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Selective Autoxidation of Some Phenols Using Salcomines and Metal Phthalocyanines[1]

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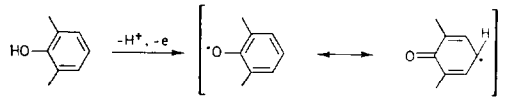
The autoxidation of 2,6-dialkyl substituted phenols has been studied using salcomines, the complexes derived from cobalt (II) and schiff bases of salicylaldehyde and ethylenediamine, and metal phthalocyanines (M-Pc) in *N,N'*-dimethylformamide. With salcomines and Co(II)-Pc, the predominant products are the corresponding 2,6-dialkylbenzoquinones along with some minor quantities of 3,3',5,5'-diphenoquinones. This is the first reported use of a phthalocyanine complex in selective oxidation of disubstituted phenols. Solvent and temperature affect the course of oxidation and the selectivity to products. With phthalocyanine complexes of Cu(II), Mn(II), or Fe(II), diphenoquinone compounds originating from the coupling of aroloxy radicals are favored over benzoquinones. Mechanistic aspects are proposed to explain the course of oxidation.

Salcomines also catalyze the oxidation of monoalkylphenols and phenol but require higher temperature and more severe conditions. Co(II)-Pc, the most active of the phthalocyanine complexes tested, also catalyzes the oxidation of monoalkylphenols to a limited degree but does not affect phenol itself.

INTRODUCTION

The catalytic oxidation of hindered phenols has been studied rather extensively during the last several years. A large number of oxidizing agents have been used with different phenols (*1–3*). A radical mechanism involving the transfer of one electron from phenol to an oxidant resulting in the formation of a phenoxy radical has almost always been postulated (*3, 4*). This can be explained by the resonance between the structures shown. After the initial step, a variety of products can be formed as



the resultant phenoxy radical undergoes a complex series of reactions. The literature (*5–8*) is extensive on autoxidation of phenols catalyzed by transition metal complexes. The catalyst is generally a cobalt-, manganese-, or copper-amine compound and the products of oxidation reactions are their corresponding benzoquinones, diphenoquinones, polyphenylene ethers or combination of them. The selectivity to a particular product depends upon the catalyst, solvent, and the phenolic compound.

The oxidation of 2,6-disubstituted phenols catalyzed by salcomine [bis(salicylaldehyde)-ethylenediamine-cobalt(II)] and its derivatives is of interest because it affords a system in which the relationship between the states of oxygen adducts and the mode of oxidation can be studied (*7–11*). It is well known that salcomine, pyridine-salcomine, and their derivatives are

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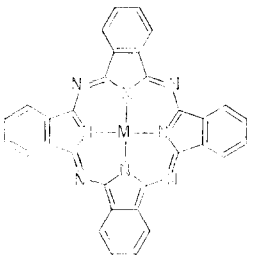
oxygen carriers (*12*) and act as homogeneous catalysts for the oxidation of phenols with molecular oxygen in organic media. The main product in many cases is the corresponding *p*-benzoquinone. This indicates the selective introduction of oxygen at *para*-position occurs and side reactions such as those leading to derivatives of diphenyl originating from coupling reactions are less important.

The use of metal-phthalocyanines in oxidation reactions has been known for a long time (*13*); however, only recently have they been studied as catalysts in autoxidation of phenols (*11*). The catalytic activity of iron(II)-phthalocyanine in autoxidation of di- and tri-*t*-butylphenols to their radical coupled dimeric products has been studied by Tada and Katsu (*11*) because of its structural similarity to a biologically important hemin, the oxygen carried in blood. They also tested other metal-phthalocyanines containing Co(II), Mn(II), Ni(II), and Cu(II) but found them to be inactive in autoxidation of phenolic compounds.



Metal (II) - Phthalocyanine

In this paper it is our objective to show that dialkylphenols can be oxidized selectively to their dialkylbenzoquinones by salcomine catalysts at a low concentration in *N*,*N*′-dimethylformamide (DMF), a polar solvent having the ability to function as a ligand. The data will show that DMF is an effective and more selective solvent. In this solvent, we also studied the oxidation of less reactive monoalkylphenols and phenol and found that corresponding *p*-quinones are formed under proper reaction conditions. We also wish to report for the first time the use of Co(II)- and Cu(II)-phthalocyanines for selective oxidation of dialkylphenols to their dialkylbenzoquinones in DMF.

EXPERIMENTAL

Materials

Phenol (Eastman and Fisher), 2-*t*-butylphenol (Aldrich), 2,6-dimethylphenol (Aldrich) and 2,6-di-*t*-butylphenol (Ethyl) were used without further purification. Reagent grade solvents used were *N*,*N*′-dimethylformamide (Aldrich), dimethylsulfoxide (MCB), 1-methyl-2-pyrrolidinone (Aldrich) and hexamethylphosphoramide (Aldrich). Cobalt(II), copper(II), manganese (II), and iron(II) phthalocyanines were purchased from Eastman. Pyr-salcomine [bis(salicylaldehyde)ethylenediamine-cobalt(II)-monopyridine] was prepared according to the procedure of Bails and Calvin (*12*). Salcomine [bis(salicylaldehyde)-ethylenediamine-cobalt(II)] (*14*) was prepared for equimolar quantities of cobaltous acetate and schiff base in DMF.

Oxidation Procedure

In a typical experiment, pyr-slacomine or metal-phthalocyanine (1.0 g or less) was dissolved or suspended in 10–20 ml of DMF and the solution of phenolic compound in 25–100 ml of DMF was added to the catalyst. In a pressure reaction, a 500 ml pressure resistant bottle containing catalyst, phenolic compound, and DMF was clamped in a Parr apparatus, evacuated and pressured with 50–80 psig of oxygen. The oxidation was started at a desired temperature with the bottle being rocked continuously so as to cause a good mixing of reactants. The oxygen pressure was recorded periodically and readjusted when a drop of 15–20 psig had occurred. The reaction was terminated after a specified length of time or when further pressure drop became negligible. When oxidation was carried out at atmo-

TABLE 1

OXIDATION OF 2,6-DIALKYLPHENOLS BY SALCOMINE[a]

Expt	Phenol	Catalyst (%)[b]	Solvent	O_2 (psig)	Temp. (°C)	Time (hr)	Phenol conv. (%)	Selectivity (%)			BQ/DPQ[c]
								BQ	DPQ	Others[d]	
1	2,6-Di-*t*-butylphenol	Pyr-salcomine (5)	Methanol	55	20	1.0	98	93.2	6.8	—	13.7
2	2,6-Di-*t*-butylphenol	Pyr-salcomine (2)	DMF	55	24–50	0.5	100	99.0	1.0	—	99.0
3	2,6-Di-*t*-butylphenol	Pyr-salcomine (1)	DMF	55	20–46	0.75	96	98.8	1.2	—	81.8
4	2,6-Di-*t*-butylphenol	Pyr-salcomine (1)	DMF	atm	20–35	20.0	89	88.0	4.5	7.5	19.6
5	2,6-Di-*t*-butylphenol	pyr-salcomine (0.5)	DMF	54	20–35	3.0	92	88.2	10.6	1.2	8.3
6	2,6-Di-*t*-butylphenol	Pyr-salcomine (0.5)	DMF	54	60–65[e]	1.0	99	46.5	54.5	—	0.85
7	2,6-Di-*t*-butylphenol	Pyr-salcomine (1)	DMSO	55	15–40	2.5	49	84.0	1.5	14.5	56.0
8	2,6-Di-*t*-butylphenol	Pyr-salcomine (1)	1-Me-2-Py[f]	55	20–40	2.5	75	95.2	4.8	—	19.8
9	2,6-Di-*t*-butylphenol	Salcomine (1)	DMF	55	20–45	0.5	100	99.5	0.5	—	199.0
10	2,6-Dimethylphenol	Pyr-salcomine (1)	DMF	55	25–45	2.5	95	98.0	2.0	—	49.0
11	2,6-Dimethylphenol	Salcomine (1)	DMF	55	20–45	0.75	100	~100.0	—	—	—
12	2,6-Di-*t*-butylphenol	Mn(II)-Salen (5)	DMF	54	22–30	<0.2	100	<0.1	99.9	—	—

[a] Co(II)-Salen. Salen is [bis(salicylaldehyde)ethylenediamine].
[b] Mole %/mole of phenol.
[c] BQ and DPQ are the corresponding 2,6-dialkylbenzoquinone and 3,3′,5,5′-tetraalkyldiphenoquinone, respectively.
[d] Unidentified heavies.
[e] Heat applied. In other experiments, rise in temperature is due to exotherm of reaction.
[f] 1-Methyl-2-pyrrolidinone.

TABLE 2

OXIDATION OF MONOALKYL AND UNSUBSTITUTED PHENOLS BY PYR-SALCOMINE[a]

Expt	Phenol	Pyr-salcomine[b] (%)	Solvent	O_2 (psig)	Temp. (°C)	Time (hr)	Phenol conv. (%)	BQ Sel. (%)[f]
1	2-*t*:Butylphenol	3.0	DMF	54	20–35	1.5	46	96
2	2-*t*-Butylphenol	3.0	Methanol	50	22–38	20.0[g]	33	68
3	2-*t*-Butylphenol	3.0	1-Me-2-Py[c]	54	20–35	2.0	40.4	98
4	2-*t*-Butylphenol	3.0	HMPA[d]	54	20–35	2.0	10.2	~100
5	2-*t*-Butylphenol	3.0	DMSO	54	20–35	2.0	35.0	98
6	2-*t*-Butylphenol	3.0	DMF	50–60	72–74[e]	2.0	64.8	~100
7	2-*t*-Butylphenol	3.0	DMF	atm	80[e]	5.0	49.0	99
8	2-*t*-Butylphenol	3.0	DMF	atm	100–105[e]	5.0	68.1	80
						8.0	75.1	65
9	2-Methylphenol	2.5	Methanol	54	22–40	22.0[g]	10.2	77
10	2-Methylphenol	3.0	DMF	54	22–40	3.0	26.5	92
11	Phenol	10.0	Methanol	54	20–75	2.5	10.5	~100
12	Phenol	6.0	DMF	90	68–73[e]	2.0	23.1	~100

[a] Co(II)-salen with pyridine.
[b] Mole %/mole of phenol.
[c] 1-Methyl-2-pyrrolidinone.
[d] Hexamethylphosphoramide.
[e] Heat applied. In other cases, rise in temperature is due to exotherm of reaction.
[f] Corresponding benzoquinone.
[g] Reaction left for overnight.

spheric pressure, oxygen was bubbled through the reaction mixture, with stirring, at a desired temperature in a 250 ml flask.

Data pertaining to temperature, reaction time, catalyst concentration, solvent, conversion of phenolic compound, and selectivity to oxidation products are recorded in Tables 1, 2 and 4. The oxidation products are the corresponding benzoquinone and/or diphenoquinone and some unidentified heavies.

VPC Analysis

The analyses of reaction products were carried out with a Hewlett–Packard F & M 700 thermal conductivity chromatograph using two 6 ft × $\frac{1}{8}$ in. 10% UC-W98 columns at 130–160°. Heavies were analyzed by programming the GC unit at 10°/min from 130–160° to 250–265° and then holding the final temperature constant. The internal standards employed were *N*-dodecane and 2,6-di-*t*-butyl-4-methylphenol in 2,6-di-*t*-butylphenol oxidation products, 2,6-di-*t*-butyl-*p*-benzoquinone in 2-*t*-butylphenol oxidation runs and 2-*t*-butyl-*p*-benzoquinone in phenol oxidation products analyses.

Since both 2,6-dimethylphenol and the

TABLE 3

RELATIVE OXIDATION POTENTIALS OF SELECTED PHENOLS

Phenol	$E_{\frac{1}{2}}$ (*E* in millivolts) (*4*)	$(OP)_0$ (*18*)
Phenol	+1004	0.92
2-Methyl	+ 556	0.85
4-Methyl	+ 543	0.84
2-*t*-Butyl	+ 552	0.81
4-*t*-Butyl	+ 578	0.84
2,6-Dimethyl	—	0.64
2,6-Di-*t*-butyl	—	0.71
2,4,6-Trimethyl	—	0.64
2,4,6-Tri-*t*-butyl	−59	0.69

TABLE 4

OXIDATION OF PHENOLS BY METAL-PHTHALOCYANINES

Expt	Phenol	Catalyst (%)[a]	Solvent	O_2 (psig)	Temp. (°C)	Time (hr)	Phenol covn. (%)	Selectivity (%)		
								BQ[c]	DPQ[d]	Others[f]
1	2,6-Di-*t*-butylphenol	Co(II)-Pc[b] (5)	DMF	50	22–27	3.0	100	73	26	1
2	2,6-Di-*t*-butylphenol	Co(II)-Pc (5)	DMF	50–60	48–50[e]	1.5	100	51	49	—
3	2,6-Di-*t*-butylphenol	Co(II)-Pc (5)	DMF	50–60	68–70[e]	1.3	100	33	67	—
4	2,6-Di-*t*-butylphenol	Co(II)-Pc (5)	DMF	90	68–70[e]	1.3	100	33	67	—
5	2,6-Di-*t*-butylphenol	Co(II)-Pc (5)	DMSO	55	22–30	3.0	22	25	54	21
6	2,6-Di-*t*-butylphenol	Co(II)-Pc (7)	Methanol	55	22–32	6.0	16.4	51	49	—
7	2,6-Dimethylphenol	Co(II)-Pc (5)	DMF	53	22–28	3.0	96	100	—	—
						5.0	100	100	—	—
8	2,6-Di-*t*-butylphenol	Cu(II)-Pc (5)	DMF	55	22–27	3.0	10.5	41	59	—
9	2,6-Di-*t*-butylphenol	Cu(II)-Pc (5)	DMF	55	71–73[e]	2.0	100	12	88	—
10	2,6-Di-*t*-butylphenol	Mn(II)-Pc (4)	DMF	52	20–30	3.0	95	0.5	99.5	—
11	2,6-Di-*t*-butylphenol	Fe(II)-Pc (4)	DMF	55	23–30	2.0	18	22	78	—
12	2-*t*-Butylphenol	Co(II)-Pc (5)	DMF	55–60	75–80[e]	3.0	17	12	—	—
13	Phenol	Co(II)-Pc (4)	DMF	90	72–75[e]	2.0	—	—	—	—

[a] Mole %/mole of phenol.
[b] Pc = phthalocyanine.
[c] Corresponding benzoquinone.
[d] Corresponding diphenoquinone.
[e] Heat applied.
[f] Unidentified heavies.

resultant benzoquinone have very close retention values, the reaction mixture was reduced with Zn–HCl and 2,6-dimethylhydroquinone was analyzed by gas chromatography.

Recovery of Products

2,6-Dimethylbenzoquinone was isolated in 95% of theoretical amount by concentrating the filtered reaction mixture to near dryness and extracting it with petroleum ether. After removal of solvent by evaporation, the material was dried in a vacuum oven, mp 70–72°, lit. 71–73° (*15*).

In the oxidation of 2,6-di-*t*-butylphenol with salcomine catalyst, the reaction mixture was filtered to remove insoluble 3,3′, 5,5′-tetra-tert-butyldiphenoquinone. It was recrystallized from hot methanol, mp. 243–244°, lit. 246° (*1*). With metal phthalocyanine as the catalyst, it is also filtered off. The diphenoquinone is separated from phthalocyanine compound by extracting it with petroleum ether. 2,6-Di-*t*-butylbenzoquinone was also isolated by concentrating the DMF filtrate, after removal of diphenoquinone, to near dryness and extracting it with petroleum ether or methanol. Upon removal of solvent by evaporation, the residue was dissolved in acetic acid; 2,6-di-*t*-butylbenzoquinone crystallized on addition of some water to hot acetic acid solution, mp 65–66°, lit. 67° (*1*). 2,6-Di-*t*-butylbenzoquinone can also be recovered by precipitating it out from filtrate by slow addition of some cold water.

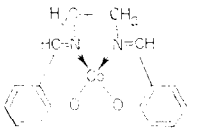
No efforts were made to isolate quinones from phenol and monoalkylphenol oxidation runs.

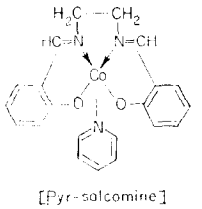
Infrared Spectra

The identity of 2,6-di-*t*-butylbenzoquinone, 2,6-dimethylbenzoquinone, and 3,3′, 5,5′-tetra-tert-butyldiphenoquinone were confirmed by infrared spectroscopy with a Perkin–Elmer 137 recording spectrophotometer.

RESULTS AND DISCUSSION

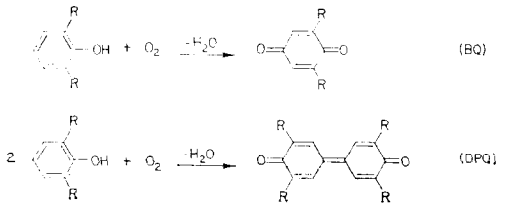
Slacomine compounds, the complexes of bis(salicylaldehyde)ethylenediamine containing cobalt(II) as the central metal ion, are known oxygen carriers and combine reversibly with molecular oxygen. The following two, salcomine and pyr-salcomine, were used in this study.





The salcomines are related to the natural oxygen carriers, hemoglobin and hemocyanin (*12*, *16*) and used as model compounds in the study of reversible oxygenation processes. In addition, the catalytic activity of oxygen carriers is an area of considerable interest (*7–11*).

Several investigators have reported the use of salcomines for the oxidation of 2,6-disubstituted phenols in methanol, chloroform, and benzene (*7–11*). The products are predominantly the corresponding benzoquinones (BQ) and/or 3,3′,5,5′-tetra-substituted diphenoquinones (DPQ) as shown below.



We, on the other hand, have found that when dimethylformamide (DMF) is employed as solvent, the oxidation process requires much less catalyst and a shorter time and is specific for BQ. Thus, from the data summarized in Table 1, it can be concluded that DMF is the most effective and efficient solvent for oxidation of dialkylphenol to its corresponding BQ.

Examination of Table 1 shows that oxygen pressure of about 50 psig is judged to be near optimum to obtain high yield of dialkylbenzoquinones. At atmospheric pressure, the reaction rate and BQ/DPQ ratio are lowered (Expt 3 vs 4). Generally, high BQ yields are favored by high catalyst concentration (Expt 2 vs 3), lower reaction temperature, and shorter reaction time (Expts 5 and 6). This indicates that the rate of aroloxy coupling increases with temperature and reaction time. If reaction time is unusually long, some unidentified heavies other than DPQ are also formed (Expt 4). It is of interest to note that the oxidation in DMF is more efficient than in DMSO at the same catalyst level (Expt 3 vs 7). Since both DMF and DMSO are excellent coordinating solvents and act as ligands (L) in the formation of complexes of type slacomine$(L)_2$ (*14*), the poor performance is attributed to some properties other than the coordination ability. On the basis of the time required to obtain high conversions, the salcomine appears to be somewhat more active than the pyr-salcomine (Expt 9 vs 3 and 11 vs 10). The rate curves of oxygen consumption by salcomine and pyr-salcomine illustrated in Fig. 1 indicate that the rate of oxygen absorption is higher for the salcomine than for the pyr-salcomine catalyst in the oxidation of dialkylsubstituted phenols.

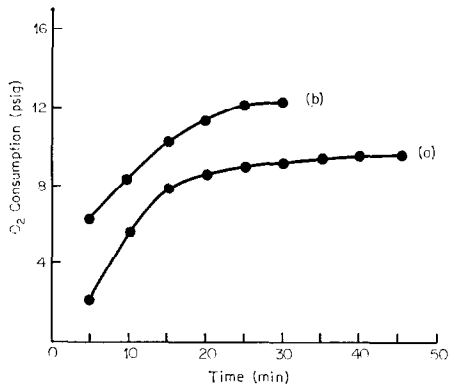


FIG. 1. Rates of oxygen consumption by (a) pyr-salcomine and (b) salcomine for oxidation of 2,6-di-*t*-butylphenol.

Mn(II)-salen [bis(salicylaldehyde)ethylenediamine-manganese(II)], previously found to be inactive (*8*), also oxidizes 2,6-di-*t*-butylphenol to 3,3′,5,5′-tetra-tert-butyldiphenoquinone (Table 1, Expt 12).

The oxidation of monoalkylphenol (*10*) and phenol (*8*), previously unsuccessful with salcomine catalysts, has also been accomplished in fairly good yields in DMF and other solvents under proper reaction conditions. These results are recorded in Table 2. As can be seen, DMF is again the best solvent for 2-*t*-butylphenol oxidation reactions (Expt 1 vs Expts 2–5). Under optimum oxygen pressure of 50–60 psig and temperature in the range of 70–80°, a good yield of 2-*t*-butyl-*p*-benzoquinone is obtained (Expt 6). Heavies start to build up with further increase in temperature and prolonged reaction time (Expt 8). The oxidation of phenol, first studied by Hutchings (*17*), is even more difficult than that of monoalkylphenol and requires still higher catalyst concentration. The selectivity to *p*-benzoquinone is nearly quantitative at low conversion (Expts 11–12). Dimethylformamide is again superior to methanol as the solvent.

The oxidation potentials of phenols are reported in the literature (*4*, *18*) and some are listed in Table 3. The oxidation potential of phenol decreases as the number of alkyl substituents on 2-, 4-, and 6-positions of the aromatic ring increases; also, steric as well as electron donating inductive effects of these alkyl groups cause changes in the oxidation potentials. Thus, the monoalkylphenols and phenol have higher oxidation potential than 2,6-dialkylphenols and, consequently, require more energy to generate aroloxy radicals. The more vigorous condition for oxidation results in an acceleratively faster rate of catalyst deactivation.

As a result, lower conversions are found with 2-alkylphenol and phenol.

Previous study has found that Co(II), Cu(II) and Mn(II) phthalocyanines are all nearly inactive for oxidation of 2,6-di-*t*-butylphenol (*11*). It can be seen from the data summarized in Table 4, that in DMF, Co(II)-Pc (hereafter, Pc for phthalocyanine) is an effective catalyst for selective oxidation of 2,6-dialkylphenols to their corresponding benzoquinones (BQ) (Expts 1 and 7). As the reaction temperature is increased, more diphenoquinone (DPQ) is formed, indicating that the rate of coupling of phenoxy radicals at *para*-position is favored as the temperature rises (Expts 1–3). The ratio of BQ/DPQ is thus temperature dependent (Fig. 2).

The oxidation of 2,6-di-*t*-butylphenol by Cu(II)-Pc and Fe(II)-Pc results in a low conversion and some benzoquinone (Expts 8 and 11). Fe(II)-Pc has been reported to catalyze the oxidation of 2,6-di-*t*-butylphenol exclusively to 3,3′,5,5′-tetratert-butyldiphenoquinone when a much greater reaction period is employed (*11*). Cu(II)-Pc requires a higher temperature for the reaction to go to completion and diphenoquinone, the coupling product, is favored (Expt 9 vs 8). Mn(II)-Pc catalyzed reaction also yields nearly all diphenoquinone (Expt 10).

Co(II)-Pc, the most active of the metal phthalocyanines, is inactive for the oxidation of phenol (Expt 13) but will catalyze

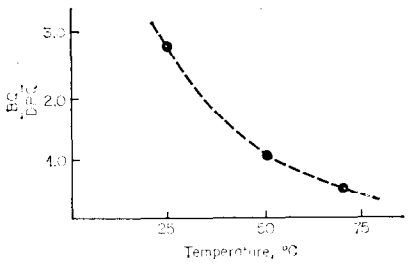


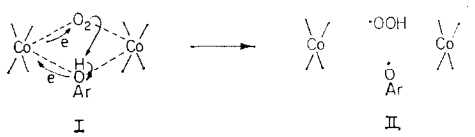
FIG. 2. A plot of BQ/DPQ vs temperature for the oxidation of 2,6-di-*t*-butylphenol with Co(II)-Pc.

the oxidation of monoalkylphenol such as 2-*t*-butylphenol to a small extent at higher temperature (Expt 12). This is, then, again due to higher oxidation potentials of monoalkylphenol and phenol.

Mechanism of Phenol Oxidation

Some theories have been proposed for salcomine (*7*) and metal phthalocyanine (*11*) catalyzed phenol oxidation.

a. Salcomine catalysts. Van Dort and Geursen (*7*) suggest that the ortho disubstituted phenol-oxygen bridged salcomine intermediates, shown below, are formed. Their proposal of intermediate I is not adequately supported and in fact can be questioned since coordination of hindered phenol such as 2,6-di-*t*-butylphenol and salcomine seems unlikely.



Another weakness of this mechanism is that it fails to account for specificity of attack at the 4-position when the 6-position is unsubstituted.

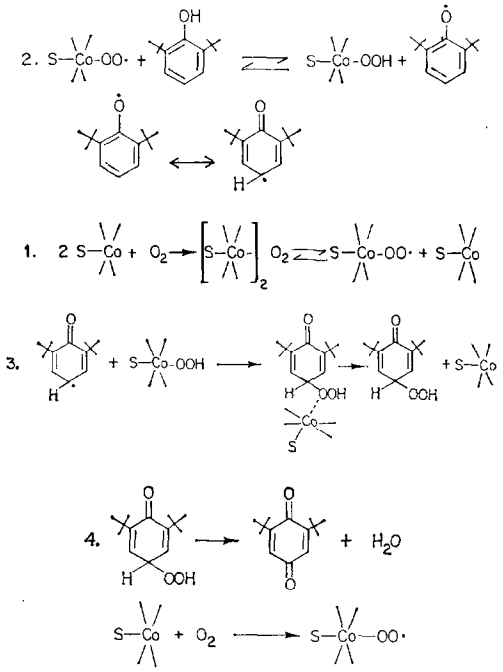
We propose an alternate four-step mechanism in which the first step is the formation of oxygen bridged salcomine or pyr-salcomine dimer, which then equilibrates with its monomeric form. Floriani and Calderazo (*14*) have reported that in a

$$2\ \text{Pyr-salcomine} + O_2 \rightleftarrows (\text{Pyr-salcomine})_2O_2$$

$$(\text{Pyr-salcomine})_2O_2 \rightleftarrows \text{Pyr-salcomine} + \text{Pyr-salcomine}:O_2$$

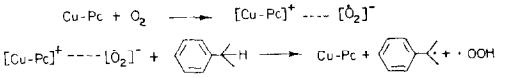
solvent such as toluene, the equilibrium is shifted toward a less soluble (Pyr-salcomine)$_2O_2$. However, in a polar solvent such as DMF, the equilibrium concentration of monomeric pyr-salcomine:O_2 adduct is much higher.

We believe that, in DMF(S), the mechanism consists of pyr-salcomine:O_2 or salcomine:O_2 adduct abstracting hydrogen from a hindered phenol such as 2,6-di-*t*-butylphenol; the resultant aroloxy radical, then, interacting with the hydroperoxide ligand of the catalyst giving rise to a hydroperoxide intermediate that rearranges to benzoquinone compound.



The arguments advanced in the above-postulated mechanism also explain the apparent specificity of the reaction at 4-position when 6-position is open as in case of 2-alkylphenol. If the complex-hydroperoxide were to be dissociated prior to attack on aroloxy radical, some formation of ortho-quinone should result. The specificity is believed to be due to the bulkiness of salcomine-hydroperoxide, which preferentially attacked the 4-position.

b. Phthalocyanine catalysts. The phthalocyanines of Co(II), Cu(II), or Fe(II) are not known to function as oxygen carriers. This would, then, tend to suggest that a one-electron transfer oxidation process like that proposed by Tada and Katsu (*11*) is operating. However, for cumene oxidation by Cu(II)-Pc, Kropf (*19*) has postulated the formation of copper-phthalocyanine-oxygen intermediate that reacts with cumene, giving rise to cumyl radical as shown below.



In a like manner, we suggest that both cobalt and copper phthalocyanines form oxygen intermediates that react with phenol, forming aroloxy and hydroperoxide radicals. Thus, the oxidation of dialkylphenols by Co(II)-Pc, yielding the corresponding benzoquinones, occurs by a pathway similar to that for the salcomine process.

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