

Photochemical fixation and reduction of sulfur dioxide to sulfide by tetraphenylporphyrin magnesium: Spectroscopic and kinetic studies

ZHANG JianBin^{1*}, LI ChunPing¹, HUO TianRui¹, LI Qiang¹,
ZHANG Tong¹ & WEI XiongHui^{2*}

¹College of Chemical Engineering, Inner Mongolia University of Technology, Huhhot 010051, China

²Department of Applied Chemistry, College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, China

Received October 28, 2011; accepted November 19, 2011; published online June 7, 2012

The photochemical reaction of sulfur dioxide (SO₂) with tetraphenylporphyrin magnesium (MgTPP) has been investigated in dichloromethane (CH₂Cl₂) solution at room temperature with illumination by visible light. Conventional fluorescence, UV-vis, and MS spectral analyses showed that under these conditions, SO₂ was initially photochemically fixed by MgTPP to form a 1:1 molecular adduct. On continued irradiation and maintaining the flow of SO₂, MS and XRD results showed that MgTPP is remarkably effective in the photochemical reduction of SO₂ to sulfide (S²⁻). The kinetics of the photochemical reaction of MgTPP with SO₂ was studied in a SO₂-saturated solution. Under irradiation, the reaction follows pseudo first order kinetics for MgTPP, having a half-life decreasing from 106 to 57 min as the illumination intensity is increased from 350 to 600 Lm. This investigation of the photochemical fixation and reduction of SO₂ by MgTPP is of key interest in elucidating fundamental photochemical reaction mechanisms associated with porphyrins in the presence of SO₂; furthermore, the analysis of the photochemical reaction may offer new opportunities for the fixation and reduction of SO₂ to less harmful species.

photoreduction, photochemical fixation, irradiation, sulfur dioxide, tetraphenylporphyrin magnesium, sulfide

1 Introduction

Sulfur dioxide (SO₂) is a conspicuous atmospheric pollutant, which results primarily from the combustion of sulfur-containing fossil fuels, and represents a major concern for public health in modern society. Consequently, its monitoring, quantification, removal, and ligand behavior in aquatic environments have been the subject of many studies, since these constitute fundamental aspects in the global natural sulfur cycle and in various chemical transformations of corrosion-inducing pollutants [1]. In order to remove SO₂, throwaway processes—such as the lime or limestone scrubbing processes—are the prevailing methods of flue gas

desulfurization (FGD) [2]. Furthermore, SO₂ treatment can be performed by the direct sulfur recovery process, in which SO₂ is converted into elemental sulfur with reducing agents, including hydrogen [3, 4], carbon monoxide [4–9], carbon [10], carbonyl sulfide (COS) [9], NH₃ [11], and hydrocarbons [12–15] (mainly CH₄), over a catalyst [4, 8, 16–20]. In addition, a number of transition metal complexes have been utilized as electron-transfer mediators to achieve electrochemical or photochemical interaction of SO₂. Previous photochemical studies also demonstrated the oxidation of SO₂ catalyzed by metalloporphyrin (MP) complexes containing peroxide ligands, or in the presence of molecular oxygen, to give sulfonato metalloporphyrin complexes [21, 22]. Electron transfer reactions between SO₂ and MP or metal(II) phthalocyanine (MPc) complexes could be used to convert harmful sulfur compounds to less harmful species

*Corresponding authors (email: xhwei@pku.edu.cn; tadzhang@pku.edu.cn)

[23–28].

Among the porphyrin complexes studied, magnesium porphyrins are typical model compounds for the reaction center of a photosynthetic system, and they have been demonstrated to be the most efficient homogenous catalysts in photochemical reduction reactions. Magnesium-containing porphyrin compounds have been extensively studied for a long time [29–36]. Mg(II) model complexes, such as tetraphenylporphyrin (TPP) and octaethylporphyrin (OEP), are still the focus of many ongoing studies because of their interesting spectroscopic and photochemical properties and their mechanistic significance. However, the photochemical reaction of MgTPP with SO₂ has not been described. Considerable research has been performed with ring-metal compounds in terms of ring-slippage processes, but far less has been done on systems containing SO₂-like ligands [37].

In the present study, MgTPP (Figure 1) was used to reduce SO₂ under irradiation. We utilize chemical, photochemical, and spectral techniques to examine the photochemical fixation and reaction of SO₂ with MgTPP, and find the reaction occurred efficiently in dichloromethane (CH₂Cl₂) under irradiation. Analysis of the photochemical reaction may offer new opportunities for the fixation and reduction of SO₂ associated with intermediates formed during the photocatalysis.

2 Experimental

2.1 Materials

MgTPP was prepared according to previous work [38–40]. SO₂ + N₂ mixture (SO₂ + N₂, Φ_{SO₂} = 1.97 × 10^{−3}) was purchased from the Beijing Zhaoge Co., Ltd., China. Dichloromethane (HPLC grade, >99.9%) was purchased from Tianjin Siyou, China). Other reagents and solvents were of reagent grade and used as received.

2.2 Characterization

Fluorescence spectra were acquired using an F-4500 fluo-

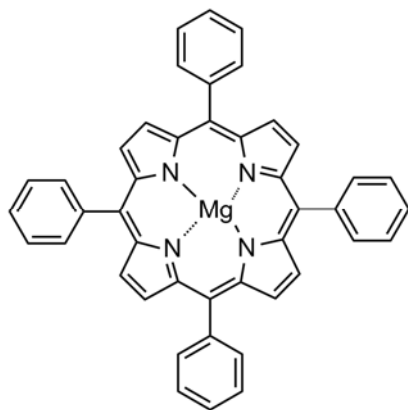


Figure 1 The structure of MgTPP.

rescence spectrophotometer employing a 500 W Hg–Xe high pressure lamp. UV-vis spectra were recorded on a Varian Cary IE UV-vis spectrometer. Mass spectra were recorded on a Bruker BIFLEX-3 matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometer and a Bruker APEX IV (7.0 T) Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS). X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-rA 12 kW X-ray diffractometer with Cu Kα radiation (40 kV, 100 mA).

2.3 Irradiation processes

Approximately 35 mL of a solution of MgTPP in CH₂Cl₂ (60 μmol L^{−1}) was put into a cold trap and irradiated using a 14 W incandescent lamp at a distance of 9 cm. The luminous flux of the lamp was 800 Lm at room temperature. Compressed SO₂ + N₂ mixtures were added to the solution continually for 6 h so that the photochemical reaction of MgTPP with SO₂ was always carried out in a SO₂-saturated solution. One mL of irradiated MgTPP solution was diluted five times with CH₂Cl₂ and the diluted solutions were used for various spectral analyses every 30 min. Meanwhile, control experiments were performed in the dark. In addition, the photochemical reaction of O₂ with MgTPP was used as another control experiment.

3 Results and discussion

3.1 Control experiment

Fluorescence emission spectroscopy and UV-vis absorption spectroscopy showed that CH₂Cl₂ solutions of MgTPP were stable in the presence of SO₂ for at least a few hours in the absence of irradiation. MALDI-TOF MS spectra of the resulting solution showed peaks at *m/z* 615.4 and 636.7 indicating that no reaction occurred between the ground state MgTPP and SO₂.

3.2 Fluorescence and UV-vis spectroscopy

Figure 2 shows photographs of the original MgTPP solution, the control solution irradiated in the presence of O₂ [41, 42], and the solution irradiated for 2 and 6 h in the presence of SO₂. After irradiation in the presence of SO₂, the color of the MgTPP solution changed from pink to blue and green which could be due to a photochemical reaction of MgTPP with SO₂. To study the reaction processes, the irradiated MgTPP solutions in the presence of SO₂ were analyzed by fluorescence and UV-vis spectroscopy every 30 min.

The fluorescence spectra (Figure 3) showed that, upon excitation at 550 nm, the fluorescence intensities of the Q* bands of MgTPP at 610 and 662 nm decreased with increasing irradiation time in the presence of SO₂. The significant quenching of the fluorescence of MgTPP can be at-

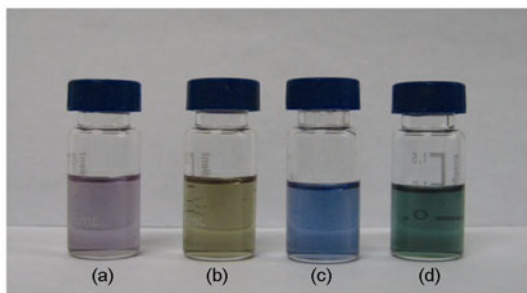


Figure 2 Photographs of MgTPP solution (a), MgTPP + O₂ solution after irradiation (b), MgTPP + SO₂ solution after 2 h irradiation (c), and MgTPP + SO₂ solution after 6 h irradiation (d).

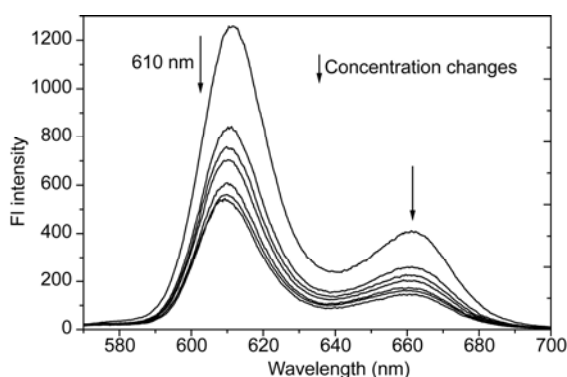


Figure 3 Changes in fluorescence emission spectra ($\lambda_{\text{ex}} = 550$ nm) of MgTPP with increasing irradiation time in the presence of SO₂.

tributed to electron transfer taking place from the porphyrin part of MgTPP to an acceptor molecule, which suggests that a photochemical interaction occurs between MgTPP and SO₂.

UV-vis absorption spectra of MgTPP solution (Figure 4) showed a typical Soret band and several Q bands. The band at 424 nm (B(0, 0)) has been assigned [43] to the Soret band of MgTPP arising from the transition $a_{1u}(\pi) \rightarrow e_g^*(\pi)$. Similar Soret absorption bands (B-bands) have been observed for most porphyrinic compounds [44, 45] and attributed to excitonic interactions between the large Soret transition di-

poles of the constituent porphyrin chromophores. Thus changes in the Soret band are a very important way to explore photochemical interaction between porphyrinic compounds and other molecules. The Q bands of MgTPP were observed at 516, 563 and 603 nm, and it has been reported [43] that these bands arise from the transition $a_{2u}(\pi) \rightarrow e_g^*(\pi)$. UV-vis spectra (Figures 4(a) and (b)) showed that the absorption intensities of the Soret band at 424 nm and the Q bands at 563 and 516 nm decreased with increasing irradiation time. A new Soret band observed at 443 nm could be due to the reaction of SO₂ with the porphyrin part of MgTPP. Meanwhile, the absorption band associated with the $n \rightarrow \pi^*$ electron transition of SO₂ was observed at 285 nm [46] and the absorption intensity of the band increased with increasing SO₂ concentration. The presence of the new Soret band at 443 nm and a new Q band at 658 nm suggest that MgTPP reacted with SO₂ resulting in the formation of a new compound. With the appearance of the final absorption spectrum, no further spectral changes were observed upon continued irradiation.

3.3 MS spectra

MS spectra of the original MgTPP solution and the MgTPP solution after irradiation for 2 and 6 h in the presence of SO₂ were recorded using a MALDI-TOF mass spectrometer and are shown in Figure 5. The spectrum of the original MgTPP solution (Figure 5(a)) showed two ion peaks at m/z 615.4 and 636.4. The peak at m/z 636.4 can be attributed to the molecular ion peak of MgTPP and that at m/z 615.4 to the fragment ion peak after loss of Mg from MgTPP. The spectrum of the MgTPP solution after irradiation for 2 h in the presence of SO₂ (Figure 5(b)) showed four ion peaks at m/z 615.3, 636.6, 648.2 and 701.3. The peak at m/z 648.2 can be attributed to the ion peak of either the TPP-S or the TPP-O₂ complex and the peak at m/z 701.3 can be related to the molecular ion peak of MgTPP-SO₂. The MS spectra indicate that under irradiation, one SO₂ molecule was photochemically fixed by one MgTPP molecule to form a stable 1:1 adduct of MgTPP-SO₂. With increasing irradiation time

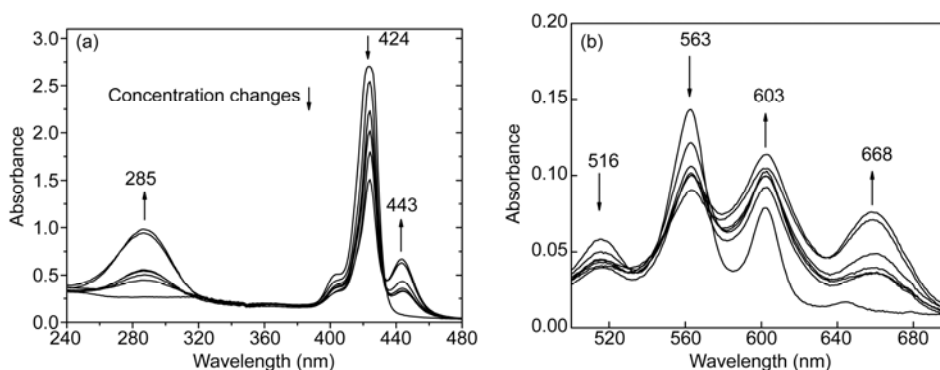


Figure 4 Changes in UV-vis absorption spectra of the original MgTPP solution diluted five times with CH₂Cl₂ with increasing irradiation time in the presence of SO₂. (a) (380–480 nm); (b) (500–700 nm).

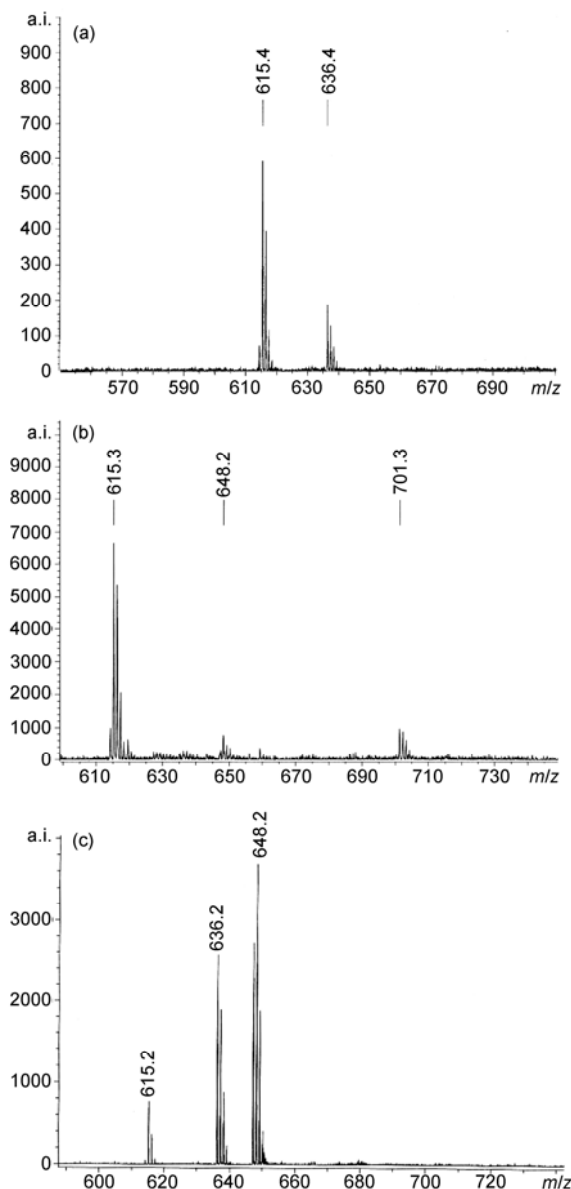


Figure 5 MALDI-TOF MS spectra of the original MgTPP solution (a), MgTPP solution in the presence of SO_2 after 2 h irradiation (b), and MgTPP solution in the presence of SO_2 after 6 h irradiation (c).

in the presence of SO_2 (Figure 5(c)), the ion peak at m/z 701.3 disappeared and that at m/z 648.2 increased in intensity.

Accurate MS detection was performed using high resolution MS and the spectra showed special ion peaks at m/z 647.2454. For the peak at m/z 647.2454 (M) in Figure 5, the intensity ratio $(M + 1)/M$ is about 0.50 and $(M + 2)/M$ is about 0.15. According to the probability relation characteristics (see the Supporting Information), the peak at m/z 647.2454 can be attributed to the ion peak of the TPP-S complex. These mass spectra indicate that one MgTPP molecule reacts with one SO_2 molecule to form a stable 1:1 adduct under irradiation; meanwhile, S^{2-} was formed.

3.4 X-ray diffraction (XRD)

After photochemical reaction of MgTPP with SO_2 , a green solid could be isolated. The solid was added to an aqueous solution of $\text{Pb}(\text{CH}_3\text{COO})_2$ and aqueous solution HCl was then added. The XRD pattern (Figure 6) of the grayish-black precipitate showed peaks characteristic of PbS at 30.50° , 46.38° , and 51.03° . 2θ , and other diffraction peaks characteristic of PbCl_2 . The XRD data thus confirm that SO_2 had been photochemically reduced to S^{2-} by MgTPP.

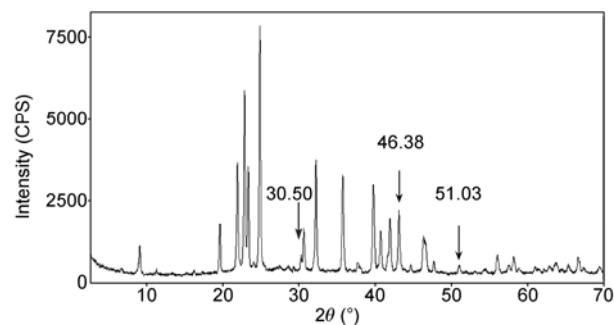
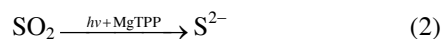
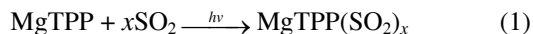


Figure 6 X-ray diffraction pattern of the sulfur-containing compound.

3.5 Photochemical reaction kinetics

According to the above results, the first product of the MgTPP with SO_2 is the species $\text{MgTPP}(\text{SO}_2)_x$ (eq. 1); meanwhile, SO_2 was photoreduced to sulfide by MgTPP (eq. 2).



The photochemical reaction (eq. 1) rate of MgTPP with SO_2 was monitored by fluorescence spectroscopy as a function of irradiation time. Approximately 35 mL of a solution of 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 at room temperature. The luminous fluxes of the lamps were 220, 400, and 600 Lm. Compressed $\text{SO}_2 + \text{N}_2$ with a flow rate of 30 mL/min was added to the solution continuously for 4 h so that the photochemical reaction of MgTPP with SO_2 was continuously carried out in a SO_2 -saturated solution. One mL of irradiated MgTPP solution was diluted five times for spectral analyses every 5–30 min. The reaction of MgTPP with SO_2 is expected to be described by the equation



The kinetic process is described by the equation

$$-d[\text{MgTPP}]/dt = k[\text{MgTPP}][\text{SO}_2]^x \quad (4)$$

where $[\text{MgTPP}]$ denotes the concentration of MgTPP, $[\text{SO}_2]$ denotes the concentration of SO_2 , t is the reaction time, and k is the rate constant.

When the concentration of SO_2 is kept constant, eq. (4) may be replaced by eqs. (5)–(8) as follows:

$$-d[\text{MgTPP}]/dt = k'[\text{MgTPP}] \quad (5)$$

$$k' = k[\text{SO}_2]^x \quad (6)$$

$$-\ln([\text{MgTPP}]_t/[\text{MgTPP}]_0) = k't \quad (7)$$

$$t_{1/2} = \ln 2/k' \quad (8)$$

where $[\text{MgTPP}]_0$ is the initial concentration of MgTPP and $[\text{MgTPP}]_t$ is the concentration of MgTPP at t min. A plot of the natural logarithm of the function on the left-hand side of eq. (7) as a function of time should yield a straight line with a slope of k' .

Figure 7 shows that when photochemical reaction took place at various irradiation intensities, the concentration of MgTPP in solution decreased with increasing irradiation time in each case. Furthermore, the concentration of MgTPP in solution decreased more rapidly with increasing irradiation intensities.

Figure 8 shows typical plots of eq. (7) for experiments in which MgTPP was irradiated at various irradiation intensities. The linear plots show that loss of MgTPP by the photochemical reaction follows pseudo first order reaction kinetics. The reaction rate constants and half lives of the photochemical reactions at different irradiation intensities are

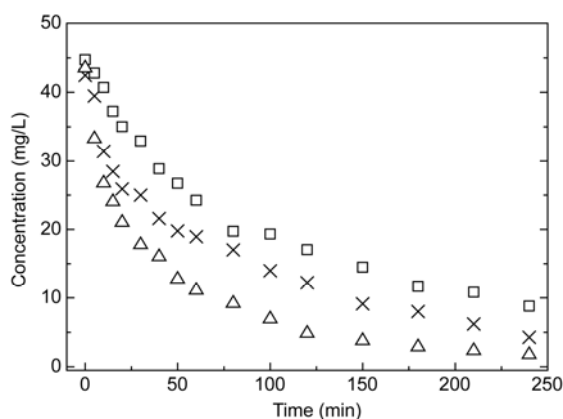


Figure 7 Dependency of the concentration of MgTPP (mg/L) on irradiation time in CH_2Cl_2 (with a gas flow of 30 mL/min and a concentration of MgTPP of 30 mg/L) at various irradiation intensities: \square , 235 Lm; \times , 400 Lm; Δ , 600 Lm.

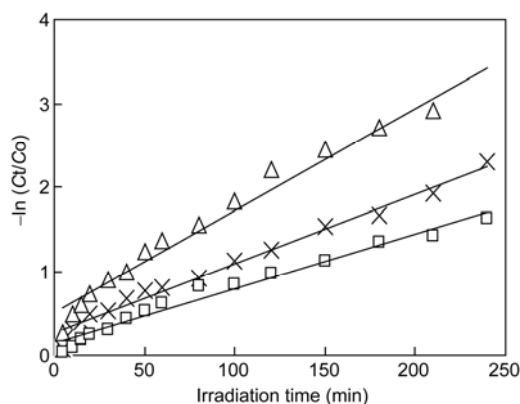


Figure 8 Photochemical kinetics of the reaction of MgTPP with SO_2 at various irradiation intensities: \square , 235 Lm; \times , 400 Lm; Δ , 600 Lm.

shown in Table 1, together with the correlation coefficients obtained from the linear regression analysis. The half-life of the photochemical reaction of MgTPP with SO_2 decreased from 106 to 57 min as the irradiation intensity was increased from 350 to 600 Lm.

Table 1 Values of the pseudo first order reaction rate constant, k' , and half life, $t_{1/2}$, for the reaction of MgTPP with SO_2 at different irradiation intensities

Irradiation intensity (Lm)	235	400	600
k' (min^{-1})	0.00654	0.00827	0.0122
Correlation coefficient (R^2)	0.9759	0.9837	0.9758
$t_{1/2}$ (min)	105.99	83.81	56.82

4 Conclusion

MgTPP is a remarkably efficient material for the photochemical fixation of SO_2 and its subsequent reduction to S^{2-} . In this process, one SO_2 molecule becomes bound to an MgTPP molecule to form a 1:1 adduct. SO_2 was subsequently photochemically reduced to S^{2-} . The half-life of the photochemical reaction of MgTPP with SO_2 decreased from 106 to 57 min as the irradiation intensity was increased from 350 to 600 Lm.

We thank Professor Wenting Hua and Professor Hongcheng Gao (Peking University, China) for their suggestions concerning the photochemical reaction of MgTPP with SO_2 . This work was supported by the Foundation of Inner Mongolia Autonomous Region's Educational Commission (NJZZ11068), the School Scientific Research Fund (ZD201004, Inner Mongolia University of Technology, China) and Yongfeng Boyuan Industry Co., Ltd. (Jiangxi Province, China).

- Zagal JH. Metallophthalocyanines as catalysts in electrochemical reactions. *Coord Chem Rev*, 1992, 119: 89–136
- Makansi J. Will combined SO_2/NO_x processes find a niche in the market? *Power*, 1990, 134: 26–28
- Bresinska I, Dudzik Z. Reduction of sulfur dioxide with hydrogen on Na-X zeolite. *React Kinet Catal Lett*, 1986, 31: 21–26
- Han GB, Park N, Ryu SO, Lee TJ. Catalytic reduction of sulfur dioxide using hydrogen or carbon monoxide over $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts for the recovery of elemental sulfur. *Catal Today*, 2008, 131: 330–338
- Han GB, Park N, Yoon SH, Lee TJ. Catalytic reduction of sulfur dioxide with carbon monoxide over tin dioxide for direct sulfur recovery process. *Chemosphere*, 2008, 72: 1744–1750
- Ma JX, Fang M, Lau NT. The catalytic reduction of SO_2 by CO over lanthanum oxysulphide. *Appl Catal A: Gen*, 1997, 150: 253–268
- Ma JX, Fang M, Lau NT. On the synergism between $\text{La}_2\text{O}_3\text{S}$ and CoS_2 in the reduction of SO_2 to elemental sulfur by CO. *J Catal*, 1996, 158: 251–259
- Liu W, Sarofim AF, Sarofim DW, Flytzani-Stephanopoulos, M. Reduction of sulfur dioxide by carbon monoxide to elemental sulfur over composite oxide catalysts. *Appl Catal B: Environ*, 1994, 4: 167–186
- Lau NT, Fang M, Chan CK. Reduction of SO_2 by CO and COS over $\text{La}_2\text{O}_3\text{S}$: A mechanistic study. *J Mol Catal A: Chem*, 2003, 203: 221–229

- 10 Zheng S, Yang Q, Zhang H, Chen Z, Liang G, Yue W. Thermodynamic equilibrium verify for carbonthermal reduction of sulfur dioxide. *Environ Chem*, 1997, 16: 300
- 11 Zhang L, Qi X, Qing Y, Song J. The effect of carrier on the catalytic property of nickel-based catalyst for reducing sulfur dioxide to elemental sulfur by ammonia. *J Environ Sci*, 2000, 20: 122
- 12 Zhang X, Haywar DO, Lee C, Mingo D. Microwave assisted catalytic reduction of sulfur dioxide with methane over MoS_2 catalysts. *Appl Catal B: Environ*, 2001, 33: 137–148
- 13 Sarlis J, Berk D. Reduction of SO_2 by CH_4 over transition oxide catalysts. *Chem Eng Comm*, 1996, 140: 73–85
- 14 Yu JJ, Yu Q, Jin Y, Chang SG. Reduction of SO_2 by CH_4 to elemental sulfur over supported cobalt catalysts. *Ind Eng Chem Res*, 1997, 36: 2128–2133
- 15 Wang C, Lin S, Sung P, Weng H. Catalytic reduction of SO_2 over supported transition-metal oxide catalysts with C_2H_4 as a reducing agent. *Appl Catal B: Environ*, 2003, 40: 331–345
- 16 Dumani TF, Bradley WE. Recovery of sulfur from sulfur dioxide in waste gases. *Ind Eng Chem*, 1944, 36: 329–332
- 17 Park JH, Han JD. Selective catalytic reduction of sulfur-dioxide with hydrogen to elemental sulfur over $\text{Co-Mo/Al}_2\text{O}_3$. *J Korean Ind Eng Chem*, 1999, 10: 1129
- 18 Han GB, Park N, Lee JD, Ryu SO, Lee TJ. A study on the characteristics of the SO_2 reduction using coal gas over $\text{SnO}_2\text{-ZrO}_2$ catalysts. *Catal Today*, 2006, 111: 205–211
- 19 Ma JX, Fang M, Lau NT. Activation of La_2O_3 for the catalytic reduction of SO_2 by CO. *J Catal*, 1996, 163: 271–278
- 20 Ma JX, Fang M, Lau NT. The catalytic reduction of SO_2 by CO over lanthanum oxysulphide. *Appl Catal*, 1997, 150: 253–268
- 21 Miksztal AR, Valentine JS. Reactivity of the peroxo ligand in metalloporphyrin complexes. Reaction of sulfur dioxide with iron and titanium porphyrin peroxo complexes to give sulfato complexes or sulfate. *Inorg Chem*, 1984, 23: 3548–3552
- 22 Scheidt NR, Lee YJ, Finnegan MG. Reactions of sulfur dioxide with iron porphyrinates and the crystal structure of (hydrogen sulfato)(tetraphenylporphinato)iron(III) hemibenzene solvate. *Inorg Chem*, 1988, 27: 4725–4730
- 23 Nensala N, Nzimande A, Nyokong T. Photochemically induced electron transfer between sulfur dioxide and tin(IV) mono- and di-phthalocyanines. *J Photochem Photobiol A: Chem*, 1996, 98: 129–135
- 24 Thamae M, Nyokong T. Interaction of sulfur dioxide and cyanide with cobalt(II) tetrasulfophthalocyanine in aqueous media. *Polyhedron*, 2002, 21: 133–140
- 25 Pasiuk-Bronikowska W, Krajewska M, Flis-Kabulska I. Transformations of manganese tetrasulphophthalocyanine in oxidative conditions. *Polyhedron*, 1998, 18: 561–570
- 26 Hoffmann MR. Trace metal catalysis in aquatic environments. *Environ Sci Technol*, 1980, 14: 1061–1066
- 27 Boyce SD, Hoffmann MR, Andrew Hong P, Moberly M. Catalysis of the autoxidation of aquated sulfur-dioxide by homogeneous metal phthalocyanine complexes. *Environ Sci Technol*, 1983, 17: 602–611
- 28 Rajendiran JS. Interaction of sulfur dioxide with zinc(II) tetrasulfo phthalocyanine in aqueous medium: Steady state fluorescence quenching studies. *Polyhedron*, 2002, 21: 951–957
- 29 Edwards WD, Head JD, Zerner MC. On the electronic excited states of model chlorophyll. *J Am Chem Soc*, 1982, 104: 5833–5834
- 30 O'Shea DF, Miller MA, Matsueda H, Lindsey JS. investigation of the scope of heterogeneous and homogeneous procedures for preparing magnesium chelates of porphyrins, hydroporphyrins, and phthalocyanines. *Inorg Chem*, 1996, 35: 7325–7338
- 31 Willigen H, Ebersole MH. ESR and ENDOR study of the photooxidation of magnesium and zinc tetrakis(4-sulfonatophenyl)porphyrins. *J Am Chem Soc*, 1987, 109: 2299–2302
- 32 Miller JR, Dorrough GD. pyridinate complexes of some metallo-derivatives of tetraphenylporphine and tetraphenylchlorin. *J Am Chem Soc*, 1952, 74: 3977–3981
- 33 Kozlowski PM, Wolinski K, Pulay P. GIAO nuclear magnetic shielding tensors in free base porphyrin and in magnesium and zinc metalloporphyrins. *J Phys Chem A*, 1999, 103: 420–425
- 34 Zaleski JM, Chang CK, Leroi GE, Cukier RI, Nocera DG. Role of solvent dynamics in the charge recombination of a donor/acceptor pair. *J Am Chem Soc*, 1992, 114: 3564–3565
- 35 Wróbel D, Boguta A, Ion RM. Mixtures of synthetic organic dyes in a photoelectrochemical cell. *J Photochem Photobiol A: Chem*, 2001, 138: 7–22
- 36 Wróbel D, Lukasiewica J, Henryk M. Fluorescence quenching and ESR spectroscopy of metallic porphyrins in the presence of an electron acceptor. *Dyes Pigments*, 2003, 58: 7–18
- 37 Shen JK, Kubas GJ, Rheingold AL. Kinetics and mechanisms of ligand and substitution reactions of molybdenum SO_2 complexes. Synthesis and X-ray structure of *trans*- $\text{Mo}(\text{CO})_2(\text{dmpe})(\text{PPh}_3)(\text{SO}_2)$. *Inorg Chim Acta*, 1995, 240: 99–104
- 38 Baum SJ, Plane RA. Kinetics of the incorporation of magnesium(II) into porphyrin. *J Am Chem Soc*, 1966, 88: 910–913
- 39 Adler AD, Longo FR, Finarelli JD, Goldmacher J, Assour J, Korsakoff L. A simplified synthesis for meso-tetraphenylporphine. *J Org Chem*, 1967, 32: 476–476
- 40 Lindsey JS, Woodford JN. A simple method for preparing magnesium porphyrins. *Inorg Chem*, 1995, 34: 1063–1069
- 41 Zhang JB, Zhang PY, Zhang ZF, Wei XH. Spectroscopic and kinetic studies of photochemical reaction of magnesium tetraphenylporphyrin with oxygen. *J Phys Chem A*, 2009, 113: 5367–5374
- 42 Zhang JB, Zhang PY, Chen GH, Han F, Wei XH. Photochemical reaction between magnesium tetraphenyl porphyrin and oxygen. *Chinese Chem Lett*, 2008, 19: 1190–1192
- 43 Zhang WQ, Shan N, Yu LX, Wang XQ. UV-visible, fluorescence and EPR properties of porphyrins and metalloporphyrins. *Dyes Pigments*, 2008, 77: 153–157
- 44 Collman JP, Yan LL, Eberspacher T, Xie XJ, Solomon EI. Oxygen binding of water-soluble cobalt porphyrins in aqueous solution. *Inorg Chem*, 2005, 44: 9628–9630
- 45 Wynne K, Lecours SM, Calli C, Therien MJ, Hochstrasser RM. Porphyrin-quinone electron transfer revisited. The role of excited state degeneracy in ultrafast charge transfer reactions. *J Am Chem Soc*, 1995, 117: 3749–3753
- 46 Leontiev AV, Rudkevich DM. Revisiting nocovalent SO_2 -amine chemistry: An indicator-displacement assay for colorimetric detection of SO_2 . *J Am Chem Soc*, 2005, 127: 14126–14127

Photochemical fixation and reduction of sulfur dioxide to sulfide by tetraphenylporphyrin magnesium: Spectroscopic and kinetic studies

ZHANG JianBin^{1*}, LI ChunPing¹, HUO TianRui¹, LI Qiang¹,
ZHANG Tong¹ & WEI XiongHui^{2*}

¹College of Chemical Engineering, Inner Mongolia University of Technology, Huhhot 010051, China

²Department of Applied Chemistry, College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, China

Received October 28, 2011; accepted November 19, 2011; published online June 7, 2012

1 Accurate MS discussion

FT-ICR-MS spectra of MgTPP solution after irradiated 6 h in the presence of SO₂ is shown in Figure S1.

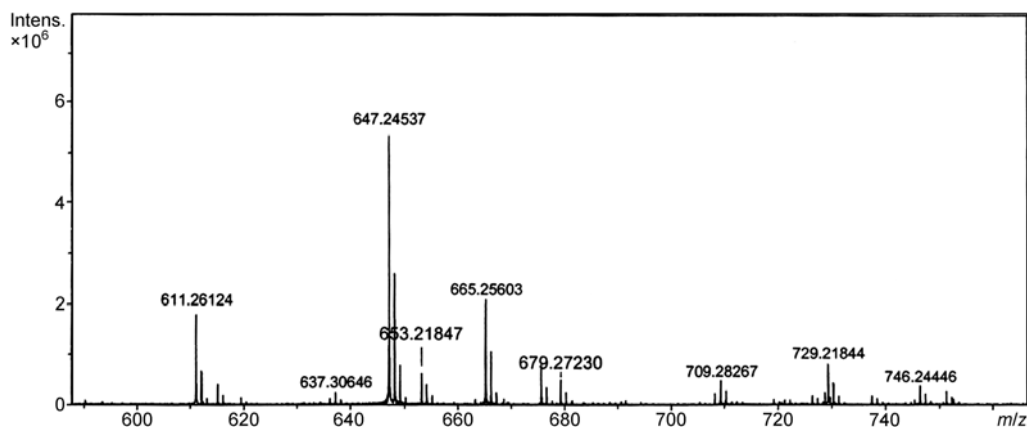
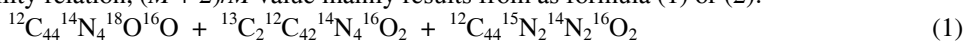


Figure S1 FT-ICR-MS spectrum of MgTPP solution after irradiated 6 h in the presence of SO₂ (the calibration compound's m/z is observed at 611.26124).

For the possible adduct at m/z of 647.2454, there are 44 carbon atoms, 4 nitrogen carbon, and 1 sulfur atom or 2 oxygen atoms. There don't consider hydrogen and magnesium atom because the $(M + 1)/M$ values of these atoms are very low. According to characteristics of probability relation, $(M + 2)/M$ value mainly results from as formula (1) or (2):

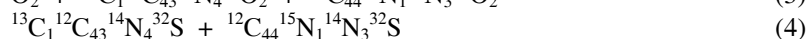


*Corresponding authors (email: xhwei@pku.edu.cn; tadzhang@pku.edu.cn)

From the formula (1), $(M+2)/M = 0.118$

From the formula (2), $(M+2)/M = 0.158$

At the same time, $(M+1)/M$ value mainly results from as formula 3 or 4:



From the formula (3), $(M+1)/M = 0.4988$

From the formula (4), $(M+1)/M = 0.4988$

2 FTIR spectra were acquired as KBr discs on a Bruker VECTOR22 FTIR spectrometer

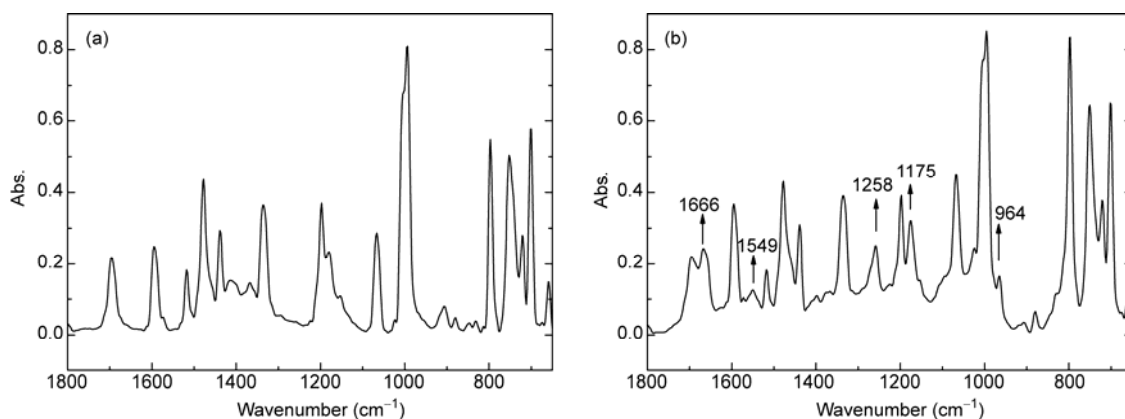


Figure S2 FTIR spectral comparison of MgTPP with MgTPP in the presence of SO_2 under irradiation. (a) Represents the FTIR spectrum of MgTPP and (b) represents the FTIR spectrum of MgTPP in the presence of SO_2 under irradiation.

3 The possible general proceeding of photochemical reaction of MgTPP with SO_2

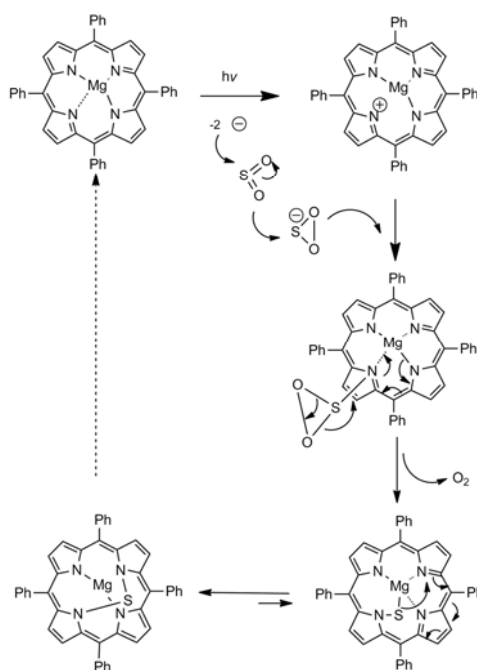


Figure S3 The possible general proceeding.