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Photochemical Reaction of Magnesium Tetraphenylporphyrin with CS_2

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The photochemical reaction of magnesium tetraphenyl porphyrin (MgTPP) with carbon disulfide (CS_2) was investigated in dichloromethane (CH_2Cl_2) by UV-vis absorption and steady-state fluorescence spectroscopic techniques to simulate the photochemical interaction of CS_2 with chlorophyll. These spectra showed that under irradiation MgTPP reacted with CS_2. The kinetics of photochemical reaction of MgTPP with CS_2 has been studied in a CS_2-saturated solution. Under irradiation the experimental rate follows a pseudo first order reaction for MgTPP, having a half-life from (31 to 69) min under various irradiation intensities. The kinetic rate constants of photochemical reaction of MgTPP with CS_2 showed a linear dependence. The photochemical reaction of MgTPP with CS_2 is of key interest in elucidating fundamental reaction mechanisms associated with this class of chlorophyll in presence of CS_2.

Key Words: Magnesium tetraphenylporphyrin (MgTPP), CS_2, Photochemical reaction, Pseudo first order reaction.

INTRODUCTION

The inorganic sulfur in the environment (*e.g.*, SO_4^{2-} in the soil and SO_2 in the air) is assimilated into cysteine mainly by the cysteine biosynthetic pathway in plants[1]. However, in particular sulfur base ligation to metalloporphyrins has been largely ignored. Especially, carbon disulfide (CS_2) is emitted by either natural or industrial sources (major sources for most industrialized countries)[2]. CS_2 is classified as a hazardous pollutant, which triggered an increasing interest in finding reliable, cost effective technologies for its control. Chloroplasts are considered as the main sites of sulfur metabolism in leaves[3] and chlorophyll is main photochemical reaction site in a chloroplast membrane, so the effects of CS_2 on photochemical characters of chlorophyll in chloroplast were studied in this work to discuss the possible sulfur metabolism.

Chlorophylls and bio-chlorophylls are compounds that contain magnesium and they also have important roles in various biological processes. Magnesium coordination chemistry in chlorophylls is of key interest in the design of biomimetic system as well as in elucidating fundamental reaction mechanisms associated with this class of chlorophyll. The photochemical reaction of magnesium-containing porphyrinic compounds with sulfur-containing complexes was not well established in previous works. Chlorophyll, however, has been seldom used as a photoreagent because the natural pigment easily loses its photostability by extractions with an organic solvent. Chlorophyll a in acetone or benzene was irreversibly bleached when exposed to visible light in presence of O_2[4]. The magnesium compound could interact with a neighboring molecule or directly with an electron-acceptor molecule, initiating the charge separation necessary for photosynthesis[5].

In this work, to simplify and simulate the photochemical reaction of chlorophyll 'a' with CS_2, magnesium tetraphenylporphyrin (MgTPP), which has a similar porphyrinic framework to the chlorophylls, was used to perform the related experiments.

EXPERIMENTAL

Fluorescence spectra were acquired using an F-4500 fluorescence spectrophotometer employing a 500 W Hg-Xe high pressure lamp. UV-vis spectra were recorded on a Varian CARY 1E UV-vis spectrometer. All solid reagents were weighed using a Sartorius BS224S electric balance.

Dichloromethane (HPLC grade, > 99.9 %) was purchased from Tianjin Siyou Co., Ltd. (Tianjin, China). All other reagents and solvents were reagent grade and used as received.

Preparation of MgTPP: The original material MgTPP was synthesized using published procedures[6] and was reported in previous work[7].

Irradiation processes: A solution of *ca.* 35 mL MgTPP in CH_2Cl_2 (60 μmol L^{-1}) was put into a cold trap and irradiated using a 11 W incandescent lamp at a distance of 9 cm. The luminous flux of the lamp was 600 Lm at room temperature. One mL of CS_2 was added to the solution so that the photochemical reaction of MgTPP with CS_2 could be maintained in a CS_2-saturated solution. 1 mL irradiated MgTPP solution was diluted 5 times with CH_2Cl_2 and the dilute solutions were used for various spectral analyses every 0.5 h.

RESULTS AND DISCUSSION

Contrast test: The contrast test was performed in dark as mentioned in irradiation processes procedure. Fluorescence emission spectra and UV-vis absorption spectra in the contrast test showed that, in the dark, the solutions of MgTPP were stable in the presence of CS_2 more than a few hours, which indicates that no reaction occurred between the ground state MgTPP and CS_2.

Fluorescence and UV-vis spectra: The original MgTPP solution irradiated for 6 h in the presence of CS_2 was taken. After irradiation, in the presence of CS_2, the colour changes of MgTPP solution from pink to blue and green could be due to a photochemical reaction of MgTPP with CS_2. To confirm the reaction processes, the irradiated MgTPP solutions in presence of CS_2 were analyzed by fluorescence and UV-vis spectroscopy every 0.5 h.

The stable state of fluorescence spectra with selective excitation of MgTPP were recorded and the spectra are shown in Fig. 1. Upon excitation at 550 nm, a strong fluorescence with maxima emission positions of Q* of MgTPP at 608 and 663 nm was observed. The fluorescence emission spectra (Fig. 1) showed a decrease in the fluorescence intensity of the solutions with increasing irradiation time and in the presence of CS_2. The fluorescence of MgTPP was significantly quenched and this phenomenon could be attributed to the photochemical interaction occurred between MgTPP and CS_2 in CH_2Cl_2.

UV-VIS absorption spectra of MgTPP solution are shown in Fig. 2. The absorption spectra showed a typical Soret band and several Q bands and the positions of their absorption peaks were identified. The band at 424 nm (B (0, 0)) was assigned to the Soret band of MgTPP arising from the transtisition of $a_{1u}(\pi)$-$e_g^*(\pi)$[8]. Similar Soret absorption bands (B-band) were observed for most prophyrinic compounds[9,10] and the band was attributed to excitonic interaction between the large Soret transition dipoles of the constituent porphyrin chromophores, so the changes of Soret band were very important to explore

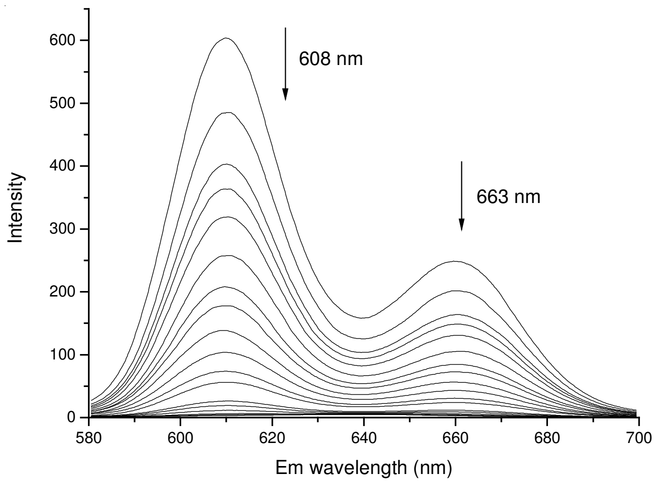

Fig. 1. Fluorescence emission (λ_{ex} = 550 nm) spectral changes of MgTPP under irradiation and in the presence of CS_2

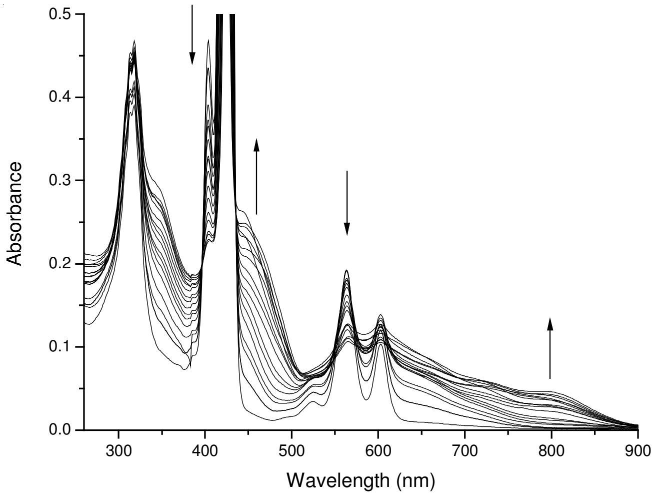

Fig. 2. UV-VIS absorption spectral changes of the original MgTPP solution in the presence of CS_2 that was diluted with CH_2Cl_2 (A) 5 times

photochemical interaction between porphyrinic compounds and other molecules. Meanwhile, Q bands of MgTPP were respectively observed at 516, 563 and 603 nm, and these bands were attributed to the Q bands arising from the transtisition of $a_{2u}(\pi)$-$e_g^*(\pi)$[8]. Meanwhile, the absorbance changes were recorded. From the absorption spectra the absorption intensity of the Soret bands at 424 and 403 nm decreased with increasing irradiation time in presence of CS_2 and the absorption bands in the range of 450-500 nm and in the range of 750-900 nm increased, indicating MgTPP had reacted with CS_2 resulting in the formation of new compound. With the appearance of the final absorption spectrum, no further spectral changes were observed upon continued irradiation.

Photochemical reaction kinetics: According to these results, the final product of the MgTPP with CS_2 is the species $MgTPP(CS_2)$ (eqn. 1). Most reported synthetic CS_2 binding systems have been studies in organic solvents such as toluene, benzene and dichloromethane[11-13].

$$MgTPP + CS_2 \xrightarrow{h\nu} MgTPP(CS_2) \qquad (1)$$

The photochemical reaction rate of MgTPP with CS_2 was monitored with the fluorescence technology as a function of irradiation time. A solution of *ca.* 35 mL MgTPP in CH_2Cl_2 (30 mg L^{-1}) was irradiated using various incandescent lamps with various irradiation intensities at a distance of 9 cm. The luminous flux of the lamp was 220-600 Lm at room temperature. 1 mL CS_2 was added to the solution continuously for 4 h so that the photochemical reaction of MgTPP with CS_2 could be maintained in a CS_2-saturated solution. 1 mL irradiated MgTPP solution was diluted 5 times for various spectral analyses every 5-30 min. The reaction of MgTPP from CS_2 is expected to be described by the equation:

$$MgTPP + CS_2 \xrightarrow{k} MgTPP(CS_2) \qquad (2)$$

The kinetic process is described by the equation:

$$-d[MgTPP]/dt = k[MgTPP][CS_2] \qquad (3)$$

where [MgTPP] denotes the concentration of MgTPP, $[CS_2]$ denotes the concentration of CS_2, t is the reaction time and k is the rate constant.

When the concentration of CS_2 keeps constant, the eqn. 3 is changed into eqn. 4-7 as follows:

$$-d[MgTPP]/dt = k'[MgTPP] \quad (4)$$

$$k' = k[CS_2] \quad (5)$$

$$-\ln([MgTPP]_t/[MgTPP]_0) = k't \quad (6)$$

$$t_{1/2} = -\ln 2/k' \quad (7)$$

where $[MgTPP]_0$ is the initial concentration of MgTPP and $[MgTPP]_t$ is the concentration of MgTPP at t min. A plot of the natural logarithm function on the left as a function of delayed time should yield a straight line with a slope of k'.

Fig. 3 shows that when photochemical reaction took place at various irradiation intensities, and the concentration of MgTPP in solution decreased with increasing irradiation time. Furthermore, the concentration of MgTPP in solution decreased obviously at the same irradiation time with increasing irradiation intensities.

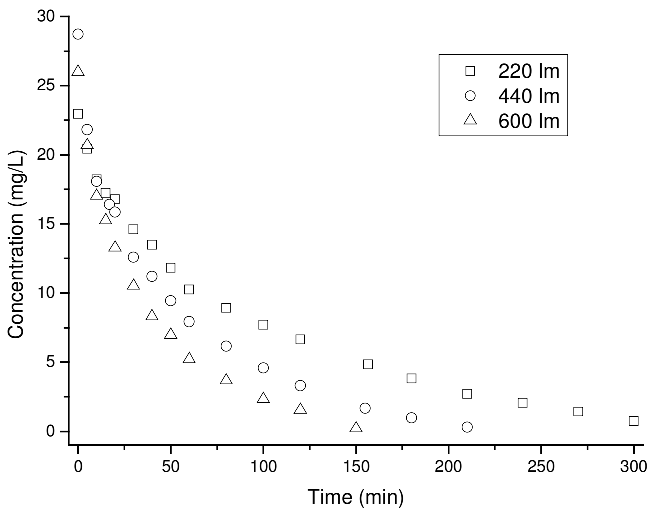

Fig. 3. Dependencies of the concentration of MgTPP (mg/L) on irradiation time in the presence of CS_2: □, 220 Lm; ○, 440 Lm; △, 600 Lm

The kinetics of the photochemical reaction of MgTPP with CS_2 is showed in Fig. 4. The figure showed that MgTPP loss by photochemical reaction follows a pseudo first order reaction kinetics. The reaction rate constants and half life of photochemical reaction are shown in Table-1, together with the correlation coefficients obtained from the linear regression analysis. Fig. 4 shows a typical plot of eqn. 6 from an experiment in which MgTPP is irradiated to various irradiation intensities.

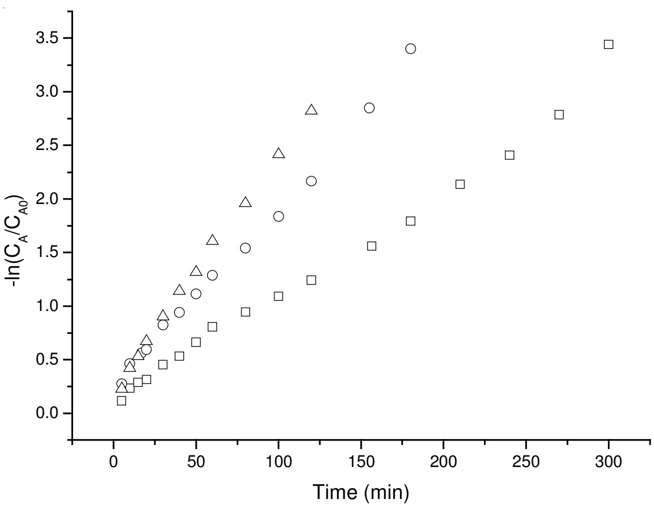

Fig. 5. Photochemical reaction kinetics of MgTPP with CS_2 at various irradiation intensities: □, 220 Lm; ○, , 440 Lm; △, 600 Lm.

TABLE-1
INTERCEPT VALUES: PSEUDO FIRST ORDER REACTION RATE CONSTANTS, k', AND HALF LIFES, $t_{1/2}$, FOR MgTPP REACTION WITH CS_2 AT VARIOUS IRRADIATION INTENSITIES

Irradiation intensity (Lm)	220	440	600
k' (min^{-1})	0.0101	0.0168	0.0212
Correlation coefficient (R^2)	0.9887	0.9954	0.9973
$t_{1/2}$ (min)	68.63	41.26	31.34

Under these conditions the experimental photochemical reaction of MgTPP with CS_2 has a half-life from 31 to 69 min under various irradiation intensities. The kinetic rate constant of photochemical reaction of MgTPP with CS_2 showed a linear dependence as $k' = 3 \times 10^{-5}$ (irradiation intensity/Lm) + 0.00303 ($R^2 = 0.9995$).

Conclusion

The photochemical reaction of MgTPP with CS_2 was investigated and our approach was to simulate the photochemical reaction processes of chlorophyll a with CS_2. The phenomena are noteworthy, although the reasons are unclear. Under these conditions the experimental rate was the pseudo first order reaction for MgTPP, having a half-life from 31 to 69 min under various irradiation intensities. The kinetic rate constants of photochemical reaction of MgTPP increases from 1.01×10^{-2} to 2.12×10^{-2} min^{-1} in various irradiation intensities and these constants showed a linear dependence.

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