Oxidation of 2,6-di-*tert*-butylphenol with *tert*-butylhydroperoxide catalyzed by cobalt(II) phthalocyanine tetrasulfonate in a methanol–water mixture and formation of an unusual product 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl

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Abstract

The oxidation of 2,6-di-*tert*-butylphenol (DTBP) with *tert*-butylhydroperoxide (Bu^{t}OOH) catalyzed by cobalt(II) phthalocyanine tetrasul-fonate ([CoPcTS]$^{4-}$) in a 4:1 methanol–water mixture gave predominantly the coupled products 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (DPQ) and 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (H$_2$DPQ) when the oxidant/substrate ratio was less than 10. The conversion of DTBP was 70% in 3 h and 86% in 8 h when the amounts of DTBP, Bu^{t}OOH, and [CoPcTS]$^{4-}$ in millimoles were 0.300, 1.52, and 3.0×10^{-3}, respectively. The yield of DPQ was 56% in 3 h and 73% in 8 h whereas that of H$_2$DPQ was about 14% in 3 and 8 h. H$_2$DPQ is not commonly encountered the oxidation product of DTBP and is considered unstable. When the oxidant/substrate ratio was over 10, 2,6-di-*tert*-butylbenzoquinone was also formed. The degradation of [CoPcTS]$^{4-}$ by Bu^{t}OOH also occurred during the oxidation of DTBP. About three-fourths of the catalyst was degraded in the first hour and about 2% of the catalyst remained after 8 h.
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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; Cobalt(II) phthalocya-nine tetrasulfonate; *Tert*-butylhydroperoxide; Oxidation

1. Introduction

Besides its relation to enzymatic systems, the oxidation of phenols has synthetic importance as well as environmental priority. Today phenol derivatives are one of the major water and soil pollutants. In addition to transition metal complexes [1–8], metalloporphyrins [9–11], and Schiff bases [12–14], metallophthalocyanines have received considerable attention as catalysts for phenol oxidations or degradations in the last two decades [10,12,15–19]. Because of their easy prepara-tions in large scale, low costs, relatively high chemical and thermal stabilities, metallophthalocyanines are also attrac-tive oxidation catalysts for the oxidations of some alkanes

[16–18,20–22], alkenes [23,24], and thiols [25–28] as well. They have also been investigated intensively in other areas such as dyes, optical and electrical materials, sensors, fuel cells and models for naturally occurring macrocycles [23].

The stabilities of metallophthalocyanines toward oxi-dants differ with the type of oxidant used in reactions. They are considered stable toward molecular oxygen. This is presumably why majority of the metallophthalocyanine-catalyzed oxidation systems use molecular oxygen as the oxygen source. Nevertheless there are some studies which report the use of stronger oxidants such as hydrogen peroxide [15,19,21,22], *tert*-butylhydroperoxide (Bu^{t}OOH) [16–18,21–24], and *meta*-chloroperbenzoic acid (*m*-CPBA) [22,24] in the metallophthalocyanine-catalyzed oxidation re-actions. The use of H$_2$O$_2$ usually leads fast destruction of metallophthalocyanines and Bu^{t}OOH looks a milder oxidant than H$_2$O$_2$. Grootboom and Nyokong [22] have used iron

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perchlorophthalocyanine and iron tetrasulfophthalocyanine catalysts ([FePcTS]$^{4-}$) and H$_2$O$_2$, *m*-CPBA, and Bu^{t}OOH oxidants in the oxidation of cyclohexane. They observed fast degradation of the phthalocyanine ring in [FePcTS]$^{4-}$ when *m*-CPBA or H$_2$O$_2$ was employed as an oxidant. The ring was relatively stable toward Bu^{t}OOH. The other phthalocyanine they used showed similar behavior toward these oxidants as [FePcTS]$^{4-}$. Balkus et al. [20] reported the oxidation of cyclohexane with Bu^{t}OOH catalyzed by zeolite-encapsulated perfluorinated ruthenium phthalocyanines. Metallophthalocyanine-catalyzed oxidation of cyclohexane with Bu^{t}OOH was reviewed recently [29]. Setletho and Nyokong [24] reported the catalytic activity of iron and cobalt phthalocyanine complexes toward the oxidation of cyclohexene using Bu^{t}OOH and chloroperoxybenzoic acid. Sorokin and Tuel [16–18] also used Bu^{t}OOH as the oxidant in the catalytic oxidation of 2,3,6-trimethylphenol and 2-methylnaphthalene by iron phthalocyanines in a sol–gel material. Although many catalytic systems and oxidants have been employed for the oxidation of 2,6-di-*tert*-butylphenol (DTBP), to the best of our knowledge, none of them has used a cobalt phthalocyanine/Bu^{t}OOH catalyst–oxidant system.

In this study, we report the oxidation of 2,6-di-*tert*-butylphenol (DTBP) catalyzed by cobalt(II) phthalocyanine tetrasulfonate ([CoPcTS]$^{4-}$) in the presence of Bu^{t}OOH as an oxygen donor.

2. Experimental

2.1. Reagents and instrumentation

Sodium salt of cobalt(II) phthalocyanine tetrasulfonate [CoPcTS]Na$_4$ was prepared by using Weber procedure (Fig. 1) [30]. 2,6-Di-*tert*-butylphenol (DTBP, Merck) and *tert*-butylhydroperoxide (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 Fisons 8560 HRGC gas chromatograph fitted
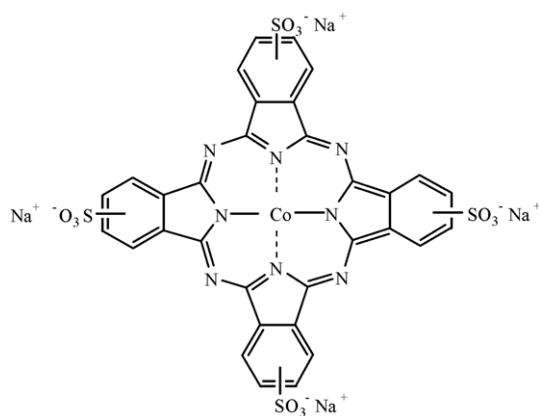

Fig. 1. Chemical structure of sodium salt of cobalt(II) phthalocyanine tetrasulfonate.

with a 25 m SE-54 Permabond fused silica capillary column and an FID detector. The identity of the products were further confirmed using a GC–MS instrument (HP 6890) and a ^{1}H NMR spectroscopy (JEOL JNM-EX90A). The degree of the cobalt phthalocyanine catalyst degradation was determined from its visible spectra obtained using a Shimadzu 2450 UV-PC spectrophotometer.

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 3.0×10^{-3} M [CoPcTS]$^{4-}$ (1.0 ml, 3.0×10^{-3} mmol) and a methanol solution of 0.075 M DTBP (4.0 ml, 0.300 mmol). The 4:1 volume ratio of methanol and water solvent mixture kept both the catalyst and the substrate soluble and this solvent mixture was used for subsequent studies. Under nitrogen atmosphere, Bu^{t}OOH (0.21 ml, 1.52 mmol) was then added to the reaction mixture and the mixture was stirred magnetically at room temperature. To stop the reaction, the reaction mixture was transferred into a separatory funnel, a few milliliters of CH$_2$Cl$_2$ was added to the funnel and the residual DTBP and the reaction products were extracted in the organic phase. The extraction process was repeated 4–6 times. Before GLC analysis, a known amount of naphthalene (about 20 mg) was added to the extract as an internal standard. The amounts of residual DTBP and reaction products in the extract were calculated using their peak areas in GC chromatograms, detector response factors and the amount of internal standard.

2.3. Product isolation and characterization

Two of the reaction products, 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (DPQ) and 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (H$_2$DPQ), were isolated together after crystallization from the dichloromethane extract of the reaction mixture with methanol. They were identified using GC–MS chromatograms and a ^{1}H NMR spectrum of the CH$_2$Cl$_2$ and CDCl$_3$ solutions of the crystals, respectively. DPQ: MS, *m/e*: 408 (molecular ion peak), 393, 366, 351, 337, 323, 309, 295, 281, 57; ^{1}H NMR (CDCl$_3$), δ: 1.35 (s, 36H), 7.69 (s, 4H). H$_2$DPQ: MS, *m/e*: 410 (molecular ion peak), 395, 190, 162, 57; ^{1}H NMR (CDCl$_3$), δ: 1.47 (s, 36H), 5.12 (s, 2OH), 7.27 (s, 4H). The product 2,6-di-*tert*-butylbenzoquinone (BQ) was identified on GC chromatograms by spiking using an authentic BQ sample.

3. Results and discussion

Metallophthalocyanine complexes are readily available oxidation catalysts and found to transfer oxygen from various oxygen donors to alkanes, alkenes, phenols and thiols in numerous studies [10,12,15–28]. Here we report the oxidation of 2,6-di-*tert*-butylphenol (DTBP) with *tert*-butylhydroperoxide (Bu^{t}OOH) oxidant using a [CoPcTS]$^{4-}$

catalyst. From our point of view it was worthwhile to investigate Bu^{t}OOH as an oxidant in a metallophthalocyanine-catalyzed phenol oxidation reaction for two reasons. (1) There is a synthetic importance as well as environmental priority for the phenol oxidations. (2) It takes hours Bu^{t}OOH to destroy [CoPcTS]$^{4-}$ and Bu^{t}OOH is expected to give a faster reaction than when molecular oxygen is used instead. Because the solubility of molecular oxygen in pure water under 1 atm oxygen pressure at 25 °C is about 1.3×10^{-3} M, which is quite low and can only be varied with pressure and/or temperature changes. On the other hand, Bu^{t}OOH is a water-soluble substance and its concentration could be adjusted in a wide range and kept high in reaction mixtures. Furthermore Bu^{t}OOH is a stronger oxidant than molecular oxygen.

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

We used a solvent mixture of CH$_3$OH/H$_2$O (4:1 v:v) in our reactions in which DTBP, [CoPcTS]$^{4-}$, and Bu^{t}OOH were found to be soluble. In a typical reaction, the relative molar ratios of Bu^{t}OOH:DTBP:[CoPcTS]$^{4-}$ were about 500:100:1, respectively. Of two papers of Tsuruya and colleagues [6,7] and a paper of Kharasch and Joshi [31], 2,6-di-tert-butylbenzoquinone (BQ) and 3,3′,5,5′-tetra-tert-butyl-4,4′-diphenoquinone (DPQ) were the only two products of DTBP oxidation reported in the literature (Fig. 2) [5,8,9]. In the Tsuruya's papers, a third compound, 4,4′-dihydroxy-3,3′,5,5′-tetra-tert-butylbiphenyl (H$_2$DPQ) (Fig. 2), was reported as one of the products of the oxidation of DTBP using Cu-impregnated MCM-41 catalysts at 313 K in 1 atm air. Kharasch and Joshi also reported the same product from the oxidation of DTBP with potassium ferricyanide [31]. We also observed the formation of H$_2$DPQ as one of the products of the oxidation of DTBP with Bu^{t}OOH in the presence of [CoPcTS]$^{4-}$ catalyst. In our oxidant/catalyst system DPQ and H$_2$DPQ obtained were the major products and a few reactions resulted with the formation of BQ. The GC–MS spectra for DPQ and H$_2$DPQ gave both the molecular ion and fragment peaks as expected for these compounds. Further identifications of these compounds was done using a ^{1}H NMR spectrum of a DPQ–H$_2$DPQ mixture in CDCl$_3$. Because of knowing ^{1}H NMR peaks of DPQ from the lit-
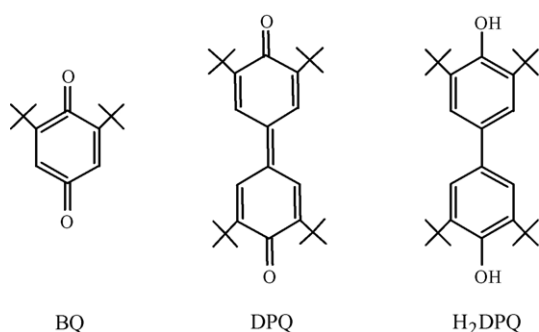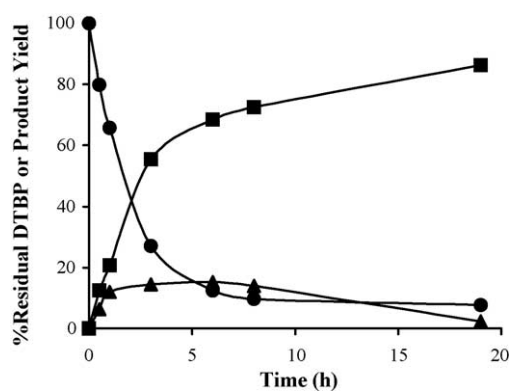

Fig. 3. Conversion and product yield vs. time in the oxidation of 0.300 mol DTBP with 1.52 mmol Bu^{t}OOH catalyzed by 3.0×10^{-3} mmol [CoPcTS]$^{4-}$ in 5 ml of 80% methanol–water mixture: (●) conversion of DTBP; (■) yield of DPQ; (▲) yield of H$_2$DPQ.

erature, having a ^{1}H NMR spectrum of an authentic sample of DPQ in our hand, and symmetrical and simple structures of DPQ and H$_2$DPQ, it was easy to pick up the peaks in the spectrum that do not belong to DPQ. Those ^{1}H NMR peaks were the ones expected for H$_2$DPQ. BQ was identified on GC chromatograms by spiking an authentic BQ sample. The GLC chromatograms were used for quantitative product and reactant analyses. Because we did not have a pure sample of H$_2$DPQ in our hand, we used the same response factor for H$_2$DPQ as that of DPQ.

Fig. 3 shows the time dependence of the percentages of residual DTBP and yields of products in the oxidation of DTBP with Bu^{t}OOH catalyzed by [CoPcTS]$^{4-}$. The conversion of DTBP to products increased fast with the increase in reaction time for the first 3 h reaching a value of about 70% then gradually levelled off. After 8 h, the conversion of DTBP was over 85%. The reaction profile shows that the yield of DPQ increased fast first 3 h (about 56%) then gradually with increasing reaction time. After 8 h, the yield of DPQ was about 73%. Also the yield of H$_2$DPQ increased fast with time in the initial stage of oxidation (about first 1 h) and nearly tended to level off at the reaction times from 1 to 6 h (maybe with a maximum around 6 h) and then gradually decreased with further reaction time. The highest yield percentage of H$_2$DPQ was about 15% after 6 h.

We also investigated how catalyst, oxidant, and substrate concentrations affect the oxidation of DTBP with [CoPcTS]$^{4-}$/Bu^{t}OOH catalyst–oxidant system (Figs. 4–6) and determined the product distribution of each experiment. The product distribution of the oxidation reaction at 8 h is given in Table 1. Fig. 4 illustrates the effect of [CoPcTS]$^{4-}$ catalyst loading on the conversion of DTBP for a reaction mixture consisting of constant concentrations of the substrate and the oxidant. In all catalyst concentrations the conversion of DTBP and yields of DPQ and H$_2$DPQ increased as the concentration of the catalyst increased (reactions 1–5, Table 1). When the concentration of the catalyst is doubled compared to that of the typical experiment (reaction 2, Table 1), the
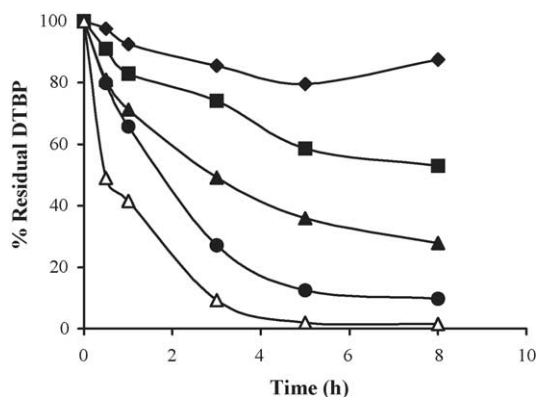

Fig. 2. Chemical structures of the products of DTBP oxidation.

Fig. 4. Effect of the amount of $[CoPcTS]^{4-}$ on the conversion of 0.300 mmol DTBP oxidized with 1.52 mmol Bu^tOOH in 5 ml 80% methanol–water mixture. The amounts of $[CoPcTS]^{4-}$: (♦) 3.0×10^{-4} mmol; (■) 7.5×10^{-4} mmol; (▲) 1.5×10^{-3} mmol; (●) 3.0×10^{-3} mmol; (△) 6.0×10^{-3} mmol.
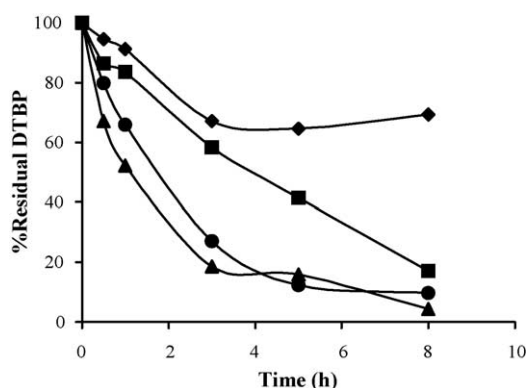

Fig. 5. Effect of the amount of Bu^tOOH on the conversion of 0.300 mmol DTBP catalyzed by 3.0×10^{-3} mmol $[CoPcTS]^{4-}$ in 5 ml 80% methanol–water mixture. The amounts of Bu^tOOH: (♦) 0.15 mmol; (■) 0.76 mmol; (●) 1.52 mmol; (▲) 4.55 mmol.

conversion of DTBP was over 96% in 5 h. Interestingly the formation of the product 2,6-di-*tert*-benzoquinone (BQ) (less than 2%) was observed in this reaction. In an attempt to oxidize DTBP with Bu^tOOH in the absence of the catalyst $[CoPcTS]^{4-}$, no oxidation product was obtained. This confirms that the catalyst is essential in the oxidation process.
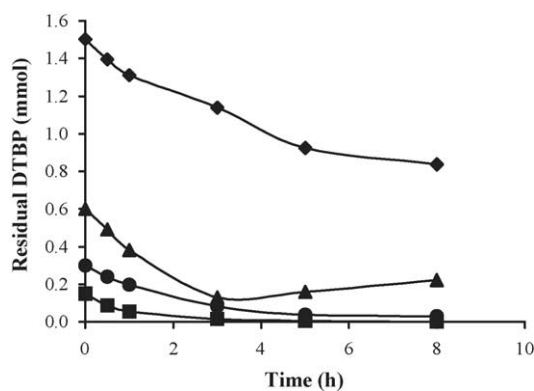

Fig. 6. Effect of the initial amount of DTBP on its conversion with 1.52 mmol Bu^tOOH catalyzed by 3.0×10^{-3} mmol $[CoPcTS]^{4-}$ in 5 ml 80% methanol–water mixture. The amounts of DTBP: (♦) 1.500 mmol; (▲) 0.600 mmol; (●) 0.300 mmol; (■) 0.150 mmol.

Furthermore, in the presence of $[CoPcTS]^{4-}$ but in the absence of Bu^tOOH we did not get any detectable amount of the oxidation product either. When this reaction (0.300 mmol DTBP) was catalyzed by 3.0×10^{-3} mmol $[CoPcTS]^{4-}$ under air (in the absence of Bu^tOOH) at room temperature, the reaction proceeded very slowly and the conversion of DTBP was only about 3.5% after 8 h. This slow reaction rate under air may be due to low solubility of dioxygen and eventually the low concentration of dioxygen in the reaction medium as well as difficulty in the activation of dioxygen by $[CoPcTS]^{4-}$ compared to that of Bu^tOOH.

Increase in the concentration of Bu^tOOH also resulted with increase in the conversion of DTBP and yields of the products formed (Fig. 5 and reactions 1, 6, 7, Table 1). When the concentration of Bu^tOOH is tripled (reaction 6, Table 1), contrary to usual finding, no biphenyl product (H_2DPQ) was obtained and instead substantial amount BQ formed (32%) (reaction 6, Table 1).

The variation of the percent conversion of DTBP with time for its different concentrations is shown in Fig. 6 and higher yields for DPQ and H_2DPQ were obtained during the course of the reaction (reactions 1, 8–10, Table 1). When the ratio of Bu^tOOH to DTBP was about 1 (reaction 8, Table 1), the amount of formed H_2DPQ was higher than DPQ. Further-

Table 1
The product distribution of oxidation of DTBP with Bu^tOOH in the presence of $[CoPcTS]^{4-}$ catalyst after 8 h

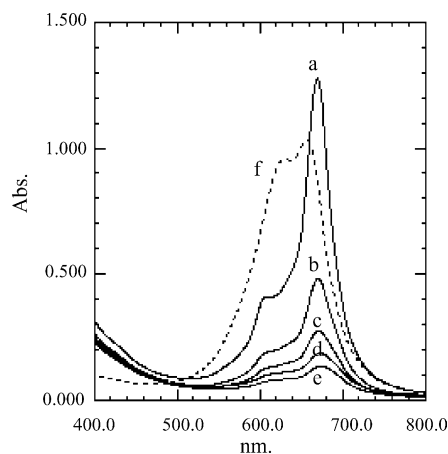| Reaction	DTBP (mmol)	$[CoPcTS]^{4-}$ (mmol)	Bu^tOOH (mmol)	Time: 8 h		
				DPQ (%)	H_2DPQ (%)	BQ (%)
1	0.300	3.0×10^{-3}	1.52	73	14	–
2	0.300	6.0×10^{-3}	1.52	60	35	<2
3	0.300	1.5×10^{-3}	1.52	42	28	–
4	0.300	7.5×10^{-4}	1.52	20	15	–
5	0.300	3.0×10^{-4}	1.52	7	3	–
6	0.300	3.0×10^{-3}	4.55	58	–	32
7	0.300	3.0×10^{-3}	0.76	31	49	–
8	1.500	3.0×10^{-3}	1.52	16	24	–
9	0.600	3.0×10^{-3}	1.52	36	24	–
10	0.150	3.0×10^{-3}	1.52	84	–	12

Fig. 7. Time-dependent changes in the visible spectrum of the oxidized $[CoPcTS]^{4-}$ observed on addition of Bu^{t}OOH oxidant (0.21 ml, 1.52 mmol) to a reaction mixture containing 0.300 mmol DTBP and 3.0×10^{-3} mmol $[CoPcTS]^{4-}$ catalyst in 5.0 ml: (a) 1 h; (b) 2 h; (c) 3 h; (d) 5 h; (e) 8 h after addition of Bu^{t}OOH. All spectra for the oxidized $[CoPcTS]^{4-}$ were taken after seven-fold dilution with water. (f) The visible spectrum of (non-oxidized) $[CoPcTS]^{4-}$.

more, we observed considerable amount of BQ formation (12%) when the [Bu^{t}OOH]/[DTBP] ratio was about 10 (reaction 10, Table 1). As in reaction 6, here also we did not observe any H$_2$DPQ formation. From Table 1 we can conclude that high oxidant/substrate ratio (about 10 or larger) leads to

the formation of substantial amount BQ and no formation of H$_2$DPQ or vice versa.

3.2. Catalyst recycling and degradation

In a recycling experiment, 0.300 mmol DTBP and 1.52 mmol Bu^{t}OOH were added to the medium from which the residual DTBP and its oxidation products from the first cycle were extracted and the reaction was carried out for 8 h. The GC analysis showed less than 5% conversion of DTBP for the second cycle. We found that this remarkable decrease in the catalytic activity of $[CoPcTS]^{4-}$ in the oxidation of DTBP with Bu^{t}OOH is due to fast degradation of the catalyst. Fig. 7 shows the absorption spectra of the catalyst as a function of time in the reaction medium after the extraction of the organics from the reaction mixture with dichloromethane. We determined that about three-fourths of $[CoPcTS]^{4-}$ was degraded in the first hour under the reaction conditions as in reaction 1, Table 1. The percentages of the remaining $[CoPcTS]^{4-}$ with time were as fallows: 24.2% after 1 h, 8.6% after 2 h, 4.7% after 3 h, 2.8% after 5 h, 2.1% after 8 h.

3.3. Reaction mechanism

Several studies proposed reaction mechanisms for the formation of dimeric products from the oxidation of DTBP

$$2Bu^tOOH \xrightarrow{[CoPcTS]^{4-}} Bu^tO^{\cdot} + Bu^tOO^{\cdot} + 2H_2O$$
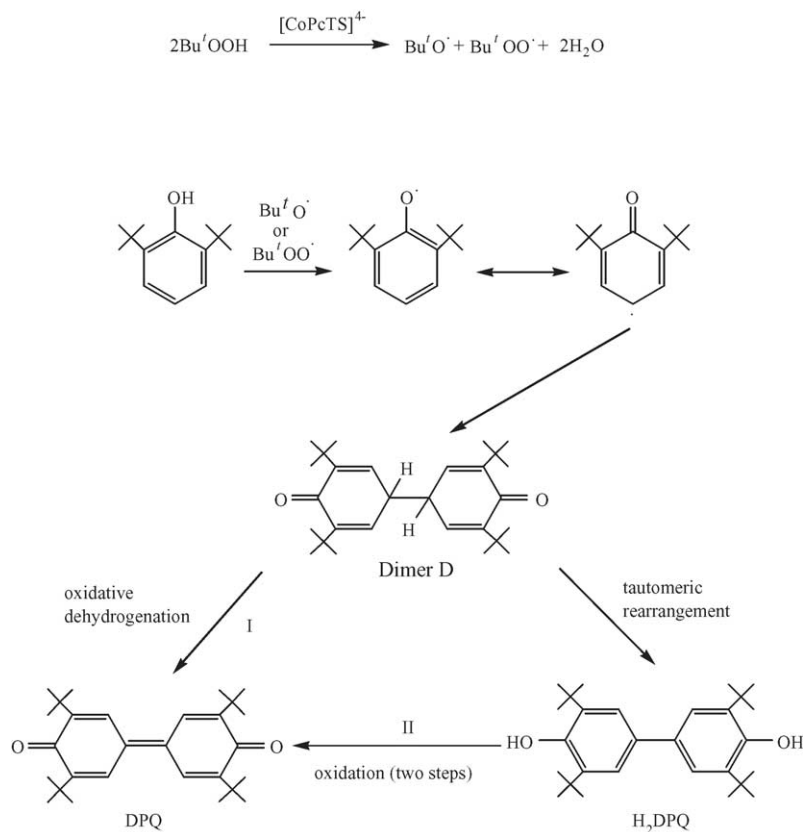
Scheme 1. Schematic representation of the possible pathways in the oxidation of DTBP with Bu^{t}OOH catalyzed by $[CoPcTS]^{4-}$ (adapted from [7]).

[1–4,6–8,12,31]. When Bu^{t}OOH is the oxidant, it is believed that interaction of the catalyst and oxidant creates Bu^{t}O$^{\bullet}$ and Bu^{t}OO$^{\bullet}$ radicals then these radicals react with DTBP and consequently 2,6-di-*tert*-butylphenoxy radicals are generated (Scheme 1).

In the formation of H$_2$DPQ, C–C coupling occurs between the resonance forms of 2,6-di-*tert*-butylphenoxy radicals with the unpaired electrons at four positions. The resulting unstable coupling product or dimer D (Scheme 1) rearranges itself into a more stable tautomeric form H$_2$DPQ. According to Kharasch and Joshi [31], the dimer D is also a stable compound when dry, and in non-polar solvents and is rapidly converted to H$_2$DPQ in polar solvents. Also many researchers have showed H$_2$DPQ in their reaction mechanism proposals for the oxidation DTBP as an intermediate or an unstable product. They proposed it further oxidize to give DPQ.

For the formation of DPQ, two plausible routes have been proposed by Tsuruya and colleagues [6,7]. First route (Scheme 1, Route I) proceeds through oxidative dehydrogenation of the unstable dimer D (C–C coupling product) which is a direct way to form DPQ. In the second route (Scheme 1, Route II), H$_2$DPQ involves as an intermediate in the formation of DPQ. In this case, DPQ forms through sequential oxidation steps of H$_2$DPQ. We believe both routes are plausible in our case. Because no induction period was observed in the formation of DPQ (see Fig. 3), this may be thought as an indication for the presence of the oxidative dehydrogenation reaction (Route I) to yield DPQ. On the other hand, the yield profile of H$_2$DPQ in Fig. 3 can be treated as the yield profile of B in A → B → C type consecutive reactions. If so, this route (Route II) also makes contribution to the formation of DPQ. An evidence for this contribution may be put forward in the late stage of the reaction (after 8 h) where the amount of residual DTBP did not change with reaction time whereas the yield of DPQ increased and the yield of H$_2$DPQ decreased about the same amounts with time (Fig. 3). Thus we can suggest that the reaction through Route II, which is a two-consecutive oxidation reactions, is working in the late stage of the reaction. Tsuruya and colleagues reported similar reaction profiles and findings in the yields in DPQ, H$_2$DPQ and conversion in DTBP with time when they used a basic unsupported CuCl$_2$ catalytic system in the oxidation of DTBP under air [7].

Acknowledgements

References

[1] S.A. Bedell, A.E. Martell, Inorg. Chem. 22 (1983) 364.
[2] S.A. Bedell, A.E. Martell, J. Am. Chem. Soc. 107 (1985) 7909.
[3] I. Mamalis, A.F. Noels, G. Tihange, R. Warin, P. Teyssié, A.J. Hubert, J. Mol. Catal. 45 (1988) 327.
[4] H. Tadakoro, S. Nishiyama, S. Tsuruya, M. Masai, J. Catal. 138 (1992) 24.
[5] R. Pathak, G.N. Gao, J. Mol. Catal. A: Chem. 130 (1998) 215.
[6] H. Fujiyama, I. Kohara, K. Iwai, S. Nishiyama, S. Tsuruya, M. Masai, J. Catal. 188 (1999) 417.
[7] I. Kohara, H. Fujiyama, K. Iwai, S. Nishiyama, S. Tsuruya, J. Mol. Catal. A: Chem. 153 (2000) 93.
[8] C. Comuzzi, A. Melchior, P. Polese, R. Portanova, M. Tolazzi, Inorg. Chim. Acta 355 (2003) 57.
[9] E. Tarnaud, A. Gaudemer, M. Frostin-Rio, C. Bied-Charreton, J. Mol. Catal. 72 (1992) 181.
[10] M. Chibwe, L. Ukrainczyk, S.A. Boyd, T.J. Pinnavaia, J. Mol. Catal. A: Chem. 113 (1996) 249.
[11] S.M.S. Chauhan, B. Kalra, P.P. Mohapatra, J. Mol. Catal. A: Chem. 137 (1999) 85.
[12] V.M. Kothari, J.J. Tazuma, J. Catal. 41 (1976) 180.
[13] D. Wöhrle, H. Bohlen, C. Aringer, D. Pohl, Makromol. Chem. 185 (1984) 669.
[14] M. Hassanein, F.I. Abdel-Hay, T. El-Hefnawy El-Esawy, Eur. Polym. J. (1994) 335.
[15] T. Ichinohe, H. Miyasaka, A. Isoda, M. Kimura, K. Hanabusa, H. Shirai, React. Funct. Polym. 43 (2000) 63.
[16] A.B. Sorokin, A. Tuel, New J. Chem. 23 (1999) 473.
[17] A.B. Sorokin, A. Tuel, Catal. Today 57 (2000) 45.
[18] A.B. Sorokin, S. Mangematin, C. Pergrale, J. Mol. Catal. A: Chem. 182–183 (2002) 267.
[19] W. Zhu, W.T. Ford, J. Mol. Catal. 78 (1993) 367.
[20] K.J. Balkus Jr., M. Eissa, R. Levado, J. Am. Chem. Soc. 117 (1995) 10753.
[21] R. Raja, P. Ratnasamy, Catal. Lett. 48 (1997) 1.
[22] N. Grootboom, T. Nyokong, J. Mol. Catal. A: Chem. 179 (2002) 113.
[23] N. Safari, F. Bahadoran, J. Mol. Catal. A: Chem. 171 (2001) 115.
[24] N. Setletho, T. Nyokong, J. Mol. Catal. A: Chem. 209 (2004) 51.
[25] J. van Welzen, A.M. van Herk, A.L. German, Makromol. Chem. 188 (1987) 1923.
[26] M. Kimura, T. Dakeno, E. Adachi, T. Koyama, K. Hanabusa, H. Shirai, Makromol. Chem. Phys. 195 (1994) 2423.
[27] M. Kimura, T. Nishigaki, T. Koyama, K. Hanabusa, H. Shirai, React. Polym. 23 (1994) 195.
[28] T.V. Rao, K.N. Rao, S.L. Jain, B. Sain, Synth. Commun. 32 (2002) 1151.
[29] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. da Cruz, M.C. Guerreiro, D. Mandelli, E.V. Spinacé, E.L. Pires, Appl. Catal. A: Gen. 211 (2001) 1.
[30] J.H. Weber, D.H. Busch, Inorg. Chem. 4 (1965) 472.
[31] M.S. Kharasch, B.S. Joshi, J. Org. Chem. 22 (1957) 1439.