical properties of $MgTBP(Py)_2$. Attempts are made to gain further information about (i) absorption spectra of $MgTBP(Py)_2$ in some organic solvents, (ii) the relationship that may exist between the stability of $MgTBP(Py)_2$ (in the solid state) and temperature, (iii) stability of $MgTBP(Py)_2$ (in solution) to sunlight, and (iv) the formation constant/thermodynamic parameters of $MgTBP(Py)_2$ with pyridine in non-aqueous solutions.

EXPERIMENTAL

Apparatus and reagents. Solvents (Aldrich Chemicals) used were reagent grade. They were utilized without further purification. For comparative studies, methanol was dried with Linde molecular sieve, type 5Å and then fractionally distilled under nitrogen at reduced pressure. Chloroform was purified by stirring over Linde molecular sieve, type 5Å, and then fractionally distilled under nitrogen at reduced pressure. It was again chromatographed on basic alumina prior to use. Pyridine was distilled over KOH before use. The results obtained in purified solvents are identical with those obtained in unpurified ones. Hence, unpurified solvents were utilized in most cases. $MgTBP(Py)_2$ was obtained by known procedure (13). All chemicals used were Analar grade. A Beckman Model 24 UV-Vis spectrophotometer equipped with 1-cm matched quartz cells or carry 14 recording spectrophotometer was used for absorbance measurements.

Absorption spectra/general procedure. The absorption spectra of bispyridylmagnesiumtetrabenzoporphin ($MgTBP(Py)_2$) were taken in saturated solutions of organic solvents - benzene, chloroform and methanol. As a result of its higher solubility, the absorption spectra were also taken in dilute solutions of pyridine and acetone (see Fig. 1).

In order to study the photobleaching effect, the dilute solutions of $MgTBP(Py)_2$ in pyridine and acetone were allowed to stand in the sunlight and in the dark. Absorption spectra data were run as a function of time.

Attempts were made to determine the stability constants for pyridine complexation. Equal concentration solutions of $MgTBP(Py)_2$ dissolved in methanol or benzene were spectrometrically titrated with large excesses of pyridine, keeping the total volume constant. A stability constant for 1:1 complex formation was calculated with the formula

$$\frac{1}{A_x - A_o} = \frac{1}{K(A_\infty - A_o)} \left[\frac{1}{(Py)} \right] + \frac{1}{A_\infty - A_o}$$

where A_o and A_∞ are the absorbance at constant wavelength of the completely complexed, and uncomplexed forms of $MgTBP(Py)_2$ respectively. A_x is the absorbance of mixtures of the complexed and uncomplexed forms. K is the stability constant for the process

$$MgTBP.\,P_y + Py \rightleftharpoons MgTBP(Py)_2$$

The plot for the determination of K is shown in Fig. 2.

The solution spectra of $MgTBP(Py)_2$ in pyridine after heating solid $MgTBP(Py)_2$ at various temperatures and two sealing pressures were also investigated. A stock solution of $MgTBP(Py)_2$ in pyridine was prepared. Aliquots were pipetted into special 1.8 cm x 10.2 cm preconstricted tubes and lyophilized (freeze dried). The tubes were evacuated and carefully sealed (without heating) at either 0.2 mm (high pressure) or 0.02 mm (low pressure). The tubes were placed in an oven and heated at different temperatures for various periods of time. The gas in the heated, sealed tubes is composed of the weakly bound pyridine vapour (14-18). The results observed have no relationship with this gas composition because after cooling, the samples were re-dissolved in pyridine to a constant volume. The absorption spectra were determined at room temperature from 350-700 nm wavelength.

RESULTS AND DISCUSSION

Fig. 1 shows the visible and soret absorption spectra of $MgTBP(Py)_2$ in pyridine, benzene, acetone chloroform and methanol. The electronic spectrum of $MgTBP(Py)_2$ in benzene showed a medium absorption band ($\varepsilon = 1.9 \times 10^5$ l. $mol^{-1} cm^{-1}$) at 628 nm and a relatively strong absorption band ($\varepsilon = 4.5 \times 10^5$ l. $mole^{-1}$ cm^{-1}) at 427 nm which are due to $\pi \rightarrow \pi^*$ and charge transfer ($L \rightarrow M$) electronic transitions respectively.

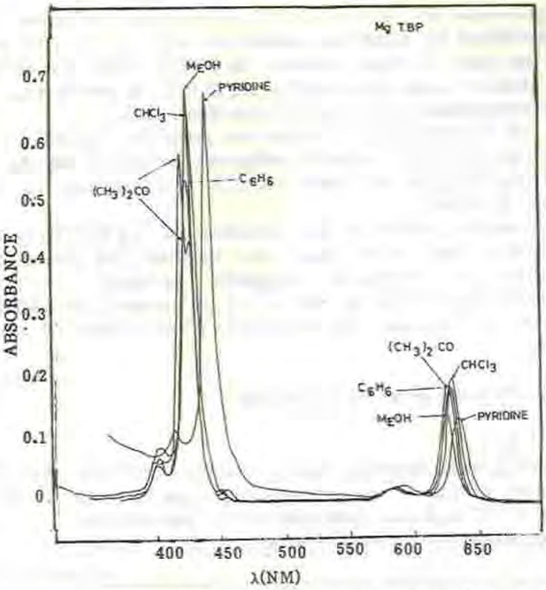

Fig. 1. Absorption spectra of MgTBP in benzene, chloroform, acetone, methanol and pyridine.

Table 1 lists the band positions in the solvents. It is noted that basic solvents like pyridine produce shifts to longer wavelengths. This is due to co-ordination of the base to magnesium. $MgTBP(Py)_2$ in acetone has a split soret band (Table 1).

Table 1. Band positions of $MgTBP(Py)_2$ in various solvents at 25°.

Solvent	Visible	Soret
Pyridine	636(m), 593 (w)	460(sh), 443(s), 416(sh)
Chloroform	630(m), 585 (w)	455(sh), 427(s) 403(sh)
Methanol	625(m) 585 (w)	455(sh) 427(s) 403(sh)
Benzene	628(m) 585 (w)	458(sh) 427(s) 402(sh)
Acetone	627(m) 585 (w)	458(sh) 428(s) 422(s) 402(sh)

Wavelength (nm); s = strong, m = medium, w = weak, sh = shoulder.

Pyridine solutions of $MgTBP(Py)_2$ in the light or dark showed little evidence of decomposition. Even when exposed to lamps of wavelengths 253.7 and 370.0 nm, pyridine solution of $MgTBP(Py)_2$ remained unchanged.

In the sunlight and under laboratory fluorescent lighting, solutions of $MgTBP(Py)_2$ in acetone were bleached. The absorption peaks of $MgTBP(Py)_2$ in acetone decreased in intensity and completely disappeared after prolonged standing. New bands did not appear in either the visible or soret region. A similar effect was noted for solutions of $MgTBP(Py)_2$ in chloroform. Stock solutions of $MgTBP(Py)_2$ in acetone showed little change in appearance in the dark for periods of up to one month.

It has been shown that methanol and acetone solutions of $MgTBP(Py)_2$ are photobleached (19). In both solvents, the photobleached pigment has a spectra similar to that produced by chemical oxidation with I_2, Fe (III) or MnO_4^-, and is attributed to the one electron product $MgTBP^+$. With Ce (IV), however, a pigment without visible bands, presumably $MgTBP^{2+}$, is produced. These results are in apparent disagreement with those of Goedheer (19).

Photobleaching of $MgTBP(py)_2$ in acetone goes to $MgTBP^{2+}$, rather than $MgTBP^+$. The presence of the solvent enhances oxidation of the porphyrin by the photon. The significance of these results with respect to chlorophyll, a similar Mg pigment, is noted.

The lack of isosbestic points in the titration of $MgTBP(Py)_2$ with pyridine in methanol indicates that more than two species are present. The weak coordinating ability of methanol suggests possibly Py-Mg, $(Py)_2$-Mg, Py-Mg-MeOH, MeOH-Mg-MeOH, or -Mg- may be present, in addition to dimers or polymeric forms. In benzene, the isosbestic points observed (Fig. 3) suggest the simple equilibra

$$MgTBP\text{-}Py + Py \rightleftharpoons MgTBP.(Py)_2$$

where $K = 10.9\ M^{-1}$ at 25°.

The enthalpy (ΔH°) and entropy (ΔS°) changes of the $MgTBP(Py)_2$ were calculated from plots of log K vs. over the range 20 - 40°C. The calculated value of log K at 25°C and the thermodynamic parameters (ΔH°, ΔS°), ΔG°) for the system studied are given below:

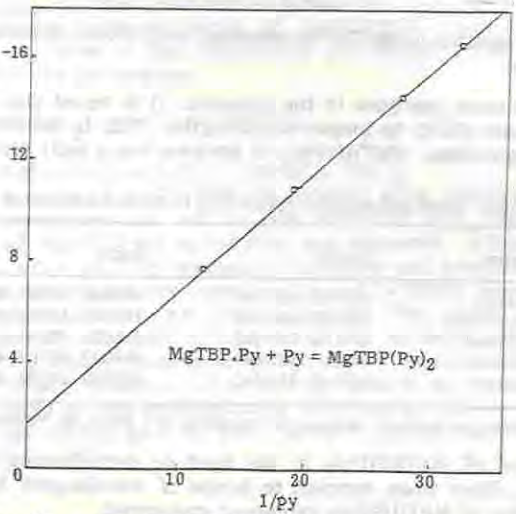

Fig. 2. Plot of $1/(A_x - A_o)$ versus 1/Py determine the formation constant of $MgTBP(Py)_2$ at 25°C benzene. $K = 10.9\ M^{-1}$

Table 2. Stability constant and thermodynamic parameters (ΔH^o, ΔS^o, ΔG^o) for $MgTBP(Py)_2$ with pyridine in benzene at 25°C.

log K	$-\Delta G^o$ KJ/mole	$-\Delta H^o$ KJ/mole	$-\Delta S^o$ J/deg mole
1.04	5.92	- 12.78	- 62.73

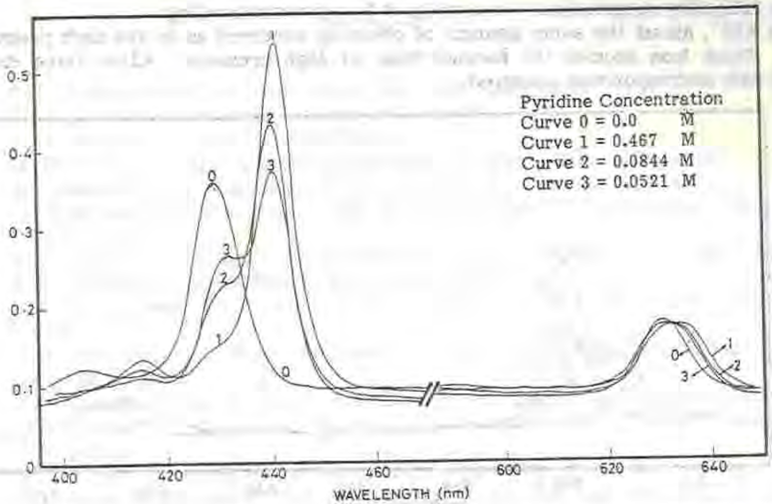

Fig. 3. Absorption spectra changes in the titration of MgTBP.Py with Pyridine in benzene solution.

This is about the order of magnitude of the stability constants found with other Mg porphyrins having different structures (20). The suggestion is that one pyridine has a great affinity for MgTBP, while the second is very weakly bound. Such is consistent with thermal data on solid MgTBP(Py)$_2$, where a 200° temperature difference was found for the separate removal of the two coordinated ligands (13).

From studies involving solution spectra in pyridine of MgTBP(Py)$_2$ after heating solid MgTBP(Py)$_2$ at various temperatures under high sealing pressures (HP) of 0.2 mm Hg, or low sealing pressures (LP) of 0.02 mm Hg, the following results were obtained independent of HP or LP:

1. MgTBP(Py)$_2$ were recovered unchanged with regard to band intensities and positions at 350° or lower.
2. There was no indication of sublimation at temperature below 350°.
3. There was no carbonation or change in solubility of MgTBP(Py)$_2$ at 350° or lower.

The following observations were made under high pressure:

1. At 450°, there was an indication of sublimation of MgTBP(Py)$_2$ but no significant amount of carbonaceous material was formed. At this temperature, a new low wavelength band appears as a shoulder on the principle Soret band (Fig. 4). A fully resolved peak was observed when the sample was heated for one hour. This indicates that the initial species of MgTBP(Py)$_2$ (I) is transformed into a new form (II) which absorbs at shorter wavelengths. For species (I), λ = 443 nm. For species (II), λ = 425 nm.
2. Charring occurs at 500°. Sublimation preceeds decomposition at this temperature. There was formation of carbonaceous material. The charred substance is insoluble in pyridine. The initial species (I) is transformed with time into a new form (II), which absorbs at shorter wavelengths.

Conclusively, species (II) is more stable to heat than species (I); but with longer heating times, species (II) also carbonizes. The spectra of (II) in pyridine is similar to that found by Geodheer (19) for the one electron oxidation product, MgTBP$^+$. The solid (II) was light blue, whereas MgTBP(Py)$_2$ was a darker greenish solid.

The following observations were made at low pressure sealing:

1. At 450°, about the same amount of charring occurred as in the high pressure case. Much less species (II) formed than at high pressure. After three days, about 25% decomposition occurred.

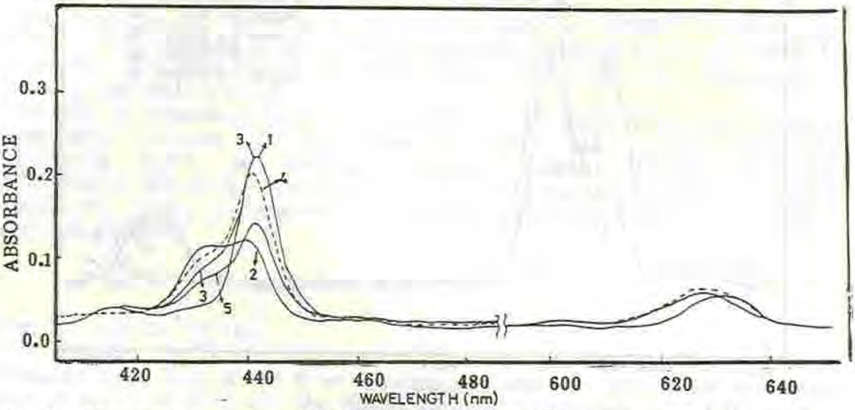

Fig. 4. Absorbance spectra of MgTBP heated at 450°C, sealed at high presure: Curve 1, time = 0 hours; Curve 2 and 5, time = 1 hour; Curve 3, time = 2 hours, Curve 4, time = 4 hours.

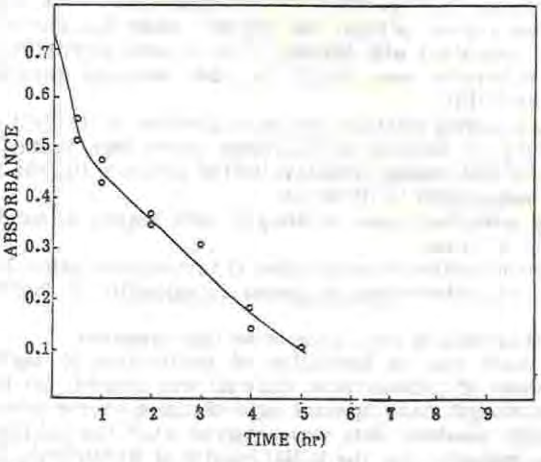

Fig. 5. Absorbance vs. Time plot of the 4430 A° peak of $MgTBP(Py)_2$ heated at 550°C.

2. When the temperature was elevated to 550°, very little species (II) was obtained. Complete decomposition occurred after eight hours at this temperature.

In conclusion, Mg is not lost from the macrocycle at either high or low pressures. The evidence is that the spectra of the demetallated porphyrin was never observed at either HP or LP, at any temperature. Finally, the results presented show the general trends found. In all heating cases, duplicate samples were removed at the same time.

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