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Oxidation of 2,6-di-*tert*-butylphenol with *tert*-butyl hydroperoxide catalyzed by iron phthalocyanine tetrasulfonate in a methanol–water mixture

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Abstract

The oxidation of 2,6-di-*tert*-butylphenol (DTBP) with *tert*-butyl hydroperoxide (Bu^{t}OOH) catalyzed by iron phthalocyanine tetrasulfonate ([FePcTS]) in a 8-to-1 methanol–water mixture resulted with about 70–80% conversion of DTBP in 3 min at ambient temperature. The mole ratios of [FePcTS]:DTBP:Bu^{t}OOH in a typical reaction were 1:400:500, respectively. The major products of the catalysis are the coupled products, namely 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (DPQ) and 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (H_2DPQ). In addition, the effect of DTBP on the monomer–dimer equilibrium of [FePcTS] and catalytically active [FePcTS] species are discussed.
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Keywords: 2,6-Di-*tert*-butylphenol; 3,3′,5,5′-Tetra-*tert*-butyl-4,4′-diphenoquinone; 4,4′-Dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl; Iron phthalocyanine tetrasulfonate; *tert*-Butyl hydroperoxide; Oxidation

1. Introduction

Metallophthalocyanines are well-known catalysts for the oxidation of various organic substrates such as phenols [1–14], alkenes [10,15–17], alkanes [16,18–26], and thiols [2,3,27–31]. Their easy preparations in large scale, low cost, relatively high chemical and thermal stabilities make them very attractive in catalysis. Metallophthalocyanine catalyzed oxidations have been investigated for the development of methods not only for the synthesis of various organic compounds [2,9,10,15–17,19,20,22] but also for the degradation of organic pollutants [1,3–5,14]. In this respect, transition metal containing and water-soluble phthalocyanines tetrasulfonates (MPcTSs) in the form of homogeneous and heterogeneous systems have been widely screened as oxidation catalysts. Among metallophthalocyanine tetrasulfonates, cobalt and iron containing ones are more effective than manganese, copper or nickel complex analogues.

As oxygen sources molecular oxygen [2,7,9–11,16,23–25], hydrogen peroxide [1,3–6,19–22,25,26], *tert*-butyl hydroperoxide [8,15,19,20,22,23,25,26], *m*-chloroperbenzoic acid [15,22], iodosylbenzene [17,32], and potassium peroxymonosulfate [33,34] were commonly employed in the metallophthalocyanine catalyzed reactions and the stabilities of metallophthalocyanines toward oxidants differ with the type oxidant used. Although MPcTSs are considered highly stable toward the molecular oxygen, the oxidation reactions with it suffer from slow reaction rates. On the other hand strong oxidants such as hydrogen peroxide and *m*-chloroperbenzoic acid destroy the phthalocyanine ring during the reaction [22]. *tert*-Butyl hydroperoxide (Bu^{t}OOH) which is a milder oxidant than H_2O_2 but stronger than dioxygen looks more active oxidant than molecular oxygen.

Bu^{t}OOH was already employed as the oxidant in the oxidation reactions of cyclohexane, cyclohexene, 2,3,6-trimethylphenol, 2-napthalene, 2,6-di-*tert*-butylphenol [8,15,19,20,22,23,25,26]. We previously reported cobalt phthalocyanine tetrasulfonate catalyzed oxidation of 2,6-di-*tert*-butylphenol

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with Bu^{t}OOH in a methanol–water system [8]. This paper presents a continuation of our previous work with the only difference in the use of iron phthalocyanine tetrasulfonate instead of cobalt phthalocyanine tetrasulfonate.

2. Experimental

2.1. Reagents and instrumentation

Sodium salt of iron phthalocyanine tetrasulfonate [FePcTS]-Na_4 was prepared by using Weber procedure (Fig. 1) [35]. 2,6-Di-*tert*-butylphenol (DTBP, Merck) and *tert*-butyl hydroperoxide (Bu^{t}OOH, 70%, Merck) were used as received. The other reagents used were research grade.

GLC analyses of the DTBP reaction mixtures were performed on a Thermo-Trace GC Ultra Gas Chromatograph fitted with a 25 m SE-54 Permabond fused silica capillary column and an FID detector. The MS spectra were obtained with a GC-MS/MS (Thermo Finnigan PolarisQ) equipped with Wiley and NIST MS libraries. The visible spectra were taken using Shimadzu 2450 UV–vis spectraphotometer.

2.2. Oxidation of 2,6-di-tert-butylphenol

In a typical experiment, a 10-mL round-bottomed-flask was charged with an aqueous solution of 6.0×10^{-3} M [FePcTS] (0.5 mL, 3.0×10^{-3} mmol) and a methanol solution of 0.3025 M DTBP (4.0 mL, 1,21 mmol). After addition of Bu^{t}OOH (0.21 mL, 1.52 mmol) to the reaction medium, the mixture was stirred magnetically at room temperature under nitrogen atmosphere. As soon as the reaction time was over, the reaction mixture was immediately transferred into a separatory funnel and worked up. The organics were extracted with 2 mL dichloromethane for five times. Before GLC analysis, known amount naphthalene was added to the extract as an internal standard. The amounts of residual DTBP and of major reaction products in the extract were calculated using their peak areas in GLC chromatograms, detector response factors and the amount of internal standard. The characterizations of the products 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (DPQ) and 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (H_2DPQ) were previously reported [8].

3. Results and discussion

3.1. Oxidation of 2,6-di-tert-butylphenol with Bu^{t}OOH catalyzed by [FePcTS]

The oxidation of 2,6-di-*tert*-butylphenol (DTBP, Fig. 2) with *tert*-butyl hydroperoxide (Bu^{t}OOH) in the presence of iron phthalocyanine tetrasulfonate ([FePcTS]) catalyst has been studied. The reactions were carried out in methanol–water (8:1 v/v) mixtures at ambient temperature and under nitrogen atmosphere. The 8-to-1 volume-to-volume ratio of methanol–water provides a homogeneous reaction medium for the catalyst, substrate and oxidant. In a typical experiment, the catalyst:substrate:oxidant mole ratios were 1:400:500. We have recently reported the results of the DTBP oxidation with Bu^{t}OOH catalyzed by cobalt phthalocyanine tetrasulfonate ([CoPcTS]) in the methanol–water mixture [8]. Changing the metal of the phthalocyanine tetrasulfonate macrocycle from cobalt to iron caused substantial consequences in the outcome of the reaction:

(i) much shorter reaction time,
(ii) more complex product composition.

It took less than 3 min to have about 70–80% conversion of DTBP for the [FePcTS] catalyzed reaction whereas this conversion time was about 3 h in the [CoPcTS] catalyzed reaction. Furthermore the substrate-to-catalyst mole ratio used in this study was typically 4 times that of in the [CoPcTS] catalyzed reaction [8]. Furthermore the [FePcTS] catalyzed reaction of DTBP produced 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (DPQ, Fig. 2) and 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (H_2DPQ, Fig. 2) as expected and major products in addition to nine minor products including 2,6-di-*tert*-butylbenzoquinone which is one of the common products of the oxidation of DTBP oxidation. Fig. 3 shows the GLC chromatogram of the reaction mixture of a typical oxidation reaction of DTBP catalyzed by

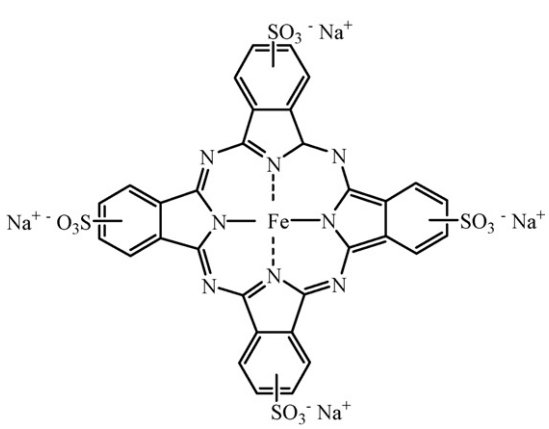


Fig. 1. Chemical structure of sodium salt of iron phthalocyanine tetrasulfonate.

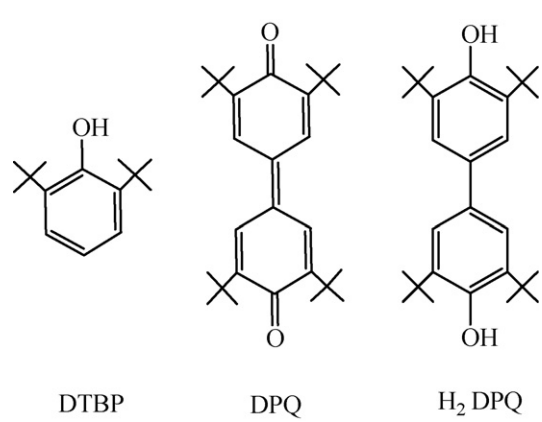


Fig. 2. Chemical structures of 2,6-di-*tert*-butylphenol and its major oxidation products.

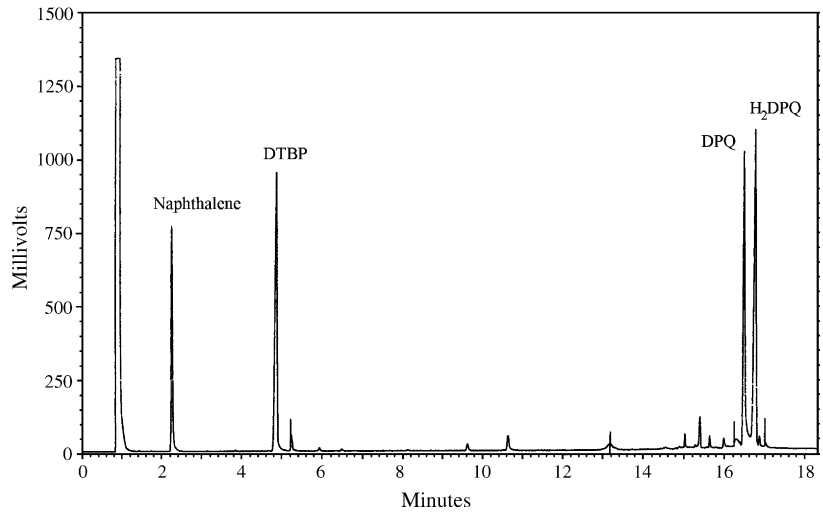
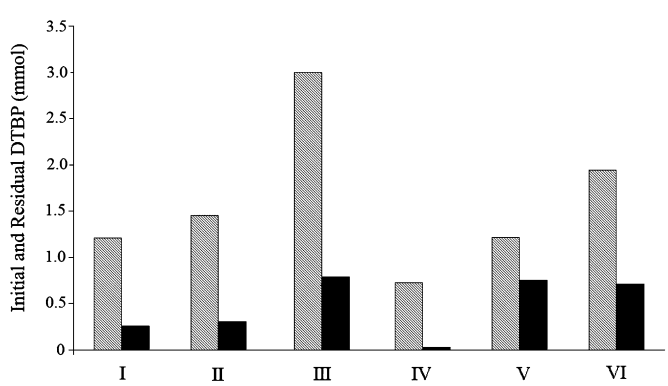


Fig. 3. The GLC chromatogram of the reaction mixture of the DTBP oxidation with Bu^{t}OOH catalyzed by [FePcTS].

[FePcTS]. On the other hand, the [CoPcTS] catalyzed oxidation of DTBP with Bu^{t}OOH generally produced DPQ and H_2DPQ as the only products. Furthermore in the absence of the catalyst [FePcTS], DTBP was not oxidized by Bu^{t}OOH.

Fig. 4 shows the graphics of the amounts of initial and remaining DTBPs after 3 min reaction time for varied substrate, oxidant and catalyst ratios for the [FePcTS] catalyzed reactions. When slight excess of the oxidant Bu^{t}OOH relative to DTBP was used (Fig. 4, I–III), the conversion of DTBP varied from 74 to 79%. On the other hand, when the amount of Bu^{t}OOH was about twice as that of DTBP (Fig. 4, IV), about 96% conversion of DTBP was achieved. In the experiments when Bu^{t}OOH was the limiting agent (Fig. 4, V and VI), 38 and 63% of the initial DTBP (which corresponds to 76 and 81% of oxidizable DTBP if 1 mol oxidant is used for per mol of DTBP) was converted. A remarkable turnover number as high as 740 was achieved for a 3 min reaction time when the DTBP to [FePcTS] ratio was 1000:1 (Fig. 4, III). The turnover number is calculated from the ratio of the amount of the reacted DTBP to the amount of the catalyst. The turnover numbers for other reactions are also given in Fig. 4 and such turnover numbers which can be considered large values for a 3 min chemical reaction time indicate a high reaction rate. Indeed we observed warming up the reaction medium just after the reaction started. Grootboom and Nyokong [22] also reported the warming up the reaction medium in the course of oxidation of cyclohexane with Bu^{t}OOH catalyzed by [FePcTS] and found that the temperature of the reaction mixture increased by 40 °C. For curiosity, we measured the temperature change in our reaction medium at 5 s intervals for a 3 min run (Fig. 5) and concluded from this temperature-time profile that this reaction may be occurring instantaneously (about in 10–20 s). It should be noted that the reaction flask was not insulated during the temperature measurements.

When the oxidation reactions were carried out at longer reaction times (up to 1 h), the conversion reaction of DTBP proceeded at slow rates beyond 3 min for different oxidant, substrate and catalyst ratios (Fig. 6). From sudden temperature change of the reaction mixture and time course of the conversion of DTBP, it can be said that this oxidation takes place in less than 1 min.



	I	II	III	IV	V	VI
[FePcTS]:DTBP:Bu^{t}OOH[a]	1:400:500	1:485:500	1:1000:1100	1:240:500	1:400:200	1:646:500
% DTBP Conversion	78	79	74	96	38	63
Turnover Number	312	383	740	230	152	407

Fig. 4. The amounts of initial DTBP (▨) and residual DTBP (■) after oxidation of DTBP with Bu^{t}OOH in the presence of [FePcTS] catalyst after 3 min at room temperature. [a]Mole ratios.

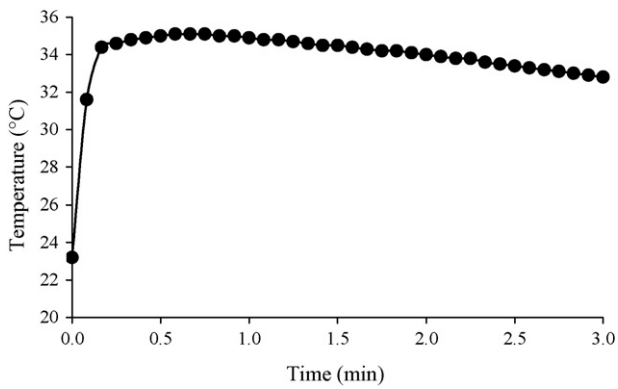


Fig. 5. The variation of the temperature of the reaction mixture with time.

Table 1 summarizes the mole percentages of the residual DTBP and the products DPQ and H_2DPQ after 3 min reaction time for different initial substrate, oxidant and catalyst amounts. The sum of the amounts of the residual DTBP, the products DPQ and H_2DPQ corresponds to 72–92% of the starting DTBP. We believe that the "unaccounted" DTBP in these reactions goes into the unidentified minor products. The GC-MS/MS search proposed names for five of the minor products: 2,6-di-*tert*-butylbenzoquinone, 2,6-di-*tert*-butylhydroquinone, 3,5-di-*tert*-butyl-4-hydroxybenzylalcohol, 2,6-bis(1,1-dimethylethyl)-4-methylphenol, and 2,6-bis(1,1-dimethylethyl)-4-methoxymethylphenol. Although the MS spectra of these products had high MS direct matching, reverse matching, and probability factors with the ones in the MS libraries, their existences should be taken cautiously. Because no further characterizations of these compounds was attempted. Furthermore, no meaningful names were proposed by the MS libraries for the other four minor products.

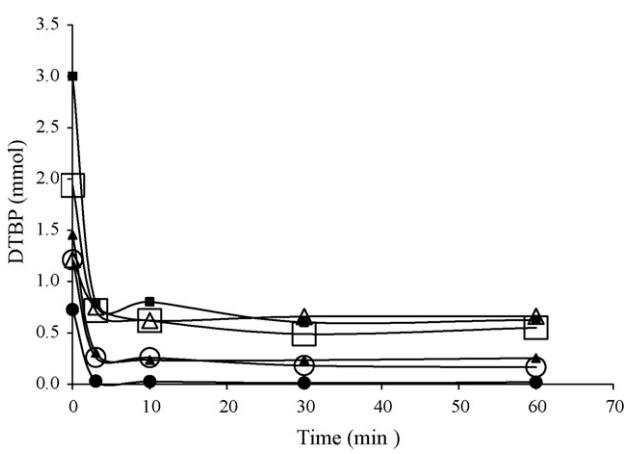


Fig. 6. The time course profile of the conversion of the varying amount of DTBP catalyzed by [FePcTS] in 4.5 mL 8-to-1 (v/v) methanol–water mixture. The amounts of DTBP, Bu^{t}OOH, and [FePcTS] are given in Table 1: (◯) I, (▲) II, (■) III, (●) IV, (△) V and (□) VI.

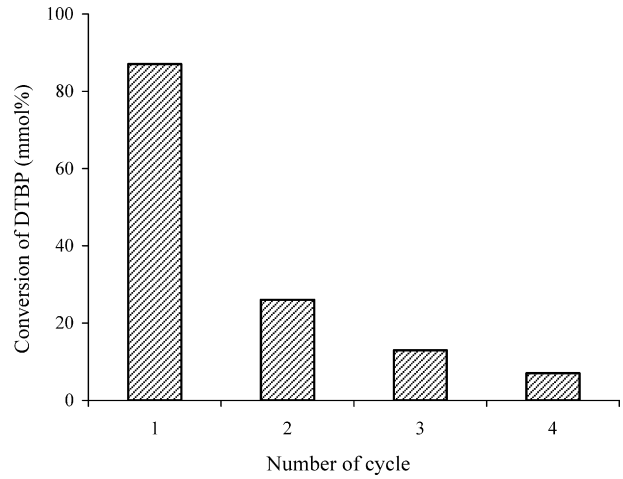


Fig. 7. Conversion of DTBP catalyzed by 3.0×10^{-3} mmol FePcTS in four recycling experiments after addition of new portions of DTBP (1.21 mmol) and Bu^{t}OOH (1.50 mmol).

3.2. Catalyst recycling and degradation

In the recycling experiment, the catalytic activity of [FePcTS] (3.0×10^{-3} mmol) was determined after addition of new portions of DTBP (1.21 mmol) and Bu^{t}OOH (1.50 mmol) to the reaction medium. The recycling reactions were carried out for 5 min. Prior to the addition of the next portions of DTBP and Bu^{t}OOH, first the organics in the reaction medium was extracted with CH_2Cl_2 for GLC analysis and then just enough amount methanol to replace its extracted portion by CH_2Cl_2 was added to the reaction medium to make the reaction medium 4.5 mL. The results for the conversion of DTBP after each cycle are given in Fig. 7. After each cycle, the conversion percentage of DTBP decreased substantially. It was 87% in the first cycle and only 7% in the fourth cycle. We also took the absorption spectrum of the catalyst for every cycle after the organics

Table 1
The product distribution of the oxidation of DTBP with Bu^{t}OOH in the presence of [FePcTS] catalyst in 4.5 mL 8-to-1 (v/v) methanol–water mixture after 3 min at room temperature

Reaction	DTBP (mmol)	Bu^{t}OOH (mmol)	[FePcTS] (mmol)	Residual DTBP (%)	DPQ (%)	H_2DPQ (%)	Accounted DTBP (%)[a]
I	1.21	1.50	3×10^{-3}	21.6	15.4	13.7	79.8
II	1.45	1.50	3×10^{-3}	21.0	11.7	14.0	76.4
III	3.00	3.30	3×10^{-3}	26.2	18.4	14.7	72.4
IV	0.73	1.50	3×10^{-3}	0.03	21.6	16.6	88.3
V	1.21	0.60	3×10^{-3}	61.9	4.5	7.2	85.3
VI	1.94	1.50	3×10^{-3}	36.9	12.4	13.3	92.4

[a] Calculated from the number of moles of residual DTBP and of DTBP used to produce DPQ and H_2DPQ.

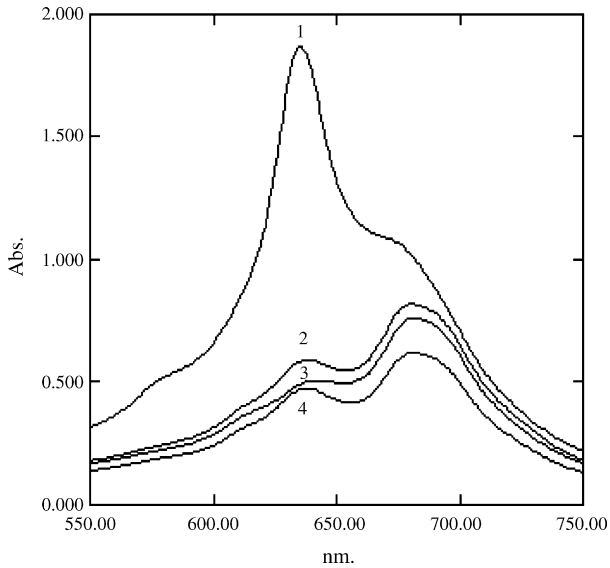


Fig. 8. The visible spectra of the catalyst [FePcTS] taken after four recycling experiments. The number on the spectrum indicates the number of the recycling. Spectrum 1 was taken after seven times dilution and spectra 2–4 were taken after five times dilution with 8:1 (v/v) methanol–water solution.

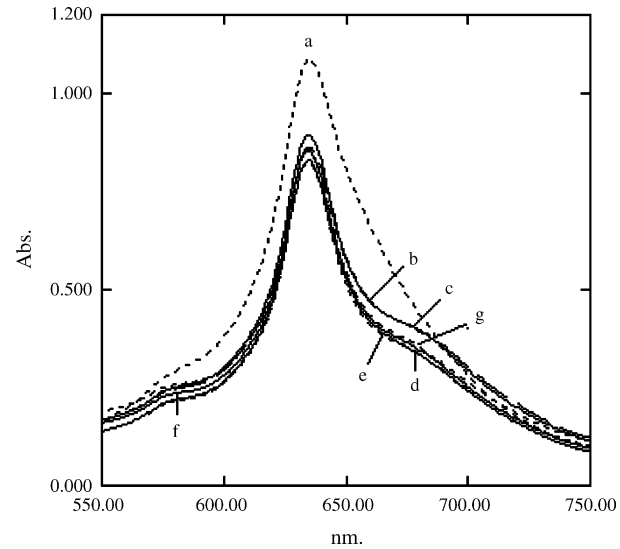


Fig. 9. The visible spectra of 3×10^{-3} mmol [FePcTS] in 1.21 mmol DTBP containing methanol–water (8:1 v/v) mixture (4.5 mL) (a) before addition of Bu^{t}OOH and after the reaction was started (b) 1 min, (c) 5 min, (d) 15 min, (e) 30 min, (f) 1 h and (g) 3 h. The spectra were taken after diluting the mixtures 10 times with 8:1 (v/v) methanol–water mixture.

were extracted (Fig. 8). The absorption spectra of the catalyst clearly indicates the partially loss (degradation) of the catalyst after each cycle. It appears that the loss of the catalyst coincides with the decrease in the conversion of DTBP after each cycle.

3.3. Catalytically active species and reaction mechanisms

During the course of the reaction, the visible spectra of [FePcTS] were taken to determine the catalytically active species. In aqueous solutions of [FePcTS], the maxima of the bands of its dimeric (or higher aggregates) and monomeric forms appear near 630 nm and 670 nm, respectively and the equilibria between the monomer and dimer forms of metallophthalocyanine tetrasulfonates in aqueous solutions are mainly concentration dependent along with other factors such as pH, temperature, ionic strength [1,22]. In the concentration range 10^{-5} to 10^{-7} M, the dimer is generally dominant species in the aqueous solutions of metallophthalocyanines. Addition of organic solvents such as acetonitrile, acetone, ethanol, and methanol to an aqueous solution of dimeric [FePcTS] shifts the equilibrium toward the monomeric form of [FePcTS] by lowering the hydrophobic interactions between the planes of phthalocyanine [1,22]. When we mixed 0.5 mL of 6×10^{-3} M aqueous solution of [FePcTS] with 1.21 mmol DTBP containing 4.0 mL methanol and took the visible spectrum of the mixture shortly after mixing, we obtained a spectrum similar to that of the dimeric form of [FePcTS] or its higher aggregates having a maximum at 636 nm with no absorbance band for the monomeric form (Fig. 9a). After leaving this mixture to stand for 5 h, no change in the spectrum occurred. Hadasch et al. [1] already reported this form of [FePcTS] and called it the stacked monomers of [FePcTS] (n[Fe^{III}PcTS(H$_2$O)]$^+$ or n[Fe^{III}PcTS(OH)]). Although our result seems contrary to general observations that organic solvents favor the formation of monomeric structure, we found that DTBP had suppressed the effect of methanol on the monomer–dimer equilibrium of [FePcTS]. Because the visible spectrum of [FePcTS] in a 8:1 methanol–water mixture without DTBP showed the maxima of both dimeric (or higher aggregates) and monomeric forms in which the dimeric form (or higher aggregates) was dominant initially and this spectrum gradually converted in 4 h to the one in which the monomeric form of [FePcTS] was dominant. When the aqueous–methanol solution of [FePcTS] contained 0.30 mmol DTBP instead of 1.21 mmol DTBP, we obtained a visible spectrum of [FePcTS] with two bands where the dimeric form (or higher aggregates) was dominant (Fig. 10a). Also in this spectrum, the band (λ_{max} 663 nm) due to the monomeric form diminished in 4 h and the new spectrum was the spectrum of the dimeric or higher aggregates of [FePcTS] (λ_{max} 636 nm). These observations clearly indicate that DTBP forces [FePcTS] in 8-to-1 methanol–water mixture to stay in the aggregated form despite of the presence of an organic solvent at large excess in the medium. Consequently, in our typical DTBP oxidation reactions the dominant form of [FePcTS] was the dimer or higher aggregates (so called the higher stacking monomers) of [FePcTS] before addition of the oxidant Bu^{t}OOH to the medium.

Addition of Bu^{t}OOH into the methanol–water solution of the higher aggregates of [FePcTS], the band at 636 nm drastically decreased and a new band with low absorption intensity appeared in 678 nm (Figs. 9b and c and 10b–g). When Grootboom and Nyokong [22] treated the monomeric [FePcTS] (λ_{max} 664 nm) in 9:1methanol–water mixture with Bu^{t}OOH, they observed a split Q band and a shift of one of the Q bands to 678 nm which they attributed to the [(Bu^{t}OO)Fe^{III}PcTS] species. We also believe that this is the species in our work which generates Bu^{t}O or Bu^{t}OO radicals (Scheme 1).

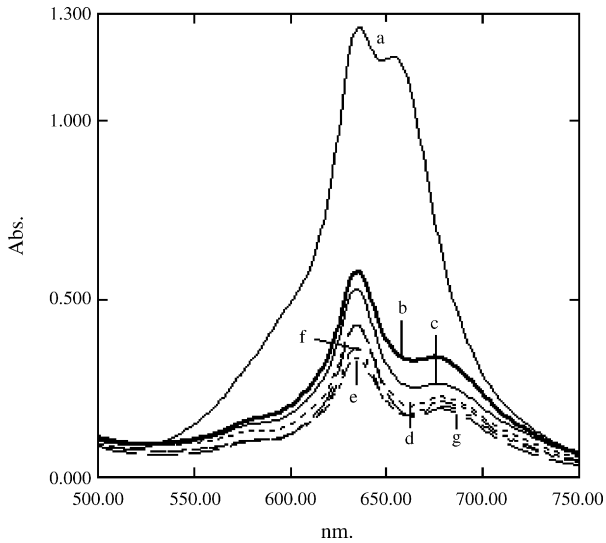
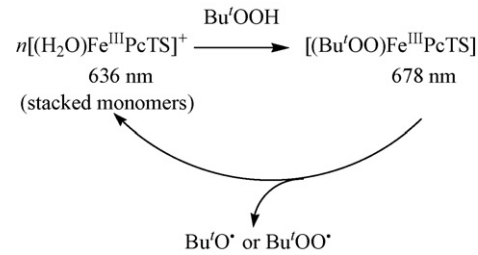


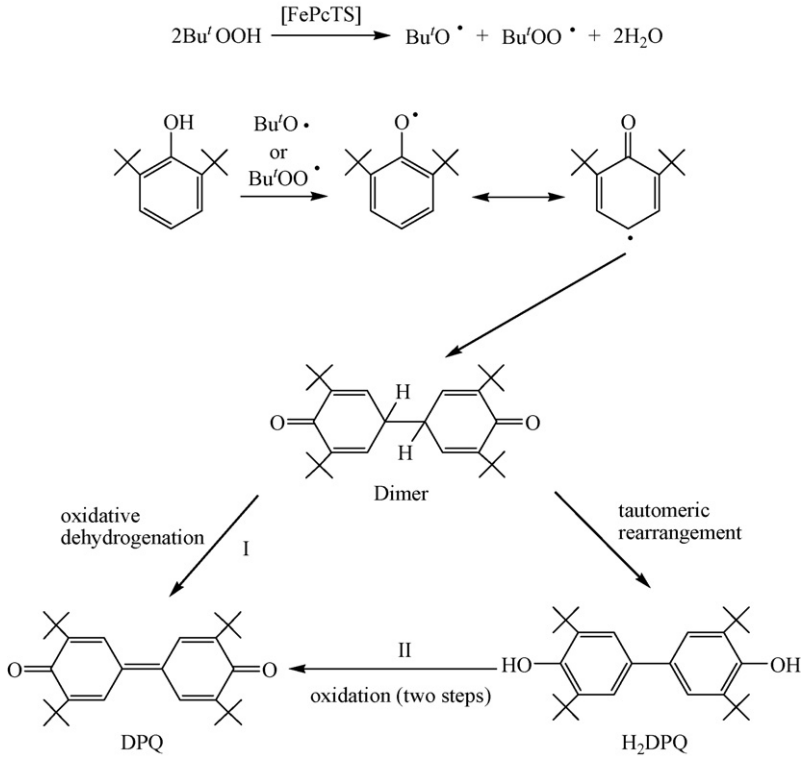
Fig. 10. The visible spectra of 3×10^{-3} mmol [FePcTS] in 0.30 mmol DTBP containing methanol–water (8:1 v/v) mixture (4.5 mL) (a) before addition of Bu^{t}OOH and after the reaction was started (b) 1 min, (c) 5 min, (d) 15 min, (e) 30 min, (f) 1 h and (g) 3 h. The spectra were taken after diluting the mixtures 10 times with 8:1 (v/v) methanol–water mixture.

After the generation of Bu^{t}O or Bu^{t}OO radicals by [(Bu^{t}OO)Fe^{III}PcTS] active species, these radicals abstract the phenolic hydrogen from DTBP and then C–C coupling occurs between the resonance forms of the phenoxy radicals with the unpaired electrons at four positions (Scheme 2). The resulting unstable coupling product or the dimer rearranges itself into a more stable tautomeric form H_2DPQ in polar media or is converted into DPQ through an oxidative dehydrogenation reaction [36]. Many researchers have showed H_2DPQ is an intermediate in the formation of DPQ in their reaction mechanisms. In that case, DPQ forms through sequential oxidation steps of H_2DPQ. The further thoughts on the oxidation reaction mechanisms of DTBP with various oxidants and catalytic systems can be found in the literature [36–39].



Scheme 1. The cycle for the generation of Bu^{t}O or Bu^{t}OO radical via [FePcTS].

As long as the supply of Bu^{t}OOH lasts during the oxidation of DTBP, the species [(Bu^{t}OO)Fe^{III}PcTS] exists in the reaction medium and can be seen as a shoulder at 678 nm of the visible spectra taken at 1 and 5 min of the reaction carried out with 1.21–1.50 DTBP–Bu^{t}OOH mole ratio (Fig. 9b and c) and even after 3 h of the reaction carried out with 0.30–1.50 DTBP–Bu^{t}OOH mole ratio (Fig. 10b–g). Because our typical oxidation reaction is quite fast and most of Bu^{t}OOH is consumed in a minute, the higher aggregates of [FePcTS] structure becomes more and more dominant species as time elapses and the spectrum gradually revert back to the spectrum of the higher aggregates of [FePcTS] (Fig. 9d–g). The same observation was reported by Grootboom and Nyokong [22].



Scheme 2. The proposed mechanisms in the formation of H_2DPQ and DPQ from the oxidation of DTBP with Bu^{t}OOH catalyzed by [FePcTS] (adapted from [38]).

Acknowledgements

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