all of the other cases, the mixture was warmed to ambient over a 3-h period after the addition of cuprous triflate at the temperature at which conjugate addition occurred. Conversion of the conjugate adducts to cyclopropanes was efficient except in the case of the adduct of **6** (R = R′ = H) with methyl vinyl ketone which, even in the presence of excess cuprous salt, gave an inseparable mixture containing substantial conjugate addition product; we suspect that the latter results from protonation of the enolate by the acidic 1,2-hydride transfer product that is formed in lieu of ring-closure product. In a few cases lowered yields resulted from the instability of the products to silica gel chromatography.

We are now studying the synthetic utility of a number of the products in Table I. The concept enunciated herein should be extendable to some other electrophilic olefins, nucleophiles, leaving groups, and Lewis acids.

Acknowledgment. We thank the National Institutes of Health for financial support, Dr. Alvin Marcus for recording the mass spectra, and Dr. Jaime Abola for the X-ray crystal structure of **5** (Z = SPh).

Registry No. **5** (Z = SPh), 112022-43-2; **5** (Z = $SiMe_3$), 112022-44-3; **6** (R = Me, R^1 = H), 112022-59-0; **6** (R = H, R′ = SPh), 112022-60-3; **6** (R = R′ = H), 111742-81-5; **7**, 101185-20-0; 7-(1-methyl-2-(phenylthio)ethenyl)bicyclo[4.1.0]heptan-2-one, 112041-64-2; 6,6-bis(phenylthio)bicyclo[3.1.0]hexan-2-one, 112022-45-4; 6-(phenylthio)-6-(trimethylsilyl)bicyclo[3.1.0]hexan-2-one, 112022-46-5; 7-[2,2-bis(phenylthio)ethenyl]bicyclo[4.1.0]heptan-2-one, 112022-47-6; 1-acetyl-2-(phenylthio)-2-(trimethylsilyl)cyclopropane, 112022-48-7; 6-[2,2-bis(phenylthio)ethenyl]bicyclo[3.1.0]hexan-2-one, 112022-49-8; 2,2-bis(phenylthio)-1-propionylcyclopropane, 83300-59-8; 2-(phenylthio)-1-propionyl-2-(trimethylsilyl)cyclopropane, 112022-50-1; 1-[2,2-bis(phenylthio)ethenyl]-2-acetylcyclopropane, 112022-51-2; 1-methyl-7,7-bis(phenylthio)-4-(propen-2-yl)bicyclo[4.1.0]heptan-2-one (1A,4B,6A), 112022-52-3; 7-[2-(phenylthio)ethenyl]bicyclo[4.1.0]heptan-2-one, 112022-53-4; 2′,3′-didehydro-3′-(phenylthio)spiro[bicyclo[4.1.0]heptane-7,1′-cyclohexan-2-one], 112022-54-5; 3′,4′-dihydro-1′-oxo-2,2-di(phenylthio)spiro[cyclopropane-1,2′(1′*H*)-naphthalene], 112022-55-6; 6-[2-(phenylthio)ethenyl]bicyclo[3.1.0]hexan-2-one, 112022-56-7; 2′,3′-didehydro-3′-(phenylthio)-2-oxospiro[bicyclo[3.1.0]hexane-6,1′-cyclohexane], 112022-57-8; 4,5-didehydro-5-(phenylthio)-1-acetylspiro[2.5]octane, 112022-58-9; cuprous triflate, 42152-44-3; tris(phenylthio)methane, 4832-52-4; [bis(phenylthio)methyl]trimethylsilane, 37891-39-7; cyclohexenone, 930-68-7; 2-cyclopentenone, 930-30-3; 3-buten-2-one, 78-94-4; 1-penten-2-one, 1629-58-9; 2-methyl-5-(propen-2-yl)cyclohex-2-en-1-one, 99-49-0; 3′,4′-dihydro-1′-oxo-2,2-bis(phenylthio)spiro[cyclopropane-1,2′(1′*H*)-naphthalene], 112022-55-6.

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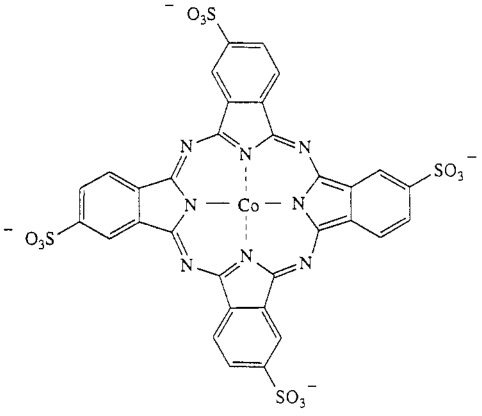
Received October 26, 1987

Autoxidation of 2,6-Di-*tert*-butylphenol in Water Catalyzed by Cobalt Phthalocyaninetetrasulfonate Bound to Polymer Colloids

Summary: Cobalt phthalocyaninetetrasulfonate (CoPcTs) bound to 54–74-nm styrene–divinylbenzene copolymer latexes substituted with quaternary ammonium ions catalyzes autoxidation of 2,6-di-*tert*-butylphenol in water ten times faster than does CoPcTs in aqueous solution.

Sir: The oxidation of organic compounds is crucial for treatment of waste water. We have found an efficient autoxidation of 2,6-di-*tert*-butylphenol in water catalyzed by cobalt phthalocyaninetetrasulfonate (**1**, CoPcTs, a mixture of isomers) bound to colloidal ion exchange resins. Previously autoxidations of 2,6-disubstituted phenols in organic solvents have produced mainly the 2,6-disubstituted 1,4-benzoquinone and the 3,5,3′,5′-tetrasubstituted 4,4′-diphenoquinone with Co catalysts[1] and certain copper catalysts.[2] CoPc derivatives have been bound to several other types of polymers for catalysis.[3]



1, CoPcTs

The colloidal polymers are prepared by emulsion copolymerization of (chloromethyl)styrene and divinylbenzene.[4] Treatment with trimethylamine converts the chloromethyl groups to quaternary ammonium chlorides.[4] The divinylbenzene prevents dissolution of the polymer in water as a polyelectrolyte. Addition of an aqueous solution of tetrasodium cobalt phthalocyaninetetrasulfonate[5] to the colloidal ion-exchange resins results in complete binding of the CoPcTs, as long as the amount of sulfonate ions of **1** does not exceed the amount of quaternary ammonium ions of the polymer. Ultrafiltration of the colloids through 0.1-μm cellulose acetate/nitrate membranes revealed no blue CoPcTs in the filtrates. The intensely blue CoPc in water is detectable by human eye to concentrations of $<10^{-7}$ M, which then is an upper limit to the concentration of CoPcTs in the aqueous phase of the heterogeneous catalysts listed in Table I.

Oxidations of 2,6-di-*tert*-butylphenol (**2**) were performed in vigorously mixed aqueous suspensions under 0.9 atm of pressure of dioxygen in flasks connected to a gas buret. The catalyst suspension was kept under air 1 h before use. With all colloidal CoPcTs catalysts except C-9 (Table I)

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Table I. Ion-Exchange Latexes and CoPcTs Catalysts

	copolymer composition[a]							
catalyst	CMS	DVB	EVB	S	wt % solids in water	DF,[b] $R_4N^+Cl^-$	R_4N^+/Co mol ratio	diam,[c] nm
C-1	91.2	4.9	3.9	0.0[d]	solid	0.61	6.7	54
C-3	98.2	1.0	0.8	0.0[d]	4.6	0.87	9.5	74
C-6	91.3	4.8	3.9	0.0[e]	9.4	0.81	8.8	55
C-8	98.2	1.0	0.8	0.0[e]	4.8	0.85	9.3	59
C-9	18.8	1.0	0.8	79.4[e]	8.4	0.21[f]	6.7	60

[a] Mole % (chloromethyl)styrenes (70/30 *m*/*p*), divinylbenzenes (55% technical grade), ethylvinylbenzenes, and styrene in the monomer mixture. [b] Degree of functionalization, the fraction of polystyrene rings substituted with quaternary ammonium groups, determined by Volhard titration of chloride. [c] Number average particle diameter of catalyst from measurement of transmission electron micrographs. [d] Polymerized in emulsion with sodium dodecyl sulfate. Conversion of chloromethyl to quaternary ammonium ions gives the colloid net positive charge. [e] Polymerized in emulsion with hexadecyltrimethylammonium bromide. [f] Complete conversion to ammonium ions within errors of measurement.

Table II. Autoxidations of 2,6-Di-*tert*-butylphenol with CoPcTs Catalysts[a]

expt	catalyst	MeOH vol fr	mix method	time, h	% conv[b]
1	soluble	0.0	shaking	24	35[c]
3	soluble	0.1	shaking	24	66[c]
4	C-1	0.0	shaking	24	100
6	C-1	0.0	stirring	6	60
7	soluble	0.0	stirring	6	6
8	soluble	0.1	stirring	6	45
23	soluble	0.1	shaking	6	30
9	C-1	0.1	stirring	6	100
10	C-1	0.0	shaking	6	100

[a] All experiments were at 70.0 ± 0.1 °C with 1.20 ± 0.01 mmol of **2**, 6.04 × 10^{-2} mmol (5.0 mol %) of CoPcTs, pH 9.0–9.1 adjusted with 4.4 mmol of AMPSO [2-hydroxy-3-[(2-hydroxy-1,1-dimethylethyl)amino]-1-propanesulfonic acid] buffer. All reaction mixtures had a volume of 150 mL and were carried out at ca. 700 mmHg (ca. 40 mmHg less than atmospheric) pressure of oxygen. [b] Percent of phenol **2** consumed according to GC analysis. [c] 3–4% yield of quinone **4** was found in addition to diphenoquinone **3**.

Table III. pH and Temperature Dependences of Oxidation of 2,6-Di-*tert*-butylphenol Using Colloidal Catalysts[a]

expt	catalyst	pH	temp, °C	time, min	% conv
11	C-1	9.0	70	120	100
13	C-1	9.0	24	120	16
14	C-1	9.0	70	80	79
15	C-1	9.0	50	120	50
16[b]	C-1	7.0	70	80	17
17[c]	C-1	9.0	70	120	55
18[d]	C-1	8.0	70	120	31
20[e]	C-1	10.0	70	80	100
21	C-3	9.0	70	80	83
22	C-6	9.0	70	80	77
24	C-8	9.0	70	80	92
25[f]	C-9	9.0	70	80	87

[a] All experiments used 0.1 volume fraction methanol, mechanical shaking, and the conditions reported in Table II unless noted otherwise. [b] Buffer was ACES [2-[(2-amino-2-oxoethyl)amino]ethanesulfonic acid]. [c] Reaction was run under air with a partial pressure of dioxygen of 150 mmHg. [d] Buffer was TAPS [3-[(2-hydroxy-1,1-bis(hydroxymethyl)ethyl)amino]-1-propanesulfonic acid]. [e] Buffer was CAPS [3-(cyclohexylamino)-1-propanesulfonic acid]. [f] Mixture contained 243 mg of C-9, instead of 123–134 mg of colloidal particles as in other experiments. All reaction mixtures contained 5 mol % Co based on phenol **2**.

the only product was 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (**3**). With soluble $CoPcTsNa_4$ as catalyst small amounts of 2,6-di-*tert*-butyl-1,4-benzoquinone (**4**) were formed also.[6] Two methods were used to add the

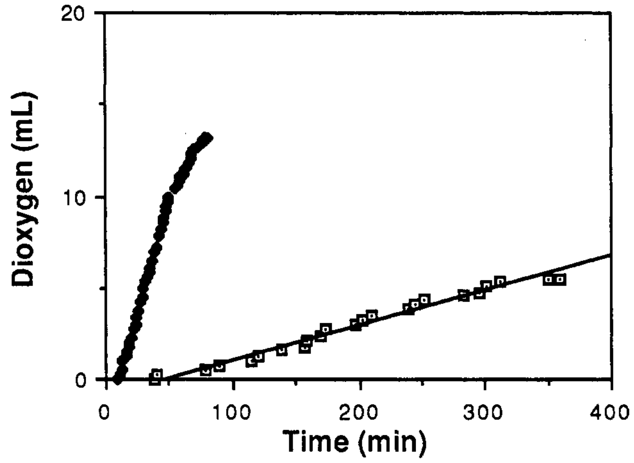
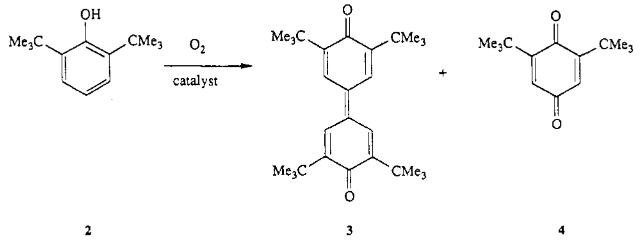


Figure 1. Consumption of dioxygen by 2,6-di-*tert*-butylphenol with soluble CoPcTs catalyst (□, experiment 23, Table II) and with latex catalyst C-9 (■, experiment 25, Table III). Consumption of 0.5 mol of O_2 per mol of **2** requires 15.2 mL of O_2.

phenol **2** to the reaction mixture. Addition of solid **2** to a mixture of catalyst in water at 70 °C gave fine droplets of melted **2** dispersed in the water. Addition of **2** dissolved in methanol gave droplets containing **2** dispersed in 0.1 volume fraction methanol in water. Some reaction mixtures were stirred rapidly with a magnetic bar. Others were shaken with a platform shaker having an amplitude of 2.5 cm and a frequency of about 1 s^{-1}. Results in Table II show that the colloidal catalyst in water is ten times as active as soluble CoPcTs under stirred conditions (experiments 6 and 7), that 0.1 volume fraction methanol enhances the rate of oxidation by factors of two (experiments 1 and 3) to eight (experiments 7 and 8), and that shaking gives faster rates than stirring with latex catalyst (experiments 6 and 10) but not with soluble catalyst (experiments 8 and 23). These results indicate that the rates of oxidation are partly limited by mass transport phenomena, at least in absence of methanol and with magnetic stirring.



Data in Table III shows the pH (experiments 11, 14, 16, 18, and 20) and temperature (experiments 11, 13, 14, and 15) dependence of the autoxidations of **2** with colloidal catalyst C-1. We conclude from increased oxidation rates

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[6] Diphenoquinone **3** was isolated from reaction mixtures and identified from its mp and IR, ^1H NMR, and ^{13}C NMR spectra. Products **3** and **4**, analyzed by GC, accounted for between 90% and 102% (±2% from duplicate determinations) of the starting 2,6-di-*tert*-butylphenol in all experiments of Tables II and III. No other products were detected by GC.

with increasing pH in the 7–10 range that the phenoxide anion is the likely reactive species. The activities of catalysts prepared from five different latexes are similar, showing 77–92% oxidation of **2** under identical conditions (experiments 14, 21, 22, 24, and 25).

Gas buret measurements of consumption of dioxygen as the reactions proceed are shown in Figure 1. After an induction period the rate of dioxygen consumption is linear with time to about 70% conversion of the phenol **2** to diphenoquinone **3**. Therefore the rate law has a zero-order dependence on substrate concentration. We have not determined yet the kinetic order in dioxygen, but in one experiment (17, Table III) the rate of oxidation is slower under air than under oxygen at atmospheric pressure. The ratio of zero-order rate constants calculated from Figure 1 for oxidation by colloidal and soluble CoPcTs catalysts is 12. The higher activity of the colloidal catalyst is most likely due to one or two factors: (1) The organic polymer concentrates the neutral phenol **2** or the phenoxide ion near the active sites in the positively-charged colloid. (2) The insoluble polymer network reduces the extent of aggregation of CoPcTs, which is known to aggregate in water.[7,8] Thus in the polymer more of the CoPcTs may exist in a monomeric form with higher catalytic activity.

We are continuing our study of the kinetics of the oxidations with colloidal catalysts in water to improve our understanding of the processes and to prepare still more active catalysts.

Acknowledgment. We thank the U.S. Environmental Protection Agency for the support of Grant R812298-01-0 and Dr. Rama Chandran for helpful discussions and assistance.

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Received August 26, 1987