Asian Journal of Chemistry; Vol. 26, No. 16 (2014), 5255-5258

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16976

Kinetic Studies of Metalloporphyrins Bonding with Nitric Oxide

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Received: 3 January 2014; *Accepted*: 14 March 2014; *Published online*: 28 July 2014; AJC-15672

At room temperature, the bonding of metalloporphyrins with nitric oxide was investigated in dichloromethane by conventional fluorescence and UV-visible techniques. Spectral analyses showed that metalloporphyrins can react with nitric oxide in a nitric oxide-saturated solution. The experimental rate follows a pseudo first order reaction for metalloporphyrins. The bonding kinetic rate constant of zinc tetraphenylporphyrin with nitric oxide for 0.01965 min^{-1} and the half-life of bonding was 35.27 min. The bonding kinetic rate constant of magnesium tetraphenylporphyrin with nitric oxide for 0.02184 min^{-1} and the half-life of bonding was 31.74 min. The experimental results showed that the coordination of magnesium tetraphenylporphyrin with nitric oxide is easier than Zinc tetraphenylporphyrin with nitric oxide.

Keywords: Zinc tetraphenylporphyrin, Magnesium tetraphenylporphyrin, Metalloporphyrin, Nitric oxide, Kinetic rate constant.

INTRODUCTION

Metalloporphyrin constitutes the active site of numbers enzymes, such as hemoglobin, (cytochromes, nitric oxide synthase, vitamin B_{12} and chlorophyll)[1,2]. These tetrapyrrol macrocycles play critical roles in a wide range of biological processes, including electron transfer, oxygen transfer, photosynthetic processes[3-5], simultaneously, porphyrins has a statement of "life pigment"[6]. Nitric oxide (NO) is a small highly diffusible gas and a ubiquitous bioactive molecule. In mammals including humans, nitric oxide is an important cellular signaling molecule involved in many physiological and pathological processes[7,8]. The present research about donors of nitric oxide, such as s-nitrosothiol and organic nitrate ester[9-11], but they exist some shortcomings, for example, they have poor stability and need metabolism by using cell. In recent years, with the understanding of the physiological function of nitric oxide, people are attempting to synthesize metalloporphyrin as molecular carrier of nitric oxide. Laverman *et al.*[12] researched 4-sulfonic acid group-phenyl metalloporphyrin which has better water solubility as molecular carrier of nitric oxide. Peretz *et al.*[13] regarded 4-*N*-methypyridyl porphyrin as donor of nitric oxide, but 4-*N*-methylpyridyl porphyrin has high toxicity and low efficiency when it released nitric oxide. Because metalloporphyrin has rigid construction, the size of the space and interactions direction of its axial ligand can be achieved by changing the position and direction. So that the metalloporphyrin can identify the size, shape, functional groups and the chiral isomer of molecules[14-16], thus metalloporphyrin has significant advantages as the carrier of nitric oxide.

This work mainly focused on providing a new potential carrier of nitric oxide. According to previous methods[17], the reaction of metalloporphyrin with nitric oxide was researched at room temperature, simultaneously and the reaction constants and half-life of the reaction were obtained.

EXPERIMENTAL

UV-visible spectra were obtained on a Shimadzu 2450 spectrometer in CH_2Cl_2. Fluorescence spectra were acquired using an F-4500 fluorescence spectrophotometer employing a 500 W Hg-Xe high pressure lamp. All solid reagents were weighed by using Sartorius BS224S electric balance.

Zinc tetraphenylporphyrin (> 99 %) was purchased from Hunan Jineng New Materials Technology Co., Ltd (Hunan province, China). Magnesium tetraphenylporphyrin was prepared by using magnesium acetate and meso-tetraphenyporphyrin (H_2TPP, > 98 %) purchased from Acros Organics (New Jersey, USA). All other reagents and solvents were reagent grade and used as received.

A solution of approximately 75 mL ZnTPP in CH_2Cl_2 (6.6068×10^{-5} mol L^{-1}) was put into a cold trap at room temperature. Nitric oxide (5000 ppm) was added to the solution continuously for 3 h so that the bonding of ZnTPP with nitric

oxide could be maintained in a nitric oxide-saturated solution. 1 mL of ZnTPP solution was diluted 5 times using CH_2Cl_2 and the dilute solutions were used for UV-visible and fluorescence spectral analyses. The same experimental method was used in the reaction of MgTPP (6.6068×10^{-5} mol L^{-1}) with nitric oxide.

RESULTS AND DISCUSSION

Fluorescence and UV-visible spectra: Fig. 1 showing the photographs of original ZnTPP solution and ZnTPP solution reacted for 5, 30 and 180 min in the presence of nitric oxide. After reaction, the color of ZnTPP solution rapidly changes from pink to reddish brown and finally to yellow. The experiments showed that the coordination reaction of metalloporphyrin with nitric oxide formed a new compound. To confirm the process, the reacted ZnTPP solutions in the presence of nitric oxide were analyzed by fluorescence and UV-visible spectroscopy, these spectra were shown in Figs. 2 and 3. The same experimental method was appeared using reaction of MgTPP with nitric oxide.

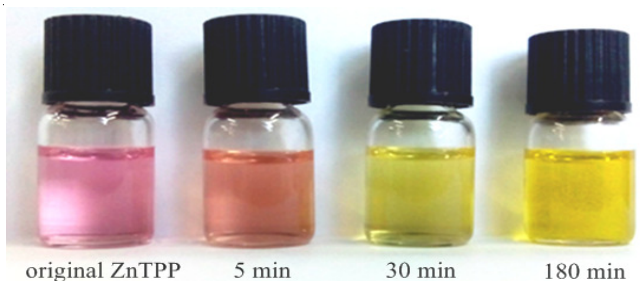

Fig. 1. Photograph of the original ZnTPP solution and the ZnTPP solution reacted for 5, 30 and 180 min in the presence of nitric oxide

The fluorescence emission spectra showed a decrease in the fluorescence intensity of the solutions at 595 nm and 644 nm with increasing reaction time. The fluorescence of ZnTPP was significantly quenched, which was attributed to electron transfer taking place from the interaction of ZnTPP with acceptor nitric oxide molecules. The fluorescence emission spectra showed a decrease in the fluorescence intensity of the solutions at 608, 650 and 715 nm with increasing reaction time. The fluorescence of MgTPP was significantly quenched and this could be attributed to electron transfer taking place from the interaction of MgTPP with acceptor nitric oxide molecules[17-19].

UV-visible spectra of the 5 times diluted solutions showed that the absorption intensity of the Soret band at 418 nm and the Q bands at 548 nm decreased with increasing reaction time, simultaneously, the Soret band at 227 nm increased. A new Soret band at 443 nm suggested that ZnTPP had reacted with nitric oxide resulting in the formation of new compound. The UV-visible spectra showed that the increasing nitric oxide concentrations resulted in red shift of 5 nm for MgTPP Soret absorption band. The Soret band at 443 nm was decreased, the Q bands at 501 nm and 656 nm increased and at 565 nm decreased with increasing reaction time. These experimental results could be due to the interaction of metalloporphyrin with acceptor nitric oxide molecules.

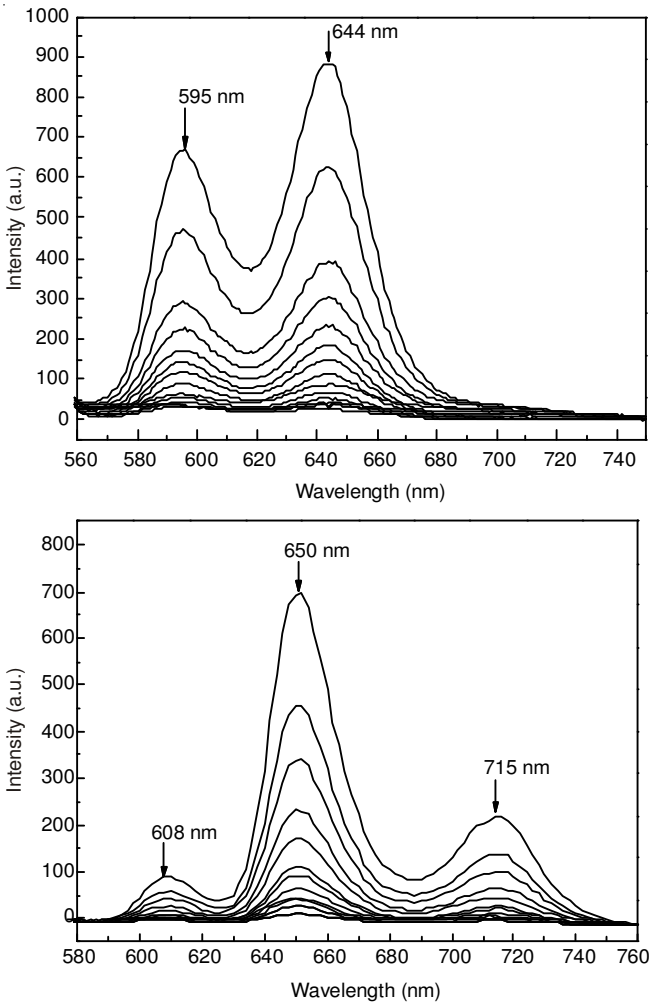

Fig. 2. Fluorescence emission spectral changes of ZnTPP (λ_{ex} = 548 nm, slit = 10 nm) and MgTPP (λ_{ex} = 515 nm, slit = 10 nm) in the presence of nitric oxide at room temperature

Kinetics of bonding: Nitric oxide is a diatomic molecule and the molecular structure is linear, nitrogen and oxygen have a lone pair of electrons. Its molecular orbital: $(\sigma 1s)^2 (\sigma 1s^*)^2 (\sigma^2 s)^2 (\sigma^2 s^*)^2 (\sigma^2 p)^2 (\pi^2 p)^4 (\pi^2 p^*)^1$, anti-bonding orbital $(\pi^2 p^*)^1$ was removed an electron easily. Because of the presence of lone pair of electrons, nitric oxide easily form complexes with metal ions. It has been reported before in the metalloporphyrin as carriers of nitric oxide[12,13], simultaneously, most reported nitric oxide binding systems were studies in organic solvents[20-23].

The bonding rate of metalloporphyrin with nitric oxide was monitored as a function of reaction time. A solution of approximately 75 mL metalloporphyrin in CH_2Cl_2 (C_{ZnTPP} = 6.6068×10^{-5} mol L^{-1} and $C_{MgTPP} = 6.6068 \times 10^{-5}$ mol L^{-1}) was put into a cold trap at room temperature. Nitric oxide (5000 ppm) was added to the solution continuously for 3 h so that the bonding reaction of metalloporphyrin with nitric oxide could be maintained in a nitric oxide-saturated solution. 1 mL reacted metalloporphyrin solution was diluted 5 times and the dilute solutions were used for spectral analyses. The reaction of metalloporphyrin with nitric oxide is expected to be described by the eqn.

$$MP + nNO \longleftrightarrow MP(NO)_n \quad (1)$$

The kinetic process is described by the equation

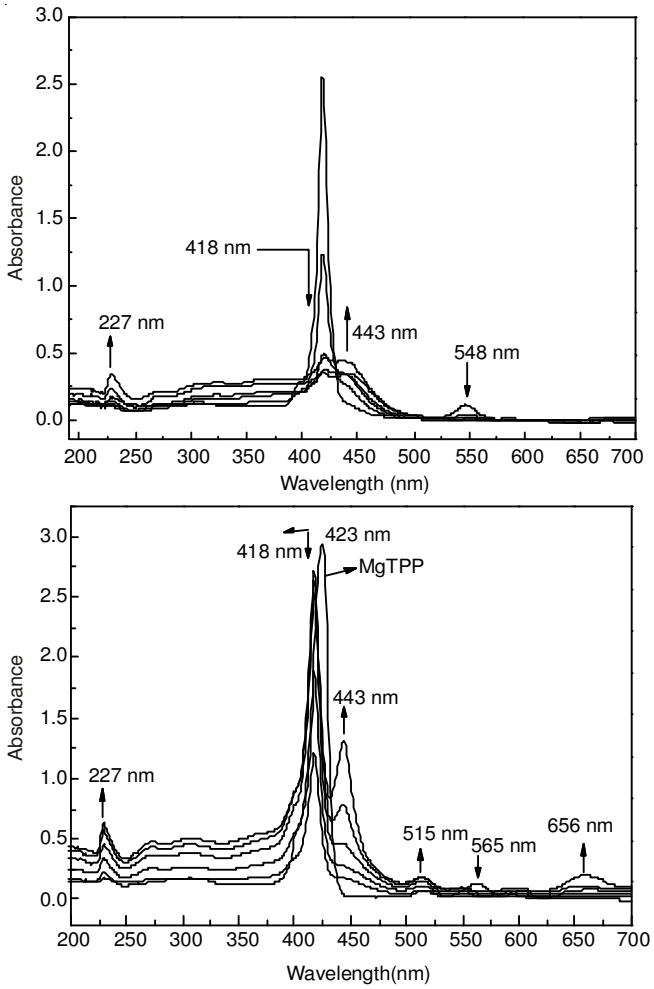

Fig. 3. UV-visible absorption spectral changes of the ZnTPP (above) solution and MgTPP (below) solution with increasing reaction time

$$-d[MP]/dt = k[MP][NO]_n \quad (2)$$

where [metalloporphyrin] denotes the concentration of metalloporphyrin, [NO] denotes the concentration of nitric oxide, t is the reaction time and k is the rate constant. When the concentration of nitric oxide keeps constant, the eqn. 2 is changed into eqns. 3 to 6 as follows:

$$-d[MP]/dt = k'[MP] \quad (3)$$

$$k' = k[NO]_n \quad (4)$$

$$-\ln([MP]_t/[MP]_0) = k't \quad (5)$$

$$t_{1/2} = \ln 2/k' \quad (6)$$

where $[MP]_0$ is the initial concentration of metalloporphyrin and [metalloporphyrin]t is the concentration of ZnTPP (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. 4 shows that concentration of metalloporphyrin in solution decreased with reaction time. The kinetics of the bonding of metalloporphyrin with nitric oxide is showed in Fig. 5. The figure showed that metalloporphyrin loss by bonding follows a pseudo first order reaction kinetics. The reaction rate constants and half life of bonding reaction are shown in Table-1. The experimental results showed that the coordination of MgTPP with nitric oxide is easier than ZnTPP. The reason of this phenomenon may be different numbers of

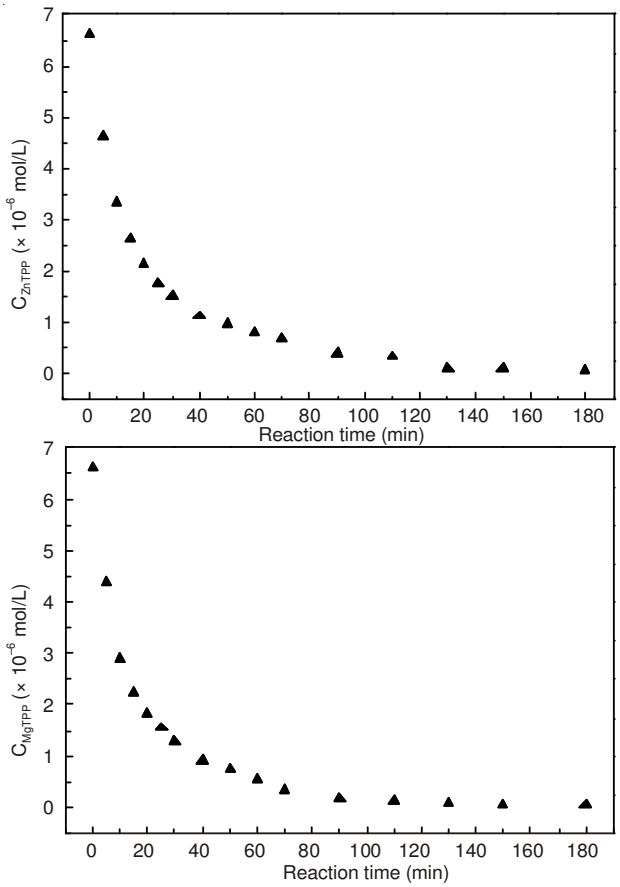

Fig. 4. Concentration of metalloporphyrin in solution decreased with reactino time [NO (5000 ppm) flow is 30 mL/min] (above: ZnTPP, below: MgTPP)

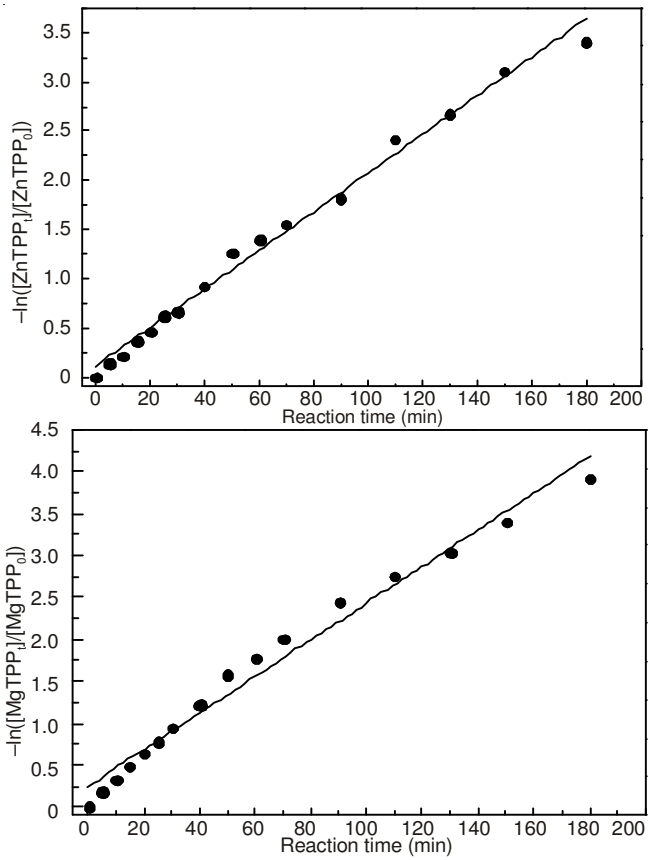

Fig. 5. Kinetics of the bonding reaction of metalloporphyrin with nitric oxide (above: ZnTPP, below: MgTPP)

TABLE-1
INTERCEPT VALUES: PSEUDO FIRST ORDER REACTION RATE CONSTANTS, k', AND HALF LIFES, $t_{1/2}$, FOR METALLOPORPHYRIN REACTION WITH NITRIC OXIDE AT ROOM TEMPERATURE

Metalloporphyrin	ZnTPP	MgTPP
k'/(min^{-1})	0.01965	0.02184
Correlation coefficient (R^2)	0.99054	0.97886
$t_{1/2}$ /min	35.27	31.74

atomic extranuclear electron of metal ion, or the different causes between the ion radius and the ionization potential[23].

Conclusion

The bonding of ZnTPP and MgTPP with nitric oxide were the pseudo first order reaction for metalloporphyrin. Under the same experimental conditions, the kinetic rate constant of bonding reaction of ZnTPP with nitric oxide for 0.01965 min^{-1} and the half-life of bonding reaction was 35.27 min. The kinetic rate constant of bonding reaction of MgTPP with nitric oxide for 0.02184 min^{-1} and the half-life of bonding was 31.74 min. The experimental results showed that the coordination of MgTPP with nitric oxide is easier than ZnTPP.

ACKNOWLEDGEMENTS

This work was supported by foundation of the "Western Light" Visiting Scholar Plan, the Program for Grassland Excellent Talents of Inner Mongolia Autonomous Region, the Inner Mongolia Science & Technology Plan, Inner Mongolia Autonomous Region's Educational Commission (No. NJZZ11068), the Inner Mongolia Talented People Development Fund and Yongfeng Boyuan Industry Co., Ltd. (Jiangxi Province, China).

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