

Autoxidation of 2,6-di-*tert*-butylphenol catalyzed by 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl]porphyrinatocobalt(II) tetraiodide in water

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Abstract

The cationic cobalt(II) porphyrin complex: 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl]porphyrinatocobalt(II) tetraiodide has been found to be an efficient catalyst for the oxidation of 2,6-di-*tert*-butylphenol by dioxygen in aqueous medium. The oxidation reaction afforded mainly the corresponding diphenoquinone and some of the 2,6-di-*tert*-butyl-1,4-benzoquinone. The initial rate constant of autoxidation reaction was found to increase with increasing pH from 7.0 to 10.0. The rate of autoxidation reaction showed linear dependence on catalyst concentration and dioxygen pressure. The rate of autoxidation reaction was found to fit a Michealis–Menten kinetic model for saturation of catalyst sites with increasing 2,6-di-*tert*-butylphenol concentration. The catalyst showed reduced activity in repeat oxidation reactions.

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1. Introduction

The development of efficient catalytic systems for oxidation reactions that mimic the action of cytochrome P-450 dependent monooxygenases has attracted much interest in recent years [1–7]. Synthetic metallo-porphyrins have been used to catalyze the transfer of an oxygen atom from a great variety of oxidizing agents into organic molecules [1–19].

The autoxidation of phenols catalyzed by transition metals is of industrial and biological importance [20]. There are only a few reports in the literature dealing with the metallo-porphyrins catalyzed oxidations and photo-oxidations of phenols [11–19,21,22].

The aim of the present work is to investigate the potential use of water soluble cationic cobalt(II) porphyrin: 5,10,15,20-tetrakis[4-(diethylmethylammonio)phenyl]porphyrinatocobalt(II) tetraiodide bearing quaternary ammonium groups as catalyst in the oxidation of 2,6-di-*tert*-butylphenol by molecular oxygen.

2. Experimental

2.1. Materials and reagents

Pyrrol (Merck), 4-(*N,N*-diethylamino)benzaldehyde (Aldrich). Methyl iodide (Aldrich) was used as received. 2,6-Di-*tert*-butylphenol (Aldrich) was recrystallized from *n*-hexane. Silica gel (Prolabo, 60–120 mesh), PLC (Silica gel plates, Merck) plates, 2 mm thickness, 20 cm × 20 cm were used for chromatographic analysis.

2.2. Measurements

Elemental microanalysis was performed by Microanalysis Center at Cairo University. ¹H NMR data were measured on Varian Germany 200 NMR instrument. Spectrophotometric measurements were carried out on Shimadzu 3101Pc UV–vis Spectrometer.

2.3. Preparation of cationic cobalt(II) tetraarylporphyrin **1**

5,10,15,20-Tetrakis[4-(diethylmethylammonio)phenyl]porphyrinatocobalt(II) tetraiodide **1** was prepared in three

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steps: fusion of 4-(*N,N*-diethylamino)benzaldehyde with pyrrole according to the published method [23] gave 5,10,15,20-tetrakis[4-(diethylaminophenyl)]porphyrin. Elemental microanalysis, found: 78.0% C; 7.30% H; 12.29% N. Calc.: 78.62% C; 7.42% H; 12.22% N. Cobalt(II) complex of 5,10,15,20-tetrakis[4-(diethylaminophenyl)]porphyrin was prepared as described previously [24]. Elemental microanalysis, found: 11.10% N. Calc. 11.72% N. Cationic complex **1** was obtained by refluxing of the cobalt(II) complex with methyl iodide in chloroform. Elemental microanalysis (found: 7.80% N. Calc.: 7.35% N). UV–vis: (MeOH) λ_{max} , nm (ϵ , mol⁻¹ L cm⁻¹) 302 (28.71 × 10³), 429.5 (12.38 × 10⁴), 537.5 (14.45 × 10³), 583.5 (8.95 × 10³).

¹H NMR (DMSO; Me₄ Si): δ 1.56 (t, 24H, -CH₃), 2.09 (s, 12H, CH₃), 4.09 (q, 16H, -CH₂), 7.96 (m, 16H, Ph), 8.97 (s, 8H, β -pyrrole).

2.4. Autoxidation reactions

Oxidation reactions of 2,6-di-*tert*-butylphenol were performed as described previously [25] by stirring of 100 ml of aqueous solution containing 0.05 volume fraction methanol in a 250 ml flask attached to a gas burette. All reactions were carried out at 40 °C and constant dioxygen pressure slightly less than 1 atm. Lower partial pressures of oxygen were obtained by use of oxygen/nitrogen mixtures at 1 atm total pressure. After completion of the reaction the mixture was extracted with ether and dichloromethane. The extract was analyzed by TLC. Reaction products were separated on PLC-G F₂₅₄ silica gel plates (Merck), 2 mm thickness, 20 cm × 20 cm, using petroleum ether (40–60)/ethyl acetate 9.5:0.5 as eluent and were identified by comparison with authentic samples. All kinetic experiments were carried out in duplicate and reproducible results were obtained.

2.5. Catalyst reuse

Reuse of catalyst **1** was performed as follows: autoxidation of 2,6-di-*tert*-butylphenol was carried out under standard reaction conditions of Table 1. The reaction was followed by dioxygen uptake. After the completion of the first run, the initial amount of phenol was again fed into reaction mixture without removal of the reaction products.

3. Results and discussion

3.1. Autoxidation of 2,6-di-*tert*-butylphenol

The catalytic activity of water soluble cationic cobalt(II) porphyrin complex **1** was investigated in the autoxidation of 2,6-di-*tert*-butylphenol. The rate of phenol consumption was determined by measuring the amount of dioxygen using a gas burette. After a short induction period, the volume of dioxygen consumed was linear with time, indicating a zero-order dependence on the concentration of the substrate.

Data summarized in Table 1 show that autoxidation of 2,6-di-*tert*-butylphenol catalyzed by the cationic cobalt(II) porphyrin

Table 1

Conversion and selectivity of the autoxidation of 2,6-di-*tert*-butylphenol catalyzed by **1**^a

Catalyst	Conversion ^b (%)	Time (h)	Selectivity ^b		$k_{\text{obs}}^{\text{c}}$, mol L ⁻¹ min ⁻¹ (10 ⁻⁵)
			DPQ ^c	BQ ^d	
–	10.0	24	–	–	–
1	100	2.10	90	10	1.829

^a All experiments were carried out at 35 °C and oxygen pressure of 740 mmHg with magnetic stirring of 1.5 mmol of phenol dissolved in 5 ml of methanol dispersed in 100 ml of distilled water containing 0.015 mmol of catalyst. The pH of the reaction was adjusted to 9.0 by using borax and HCl.

^b Conversion and selectivity are based on isolated products after completion of the reaction. Reaction products have been separated on PLC (Silica gel plates, Merck) plates, 2 mm thickness, 20 cm × 20 cm using petroleum ether and ethyl acetate (9.5:0.5) as eluent.

^c DPQ: 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenquinone.

^d BQ: 2,6-di-*tert*-butyl-1,4-benzoquinone.

^e Initial zero-order rate constant calculated from the plot of oxygen consumption vs. time.

complex **1** in water gave 100% conversion of 2,6-di-*tert*-butylphenol to 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenquinone (DPQ) in 90% yield and 2,6-di-*tert*-butyl-1,4-benzoquinone (BQ) in 10% yield within about 2 h. In absence of catalyst **1**, the reaction was slow and only 10% conversion of 2,6-di-*tert*-butylphenol was observed in 24 h.

The rate enhancing effect of the cationic catalyst **1** could be attributed to direct binding of the 2,6-di-*tert*-butylphenoxide ion to the quaternary ammonium groups at the active site.

3.2. Effect of pH on the autoxidation of 2,6-di-*tert*-butylphenol

The autoxidation of 2,6-di-*tert*-butylphenol was studied in the pH range 7.0–10.0 (Fig. 1). Data summarized in Table 2 show that the zero-order rate constant of autoxidation of 2,6-di-*tert*-butylphenol increased with increasing pH of the reaction mixture from 7.0 to 10.0. The pH has a direct effect on the concentra-

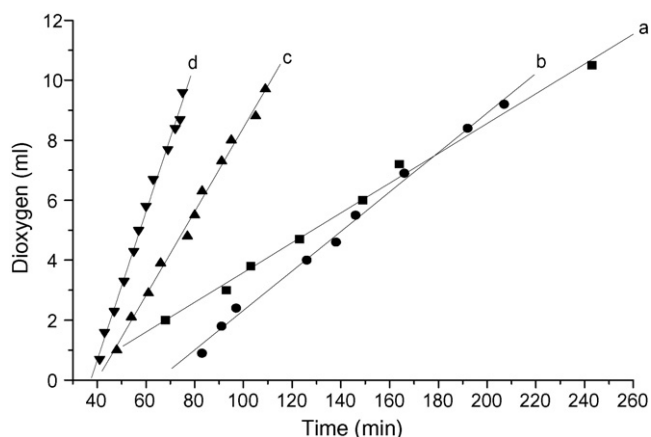


Fig. 1. Effect of pH on the autoxidation of 2,6-di-*tert*-butylphenol catalyzed by cobalt(II) porphyrin complex **1**. (a) pH 7, (b) pH 8, (c) pH 9, (d) pH 10. The pH was adjusted to 8 and 9 using NaB₄O₇ and HCl buffer mixture and the pH was adjusted to 10 using NaHCO₃ and NaOH buffer mixture. A phosphate buffer was used to adjust pH to 7.

Table 2
Effect of pH on the rate of autoxidation of 2,6-di-*tert*-butylphenol^a

pH	k_{obs} , mol L ⁻¹ min ⁻¹ (10 ⁻⁵)
7.0	0.621
8.0	0.960
9.0	1.829
10.0	2.706

^a All reactions were carried out under conditions reported in Table 1. Initial zero-order rate constant calculated from the plot of oxygen consumption vs. time.

tion of 2,6-di-*tert*-butylphenoxide ion. The rate enhancement of autoxidation of 2,6-di-*tert*-butylphenol with increasing pH of the reaction medium indicates that 2,6-di-*tert*-butylphenoxide ion is probably the active species [26].

3.3. Effect of concentration of the catalyst **1** on the autoxidation of 2,6-di-*tert*-butylphenol

The dependence of the initial rate constant k_{obs} on the concentration of the cationic porphyrin complex **1** was investigated in the concentration range 0.75×10^{-5} to 3.75×10^{-5} M (Fig. 2). Data illustrated in Fig. 3 show the increase of the initial rate constant k_{obs} of the oxidation reaction with increasing of the concentration of the catalyst **1** which could be attributed to increase of available quaternary ammonium sites for phenoxide ion binding.

3.4. Effect of temperature on the autoxidation of 2,6-di-*tert*-butylphenol

The temperature dependence of the reaction rate constant k_{obs} from 29 to 55 °C gave an Arrhenius activation energy of 40.16 kJ/mol (Fig. 4).

3.5. Effect of concentration of 2,6-di-*tert*-butylphenol on the rate of autoxidation

The dependence of reaction rate constant k_{obs} on the concentration of 2,6-di-*tert*-butylphenol was investigated in the

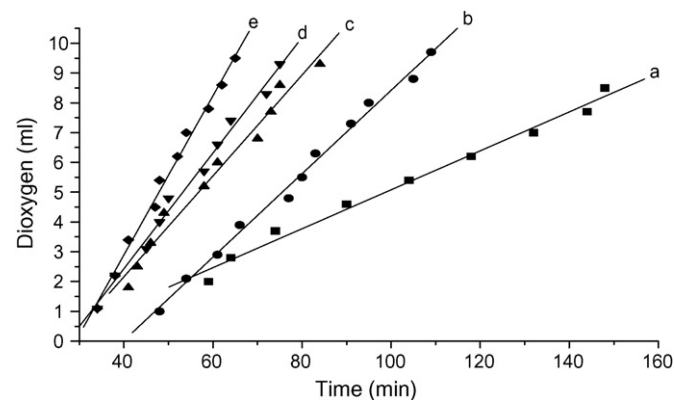


Fig. 2. Effect of the concentration of cobalt(II) porphyrin complex **1** on the autoxidation of 2,6-di-*tert*-butylphenol. For reaction conditions, see footnote 'a' of Table 1.

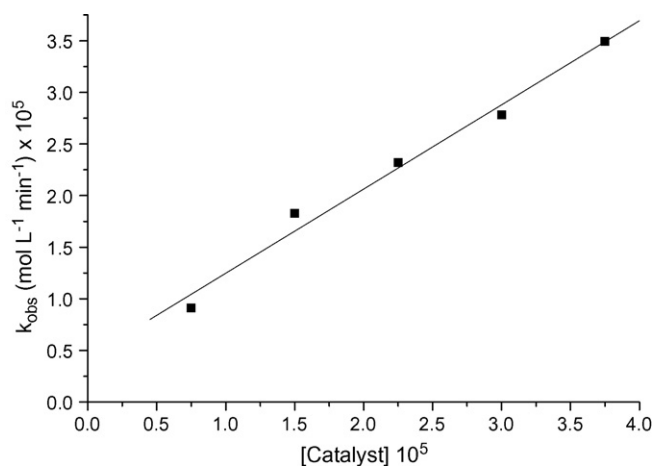


Fig. 3. Dependence of rate constant on catalyst **1** concentration. For reaction conditions, see footnote 'a' of Table 1.

concentration range 0.5×10^{-3} to 5×10^{-3} M. The rate constants k_{obs} depend on the as shown in Fig. 5. A double reciprocal Lineweaver–Burk plot (Fig. 6) showed that the rate fit a Michealis–Menten kinetic model for saturation of catalyst sites with increasing concentration of 2,6-di-*tert*-butylphenol [27].

3.6. Effect of partial pressure of dioxygen on the autoxidation of 2,6-di-*tert*-butylphenol

The effect of partial pressure of dioxygen was investigated by using oxygen/nitrogen mixture to obtain reduced partial pressure of 1 atm total pressure on the reaction mixture. The linear increase of rate constants with increasing partial pressure of dioxygen (Fig. 7) suggests that mass transfer of dioxygen from gas phase to the active site does not limit the rate of the reaction.

The oxidation of phenols by molecular oxygen catalyzed by cobalt(II) porphyrin complexes represents a typical example for a reaction involving the activation of dioxygen by a transition metal cation [11]. It is known that metal-bound oxy-

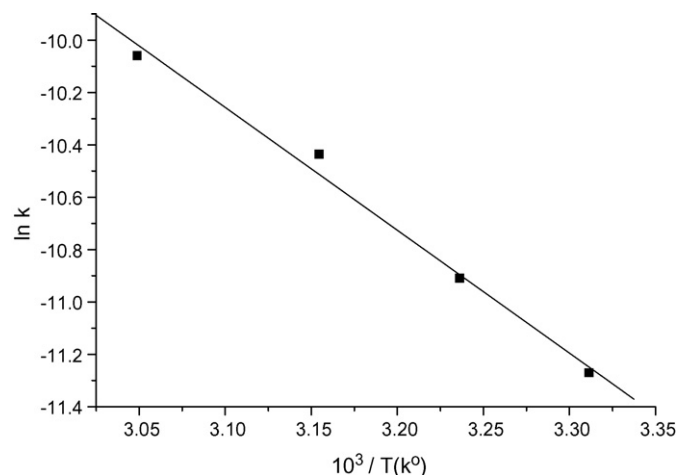


Fig. 4. The Arrhenius plot of rate data at 29–55 °C under the conditions given in Table 1.

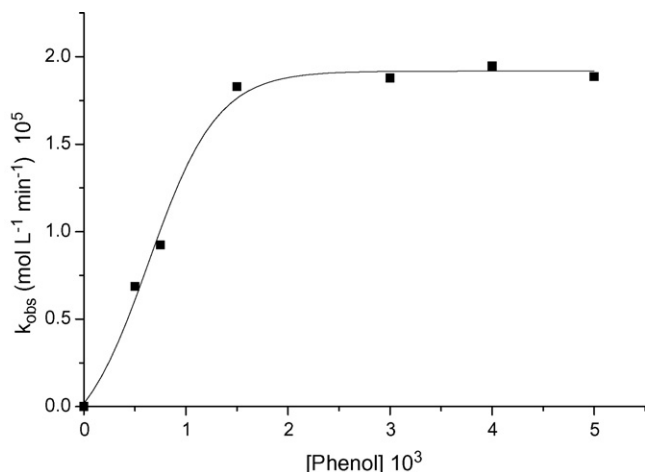


Fig. 5. Dependence of rate of autoxidation on 2,6-di-*tert*-butylphenol concentration. For reaction conditions, see footnote 'a' of Table 1.

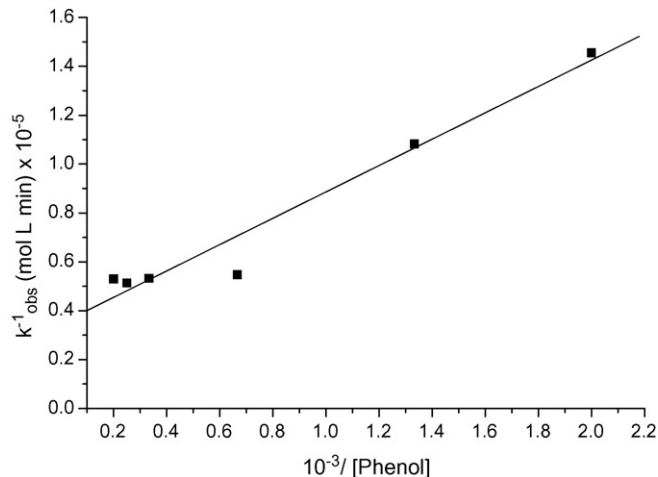


Fig. 6. Lineweaver–Burk plot for the data in Fig. 5.

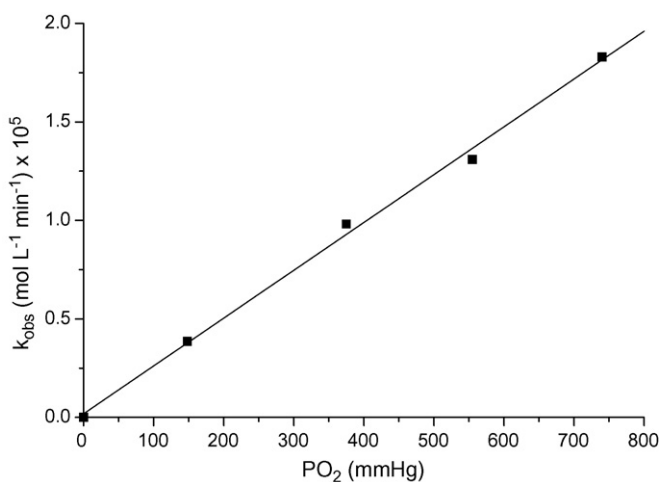
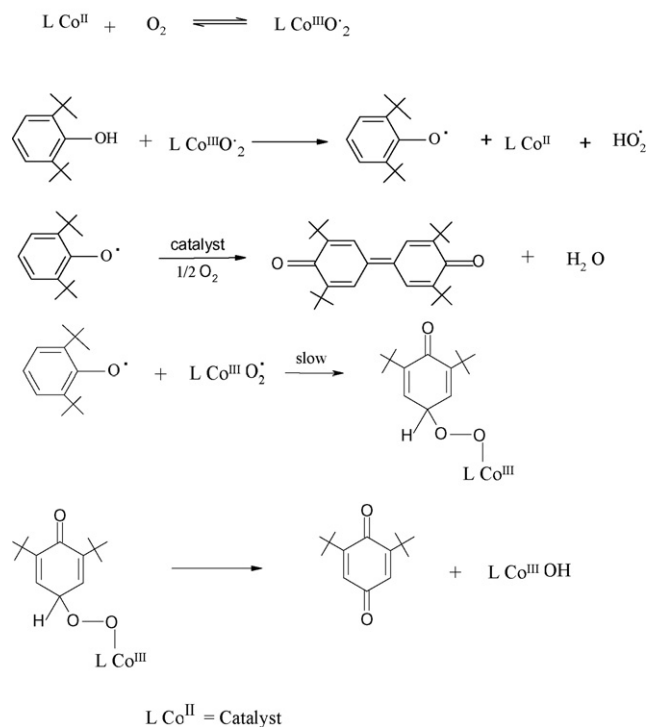


Fig. 7. Dependence of rate constant k_{obs} in autoxidation of 2,6-di-*tert*-butylphenol on partial pressure of dioxygen. For reaction conditions, see footnote 'a' of Table 1.



Scheme 1.

gen (Scheme 1) is an active species in the autoxidation of phenols catalyzed by cobalt(II) porphyrin complexes [11]. The coupling product 3,5,3',5'-tetra-*tert*-butyl-4,4'-diphenylquinone, which is the major product in the reaction catalyzed by cobalt(II) porphyrin complex **1** is formed by dimerization of the phenoxy radical via reaction of the oxygen adduct with 2,6-di-*tert*-butylphenol (Scheme 1) [11]. The oxygen insertion product, 2,6-di-*tert*-butyl-1,4-benzoquinone is formed through the cobalt(III) complex (Scheme 1) [11].

3.7. Catalyst reuse

The cationic cobalt(II) porphyrin complex **1** was tested for its stability in successive experiments. Reuse of the catalyst was followed by dioxygen uptake under experimental conditions of Table 1. After 100% conversion of 2,6-di-*tert*-butylphenol, the initial amount of phenol was added to reaction mixture without separation of reaction products. The porphyrin complex **1** showed reduced activity after the second run and the recycled catalyst was found to be 0.3 times as active as the fresh catalyst (Fig. 8). Deactivation of the cationic cobalt(II) porphyrin complex **1** could be due to the aggregation of the complex **1** in solution favoring intermolecular self-oxidation of the catalyst [10].

Previously reported results on the autoxidation of 2,6-di-*tert*-butylphenol catalyzed by sulfotetraaryl porphyrins supported on cationic polystyrene latex bearing quaternary ammonium groups [28] indicated that these catalysts showed higher stabilities than cationic cobalt(II) porphyrin complex **1**. However, catalyst **1** exhibited higher catalytic reactivity compared to previously reported catalysts.

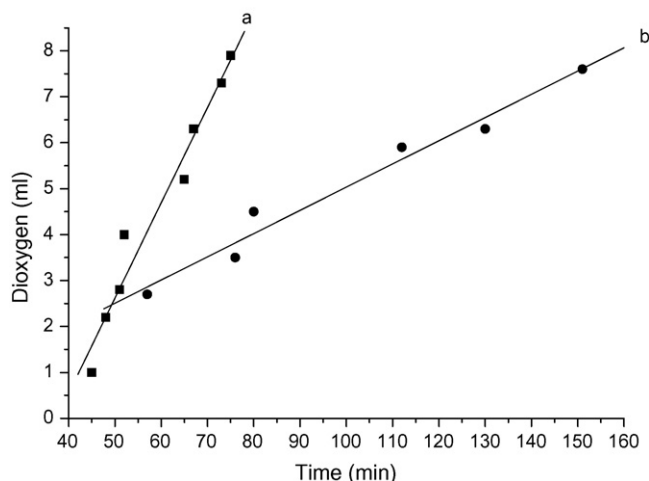


Fig. 8. Catalyst reuse in the autoxidation on 2,6-di-*tert*-butylphenol. (a) Catalyst 1, (b) reused catalyst. For reaction conditions, see footnote 'a' of Table 1.

Acknowledgement

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.11.045.

References

- [1] J.T. Groves, T.E. Nemo, R.S. Myers, *J. Am. Chem. Soc.* 101 (1979) 1032.
- [2] B. Meunier, *Chem. Rev.* 92 (1992) 1411.
- [3] D. Mansuy, P. Battioni, J.P. Battioni, *Eur. J. Biochem.* 184 (1989) 267.

- [4] D. Mansuy, *Pure Appl. Chem.* 59 (1987) 759.
- [5] J.R. Lindsay Smith, in: R.A. Sheldon (Ed.), *Metalloporphyrins in Catalysis Oxidation*, Marcel Dekker, New York, 1994 (Chapter 11).
- [6] D. Mansuy, *Coord. Chem. Rev.* 125 (1993) 129.
- [7] B.A. Arndtsen, R.G. Bergamm, T.A. Mobley, T.H. Petreson, *Acc. Chem. Res.* 28 (1995) 154.
- [8] K.A. Jorgensen, *Chem. Rev.* 89 (1989) 431.
- [9] B. Meunier, in: R.A. Sheldon (Ed.), *Metalloporphyrins in Catalysis Oxidation*, Marcel Dekker, New York, 1994 (Chapter 5), p. 133.
- [10] M. Hassanein, S. Gerges, M. Abdo, S. El-Khalafy, *J. Mol. Catal. A: Chem.* 240 (2005) 22.
- [11] X.Y. Wang, R.J. Moterkaitis, A.E. Martell, *Inorg. Chem.* 23 (1984) 271.
- [12] M. Forstin-Rio, D. Pujot, C. Bied-Charreton, M. Perree-Fauvet, A. Gaude-mer, *J. Chem. Soc. Perkin Trans. 1* (1984) 1971.
- [13] B. De Vismes, F. Bedioui, J. Devynck, C. Bied-Charreton, M. Perree-Fauvet, *Nouveau J. Chem.* 10 (1986) 81.
- [14] E. Tarnaud, M. Forstin-Rio, C. Bied-Charreton, *J. Mol. Catal.* 72 (1992) 181.
- [15] N. Colclough, J.R. Lindsay Smith, *J. Chem. Soc. Perkin Trans 2* (1994) 1139.
- [16] N.W.J. Kamp, J.R. Lindsay Smith, *J. Mol. Catal. A: Chem.* 113 (1996) 131.
- [17] H. Saleem, L.S. Kerry, *Appl. Bio. Chem. Biotechnol.* 63–65 (1997) 845.
- [18] M. Fukushima, K. Tatsumi, *J. Mol. Catal. A: Chem.* 245 (2006) 178.
- [19] H. Zeng, Q. Jian, Y. Zhu, X. Yan, X. Liang, H. Hu, Q. Liu, W. Lin, C. Guo, *J. Porphyrins Phthalocyanines* 10 (2006) 96.
- [20] R.A. Sheldon, J.K. Kochi, *Metal Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1981, p. 71.
- [21] C.W. Carter, *Biochem. J.* 22 (1928) 575.
- [22] R. Gerdes, O. Bartels, G. Schneider, D. Worchle, G. Schulz-Ekloff, *Int. J. Photoenergy* 1 (1999) 1–9.
- [23] N. Datta-Gupta, T.J. Bardos, *J. Heterocycl. Chem.* 3 (1991) 495.
- [24] A.D. Adler, F.R. Longo, F.J. Kamps, J. Kim, *J. Inorg. Nucl. Chem.* 32 (1970) 2443.
- [25] S. Takagi, T.K. Miyamoto, Y. Sasaki, *Bull. Chem. Soc. Jpn.* 59 (1986) 2371.
- [26] M. Hassanein, A. Selim, H. El-Hamshary, *Macromol. Chem. Phys.* 195 (1994) 3845.
- [27] L. Michealis, M.L. Menten, *Biochem. Z.* 49 (1913) 1333.
- [28] M. Hassanein, S. Gerges, M. Abdo, S. El-Khalafy, *J. Porphyrins Phthalocyanines* 9 (2005) 621.