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Catalysis of Autoxidation of 2,6-Di-*tert*-butylphenol in Water by Metallophthalocyanine Tetrasulfonates Bound to Polyelectrolyte Supports

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2,6-and 2,10-Ionenes and soluble poly(vinylbenzyl)trimethylammonium chloride polyelectrolytes were synthesized and used as catalyst supports for cobalt-, iron- and copper-phthalocyanine tetrasulfonates on the autoxidation of 2,6-di-*tert*-butylphenol in water by molecular oxygen. Polyelectrolyte supported cobalt-phthalocyanine tetrasulfonate showed the highest activity in comparison with the supported analogous of iron- and copper-phthalocyanine tetrasulfonates. The supported metallophthalocyanine tetrasulfonates had better catalytic activities than the unsupported analogous for the reaction. The reaction yielded 3,3',5,5'-tetra-*tert*-butyl- 4,4'-diphenoquinone as the only oxidation product of 2,6-di-*tert*-butylphenol. The extent of the reaction was affected by time, temperature, pH, the types and concentrations of supports and metallophthalocyanine tetrasulfonates.

Introduction

Polymer supported catalysis has been the subject of many investigations during the last two decades. As polymeric catalyst support, a wide range of supports such as polymers with organic and organometallic functional groups, ion-exchange resins, membranes, and polyelectrolytes have been employed and several methods have been developed to functionalize polymers for catalyst attachement[1–5].

In the literature, a wide variety of transition metal-containing compounds and their supported analogs have been used as catalysts for oxidations, reductions and other transformations. For example metallophthalocyanines, metalloporphyrins and metallo-Schiff bases were the most commonly used macrocycle-metal compounds for oxidation catalysts[5–9]. Catalytic activity closely depends on the central metal ion and cobalt(III) is the most generally active metal ion catalyst for autoxidation of organic compounds[6]. Cobalt-phthalocyanine tetrasulfonate bound to cationic latexes have been employed as colloidal catalysts for the autoxidation of water insoluble 2,6-di-*tert*-butylphenol, 1-decanethiol and of water soluble 2-mercaptoethanol in water[10–13]. The A. L. German group has extensively studied the catalytic activity of ionene bound cobalt-phthalocyanine tetrasulfonate for the autoxidation of water soluble 2- mercaptoethanol[13–18].

In this study, the effects of polymeric media were investigated by using ionene and soluble poly(vinyl benzyl)trimethylammonium chloride polyelectrolytes as catalyst supports on the autoxidation of water insoluble 2,6-di-*tert*-butylphenol in water. Tetra sodium salts of cobalt-, iron- and copper-phthalocyanine tetrasulfonates were used as catalysts.

Experimental

Reagents and Instrumentation

N,N,N',N'-Tetramethylethylenediamine (TMEDA, Merck), 1,6-dibromohexane (Merck), 1,10-dibromodecane (Merck), 2,6-di-*tert*-butylphenol (DTBP, Merck) were used as received. Vinylbenzyl chloride (70/30 meta/para, Aldrich) was used after the removal of inhibitor and vacuum distilation. The other reagents used were research grade. Sodium salts of cobalt(II)-, iron(III)- and copper(II)-phthalocyanine tetrasulfonates were from a previous work[19] and prepared by via the Weber procedure[20].

GLC analyses of DTBP reaction mixtures were performed on a Shimadzu GC-9AM equipped with a 2 mx3 mm ID 1.5 % Silicon OV-1 glass packed column on Chromosorb W column support and an FID detector. The spectra were taken using Hitachi 150-20 Ultraviolet-visible spectrophotometer and Hitachi 270-30 Infrared spectrophotometer.

Preparations of 2,6-Ionene and 2,10-Ionene

2,6-Ionene was synthesized according to Van Herk et al[14]. Stoichiometric amounts of TMEDA (4.07 g, 35 mmol) and 1,6-dibromohexane (8.54 g, 35 mmol) were added to equivolume mixtures of N,N-dimethylformamide (25 mL) and methanol (25 mL) in a 250 mL Erlen-Meyer. The solution was left at room temperature for 12 days under nitrogen atmosphere. TMEDA (1.93 g, 16.6 mmol) was then added to the solution to aminate the end-groups and the solution was kept at room temperature for 3 more days. The ionene formed was precipitated in acetone, filtered, purified by extensive washing with acetone and dried to remove acetone. The stock solution of the ionene in water was prepared to be used for characterization and experiments.

The same procedure was used to prepare 2,10-ionene.

The M_n Determinations of 2,6-Ionene and 2,10-Ionene

The molecular weight of 2,6-ionene was determined by using the values of the equivalence points and the mass of the ionene in the solution as given in the literature[17]. For the titration of the end-groups of 2,6-ionene, 10.0 mL 1.0 M NaCl solution was added to 3.0 mL of the stock ionene solution containing 249 mg ionene. Under nitrogen, 3.1 mL 0.10 M HCl solution was added until pH below 3. While the pH of the solution was monitored with a pH-meter, the solution was titrated with a 0.0096 N NaOH solution and the equivalence points were determined.

Preparations of Soluble and 5% Cross-linked Poly(vinylbenzyl)trimethylammonium chloride (PVBTMA Cl)

The preparation of soluble PVBTMA Cl was done in two-steps using the emulsion polymerization technique of Campbell et al [21]. First, poly(vinylbenzyl)chloride was prepared and then this polymer was converted to poly(vinylbenzyl)trimethylammonium chloride. Poly(vinylbenzyl) chloride was prepared by using a semi-continuous method. A 250 mL round-bottomed flask was equipped with an overhead stirrer, a condenser and an addition funnel. The reaction flask was charged with sodium dodecyl sulfate (SDS, 70 mg, 0.24 mmol) and distilled water (50 mL) and heated to 65° C. During the entire polymerization process, the flask content was stirred at 1100 ± 50 rpm. The addition funnel was charged with SDS (200 mg, 0.69 mmol), vinylbenzyl chloride (5.08 g, 33 mmol), sodium bisulfite (10 mg, 0.096 mmol) and distilled water (15 mL). By shaking this mixture, a white pre-emulsion was obtained. After potassium persulfate (32 mg, 0.12 mmol) and sodium bisulfite (2 mg, 0.019 mmol) were added to the reaction flask at 65° C, the pre-emulsion in the addition funnel was added dropwise to the stirred solution in the flask over 10 min. After addition was completed, the polymerization was continued for 1.5 h at 65° C.

After the temperature of the poly(vinylbenzyl) chloride emulsion was brought to around 40° C in 30 minutes, a solution of 5.5 mL of 45% aqueous trimethylamine diluted with 70 mL of distilled water was added dropwise to the emulsion over 15 min. The quaternization reaction was continued for 4 h at 40° C. To calculate the number of quaternary ammonium sites in the emulsion, the solid content of the emulsion and the amount of liberated chloride ions were determined using the Volhard titrimetric method[22].

The same procedure as for soluble PVBTMA Cl was applied to prepare 5% crosslinked poly(vinylbenzyl)-trimethylammonium chloride colloidal anion exchange resin (CAER). The cross linking agent was divinylbenzene.

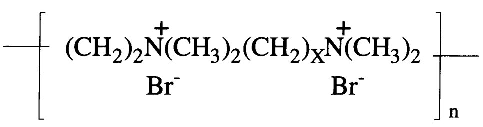
General Procedure for Autoxidation of 2,6-Di-*tert*-butylphenol

In a typical experiment, a 50 mL round-bottomed flask was charged with 2,6-ionene (64.8 mg, $9.3\text{x}10^{-2}$ mmol N^+ group) and sodium borate (0.5 mmol) buffer. The pH of the mixture was adjusted to 9.3. The flask was immersed in an oil bath at 75±2° C. After 5 minutes, DTBP (0.98 mmol) was added to the flask as solid and a condenser attached to the flask. The reaction mixture was stirred with a magnetic bar for 2 h under 0.90±0.05 atmosphere pressure of oxygen. After the reaction stopped, the organic components of the reaction mixture were extracted into about 10 mL $CHCl_3$. The extraction process was repeated 5-6 times to ensure no organics were left in the aqueous phase. Before quantitative GLC analysis, a known amount napthalene (about 100 mg) was added to the extract as an internal standard.

The analyses of reaction mixtures were done by GLC. Temperature programming from 160° C to 275° C at 25° C/min was employed and the flow rate of carrier gas nitrogen was 50 mL/min. The initial and final temperatures were kept constant for 3 min and 5 min respectively.

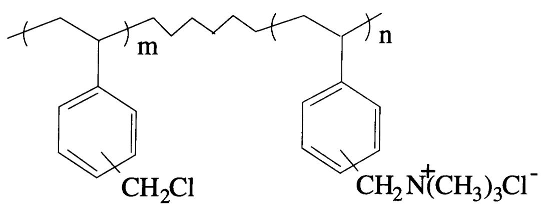
Results and Discussion

Molecular Weigths of the Supports: The molecular weights (M_n) of 2,6- and 2,10-ionenes (1a,b) were 1440 and 1400, respectively, as determined by titration with sodium hydroxide after bringing the pH of the ionene solution below 3. The obtained M_n values for the ionenes were in the expected range which is about $10^3 - 10^4$. The M_n of the soluble and 5% cross-linked PVBTMA Cl were not determined, and due to the polymerization method used, they should be much higher than those of the ionenes. The anion exchange capacities of the soluble and 5% cross-linked PVBTMA Cl were determined as 3.75 and 3.58 meq/g polymer respectively. The ionenes and soluble PVBTMA Cl gave clear solutions and no solubility problem of these supports occurred during the experiments.



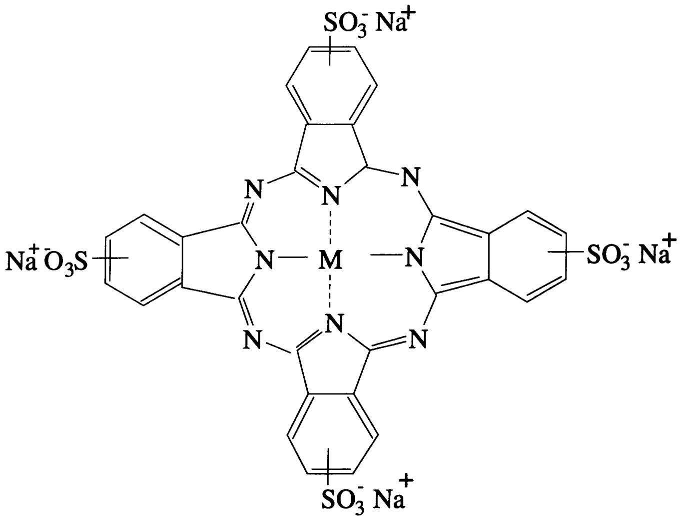
$$-\!\!\left[(CH_2)_2\underset{Br^-}{\overset{+}{N}}(CH_3)_2(CH_2)_x\underset{Br^-}{\overset{+}{N}}(CH_3)_2\right]_n\!\!-$$

1a =6
1b =10

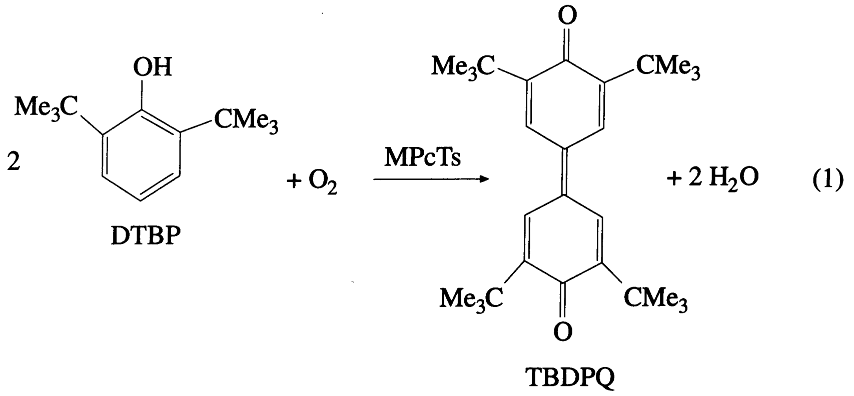


The Autoxidation of 2,6-Di-*tert*-butylphenol: The autoxidation of 2,6-di-*tert*-butylphenol (DTBP) in water catalyzed by water soluble polymer supported and soluble metallophthalocyanine tetrasulfonates (MPcTs, 3a-c) are heterogeneous reactions. The water insoluble DTBP was oxidized by O_2 gas dissolved in aqueous phase where the supported or unsupported MPcTs were found (Eq.1). When homogeneous and supported MPcTs were not present in the reaction mixture, no reaction was observed which means that the catalyst is vital for the transfer of the oxygen to the phenol. For this particular reaction, mass transport phenomena as well as activity of the catalyst are important. The ionenes and polymers used in the reaction mixtures serve as support for MPcTs and in addition they attract DTBP due to their organic nature. On the other hand, in the homogeneous catalyst case, the only mass transfer step is the transport of the phenol from the bulk phase to the catalyst dispersed in the aqueous phase. In order to obtain mechanistic information on these supported MPcTs catalysts, we studied some parameters independently. All reactions were carried out under about 0.9 atmosphere pressure of oxygen or air. Dark-red crystals were obtained as the only oxidation product of DTBP and the product was identified as 3,3',5,5'-tetra-*tert*-butyl-4,4'-diphenoquinone (TBDPQ) based on comparison with the Uv/Vis and IR spectra and the melting point given in the literature (Eq.1). The other possible product 2,6-di-*tert*-butyl-1,4-benzoquinone was not detected. The extent of the reaction was determined quantitatively by GLC and the extent of the reaction was affected by time, temperature, pH, oxygen pressure, the types and concentrations of supports and metallophthalocyanine tetrasulfonates.

The Catalytic Activities of the Soluble and Supported MPcTs's: First, in order to see the effects of the central metal atoms on the reaction, soluble Co-, Fe- and Cu phthalocyanine tetrasulfonates and their supported analogous were used as catalysts for the oxidation of DTBP in water. All three MPcTs showed certain degree catalytic activities (Table 1). Among 2,10-ionene bound MPcTs's, CoPcTs showed the highest whereas the CuPcTs showed the lowest catalytic activity. We also observed that the conversions of the reaction were higher when ionene bound CoPcTs and FePcTs were used as catalysts than the conversions when unsupported CoPcTs and FePcTs were used (Table 1). This may result from either the attraction of DTBP to the organic support where the catalyst is immobilized or the change of the monomer-dimer equilibrium of MPcTs due to immobilization or both.



3a $CoPcTsNa_4$
3b $FePcTsNa_4$
3c $CuPcTsNa_4$



Eq.1

Table 1. Autoxidation of DTBP with supported and unsupported metallophthalocyanine tetrasulfonate catalysts[a]

Expt.	Catalyst (mmol)	Support (mg)	% Conversion[b]
1	CoPcTs N^+R_4 (0.020)	2,10-Ionene (64.8)	61
2	FePcTs N^+R_4 (0.020)	2,10-Ionene (64.8)	39
3	CuPcTs N^+R_4 (0.020)	2,10-Ionene (64.8)	5
4	CoPcTs Na_4 (0.020)	-	7
5	FePcTs Na_4 (0.020)	-	10
6	CoPcTs N^+R_4 (0.040)	2,10-Ionene (64.8)	58
7	CoPcTs N^+R_4 (0.020)	2,10-Ionene (129.6)	40

[a] 0.5 mmol sodium borate, 0.98 mmol DTBP, volume 12 mL, temperature 75±2° C, pH 9.3±0.1, time 2 h. [b] Based on DTBP

UV/Vis studies have indicated that when CoPcTs are immobilized on the ionenes and PVBTMA Cl, the monomer-dimer equilibrium of CoPcTs shifts toward the monomeric species making it dominant. However at the same concentration of the soluble $CoPcTsNa_4$, the dominant species is the dimer. Although UV/Vis spectra of the supported or unsupported CoPcTs were taken at room temperature, it was expected that the monomeric species should be dominant at the reaction temperature. However the nature of the $CoPcTsNa_4$-oxygen adduct is not well-known and the dimeric $CoPcTsNa_4$ is believed to bind oxygen and transfer it to a substrate[15].

Effect of Support Types and Concentrations: The activities of CoPcTs attached to 4 different water soluble supports were quite close, showing 57- 73% conversion of the phenol under identical conditions (Table 2). However, when the homogeneous catalyst was used, the conversion % was much lower (7%). When the colloidal anion exchange resin (CAER) was used, the conversion was complete (Table 2). Within experimental error, the same activity of 2,10-ionene bound CoPcTs catalyst was observed when the phthalocyanine concentrations were doubled from 2 mol % to 4 mol % of the phenol keeping the ionene concentration constant (Table 1). When the amount of the ionene was doubled and the CoPcTs concentration was kept constant (as of 2 mol % of the phenol) the conversion of the phenol decreased from 61 % to 40% (Table 1).

Table 2. The effect of the supports on autoxidation of DTBP[a]

Expt.	Support[b]	% Conversion[c]
1	2,10-Ionene	61
2	2,6-Ionene	57
3	PVBTMA Cl	72
4	CTAB[d]	73
5	-	7
6	CAER[e]	100

[a] 0.020 mmol $CoPcTsNa_4$, 0.5 mmol sodium borate, 0.98 mmol DTBP, volume 12 mL, temperature 75 ± 2° C, pH 9.3± 0.1, time 2h.

[b] Each support contains 0.280± 0.010 mmol quaternary ammonium group.

[c] Based on DTBP.

[d] Hexadecyltrimethylammonium bromide.

[e] Colloidal Anion Exchange Resin

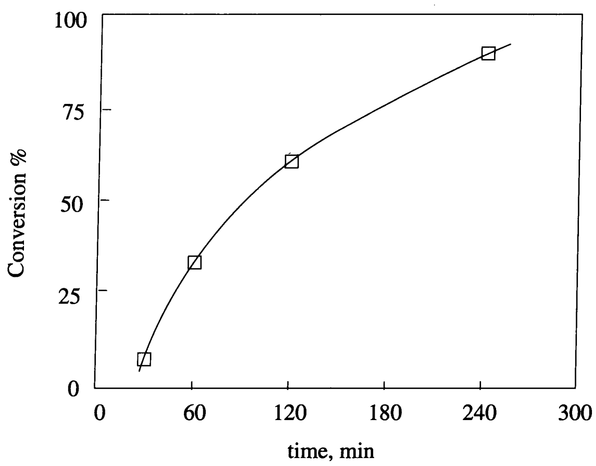


Figure 1. The time course of the autoxidation of DTBP catalyzed by CoPcTs bound to 2,10-ionene. Conditions were 0.020 mmol $CoPcTsNa_4$, 64.8 mg 2,10-ionene, 0.5 mmol sodium borate, 0.98 mmol DTBP, volume 12 mL, temperature 75±2° C, pH 9.3±0.1

Effect of Time: Figure 1 shows time dependence of the autoxidation of the phenol catalyzed by 2,10-ionene bound CoPcTs. The phenol was oxidized about 30% in 1 h, 60% in 2 h and 90 % in 4 h. The decrease in the phenol conversion after 2 h can be attributed either or both the decrease in the concentration of the unreacted phenol and in the activity of the catalyst. It seems that the conversion profile shows an induction period and then the conversion of the phenol shows linearity with time to about 60%.

Effect of Temperature and pH: Data in Table 3 show the temperature and pH dependences of the autoxidation of the phenol with 2,10-ionene supported CoPcTs. Autoxidation proceeded at a reasonable rate at 75°C. As the temperature was lowered, the reaction became slower and at room temperature the conversion almost did not take place. The conversion of the reaction increased with increasing pH in the 7.6-12.5 range.

However in the literature for the role of cobalt complexes in the autoxidation of substituted phenols by O_2 in organic media, some authors reported that the phenoxy radical is the first intermediate in the mechanism of formation of the oxidized coupled product[23,24]. So in the aqueous phase autoxidation of DTBP, a different mechanism may be taking place and as the pH increases, the increase in the concentration of the phenolate ions may be responsible for the increase in the conversion. The effect of the pH in the autoxidation of DTBP may be related to the stability of the Co-O_2 species.

When the reaction was run under air instead of oxygen, the conversion only dropped from 61% to 33% which is about half the conversion obtained with pure oxygen. This shows that the reaction is not strictly dependent on the oxygen pressure.

Table 3. Temperature and pH dependences of autoxidation of DTBP using 2,10-ionene supported CoPcTs catalyst.[a]

Expt	Temperature (°C)[b]	pH[c]	% Conversion[d]
1	23	9.3	3
2	50	9.3	11
3	75	9.3	61
4	75	7.6	9
5	75	10.9	82
6	75	12.5	92

[a] 64.8 mg 2,10-Ionene, 0.020 mmol $CoPcTsNa_4$, 0.5 mmol sodium borate, 0.98 mmol DTBP, volume 12 mL, time 2h. [b] $\pm 2°C$. [c] ± 0.1 unit. [d] Based on DTBP

Conclusions

-In the autoxidation of water insoluble 2,6-di-*tert*-butylphenol in water by molecular oxygen, polymers used as a support for the catalyst increase the catalytic activity of the catalyst. Presumably this effect occurs due to the attraction of the phenol molecules or the phenolate ions to the polymer and the change of the aggregation of metallophthalocyanine tetrasulfonates.

-Only oxidation product of 2,6-di-*tert*-butylphenol was 3,3',5,5'- tetra-*tert*-butyl-4,4'-diphenoquinone.

-When metallophthalocyanine tetrasulfonate catalysts were not present in the rection mixture, the autoxidation of 2,6-di-*tert*-butylphenol did not take place.

-Among ionene bound Co-, Fe- and CuPcTs's, CoPcTs showed the highest whereas CuPcTs showed the lowest activity.

-The activities of CoPcTs attached to 4 different water soluble supports were quite close.

-The conversion of 2,6-di-*tert*-butylphenol increased with increasing pH, temperature and reaction time.

-To gain better understanding on the activites of the supported and soluble metallophthalocyanine tetrasulfonate catalysts, further investigations are needed.

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