EFFECT OF STRUCTURE OF METAL SCHIFF BASE COMPLEXES ON THE OXIDATION OF 2,6-DI-TERT-BUTYLPHENOL*

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ABSTRACT

2,6-Di-tert-butylphenol (2,6-DTBP) was oxidized under homogeneous conditions with various metal Schiff base complexes, capable of activating molecular oxygen through dioxygen binding. Different Schiff base complexes were prepared by varying the ligand (Salen I, Saloph II, SAP III, SalMe IV, Sal n-Bu V, Salcea VI, SalMDPT VII); central metal atom (Co, Mn, Ni) and axial donor base (pyridine, 4-dimethylaminopyridine, quinoline and imidazole). Selectivity towards 2,6-ditert-butyl-1,4-benzoquinone formation decreased in the order Co(SalMDPT) > Co(Salen)Py > Co(Saloph)Py. In constrast, Co(SalMe)Py, Co(Sal n-Bu)Py, Co(Salcea) and Co(SAP)Py gave rise to 3,3'5,5'-tetra-tert-butyl-4,4'- diphenoquinone only. Whereas Co(Salen) gave benzoquinone (58%) and diphenoquinone (39%), Mn(Salen) gave exclusively diphenoquinone (93%) and Ni(Salen) showed no catalytic activity. The nature of axial donor also had a marked influence on the selectivity of oxidation products. The nature of products appear to be indicative of the mechanism of oxidation of metal Schiff base- dioxygen complexes.

INTRODUCTION

Natural oxygen carries like hemoglobin, hermerythrin and hemocyanins activate molecular oxygen and perform selective biological oxidations. Synthetic analogs can also be used for practical catalytic oxidation of organic substrates to oxygenated derivatives under mild conditions using abundantly available oxidant, oxygen. Such conversions continue to pose a formidable challenge to the synthetic organic chemists. Catalytic activation and transfer of molecular oxygen are more efficient than stoichiometric oxidation using conventional oxidants.

Oxidation of hindered phenols using molecular oxygen and cobalt Schiff base complex, Cobalt (II) bis(salicylidene) ethylenediamine, Co(Salen) was first reported by van Dort and Geursen (1) Later Vogt et.al. (2) used Co(Salen), Co(Salen)Py and oxygenated Co(Salen) for the oxidation of various 2,6-disubstituted phenols. Fullerton and Ahern (3) used Co(4-OH Salen) for oxidation of 2,6-DTBP and found it superior to Co(Salen). The effect of introduction of electron withdrawing substituents like F, No_2 in the aromatic ring of Co(Salen) on oxidation of 2,6-disubstituted phenol was studied by

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Tomaja et al. (4). Basolo and coworkers (5) studied the effect of different inplane ligands in cobalt (II) complexes on its ability as an oxygen carrier. They showed that electron withdrawing substituents in the ligand make a poor oxygen carrier. Walter (6) has reported the effect of changing axial donor base in cobalt (II) porphyrin complexes on their oxygen carrying capability. In the course of systematic study on the metal catalysed oxygen activation and transfer to organic substrates, we have investigated the effect of the nature of metal Schiff base complexes on the oxidation of 2,6-di-tert-butyphenol. The present paper reports the results of this study.

EXPERIMENTAL

Materials

2,6-Di-tert-butylphenol (Aldrich) was used as supplied. Methanol, chloroform, benzene and DMF used were of high purity grade. Metal Schiff base complexes were prepared by using known methods (7-9) and satisfactory elemental analysis were obtained. High purity oxygen gas from M/s Indian Oxygen Ltd., was used. IR was recorded on Beckman 4220 spectrophotometer and C,H,N elemental analysis was carried out on Coleman analyser.

Apparatus and procedure

2,6-Di-tert-butylphenol (10.3 g, 50 m mol) was dissolved in solvent (500 ml) and placed in tubular glass reactor. Metal Schiff base complex (2.5 m.mol) was added and oxygen was bubbled through the solution. The outgoing oxygen was throttled in such a way as to generate 1 atm. pressure inside the reactor. After 6 hr, the pressure was released and solvent removed by distillation. The residue obtained was triturated with 400 ml of warm petroleum ether (40-60°C) and filtered to remove the catalyst residues. The filtrate was evaporated and the resulting mass was subjected to column chromatography over silica gel. Elution with petroleum ether gave 2,6-di-tert-butyl-1,4-benzoquinone. Further elution with petroleum ether-benzene (95:5) gave 3,3'5,5'-tetra-tert-butyl-4,4'-diphenoquinone. Yields refer to pure isolated materials. The results are shown in tables 1 to 3.

2,6-Di-tert-butyl-1,4-benzoquinone was crystallized from methanol to give orange needles, mp 64-65°C (lit.(10) 66°C) IR (KBr) 1640 cm^{-1} (Ketone).3,3',5,5'-Tetra-tert-butyl-4,4- diphenoquinone was obtained as dark brown needles from methanol, m.p. 240-244°C (lit. (10) 246°C), IR (KBr) 1625 cm^{-1} (Ketone).

SULTS AND DISCUSSION

Oxidation of 2,6-DTBP catalyzed by different Schiff base metal chelates was carried out under identical reaction conditions (25°C, 1 kg/cm^2 oxygen pressure, 6 hr, catalyst to substrate ratio 1:20). Oxidation of 2,6-DTBP with Co(Salen)Py (I) in methanol gave 90% 2,6-di-tert-butyl-1,4-benzoquinone (BQ) in isolated yield. No other product could be detected indicating the high selectivity of this catalyst. The formation of benzoquinone can be understood based on the intermediacy of a phenoxy radical and its interaction with monomeric metal-dioxygen adduct (11). Isolation of intermediate (peroxy-p-quinolato) cobalt (III) complex in high yield by Nishinaga et al. (12) further confirmed this mechanism. The selectivity of Co(Salen)Py towards oxidation of 2,6-DTBP led to systematically examine the effect of ligand, central metal ion and axial donor in metal Schiff base complex on selectivity and reactivity towards oxidation.

Effect of Ligands

Co(Salen)Py(I), Co(Saloph)Py(II), Co(SAP)Py(III), Co(SalMe)Py(IV), Co(Sal n-Bu)Py(V), Co(Salcea)(VI) and Co(SalMDPT)(VII) figure 1 all cobalt (II) Schiff base complexes differing in the nature of amine were used for oxidation of 2,6-DTBP under identical conditions. The results are shown in table 1. The nature of the amine in the Schiff

TABLE 1

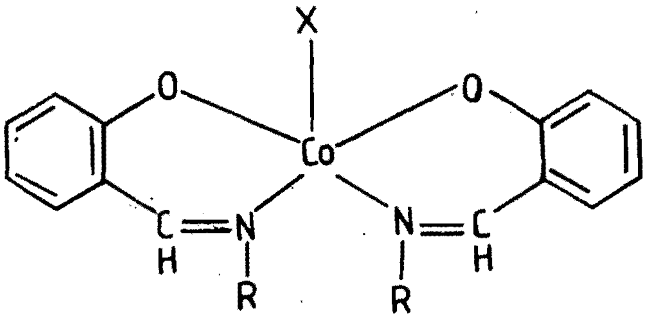
Oxidation of 2,6-DTBP with cobalt complexes containing various Schiff base ligands[a]

Catalyst	Products % yield	
	BQ	DPQ
Co(Salen)Py (I)	89.0	-
Co(Saloph)Py (II)	63.0	25.2
Co(SAP)Py[b] (III)	-	25.2
Co(SalMe)Py (IV)	-	92.6
Co(Sal n-Bu)Py (V)	-	92.6
Co(Salcea)[c] (VI)	-	98.0
Co(SalMDPT) (VII)	96.0	2.4

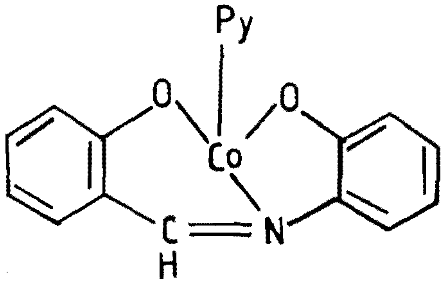
[a] Conditions: 2,6-DTBP (50 m mol), catalyst (2.5 m mol), solvent methanol (500 ml), temperature 25°C, time 6 hr, oxygen pressure 1 kg/cm^2

[b] DMF was used as solvent

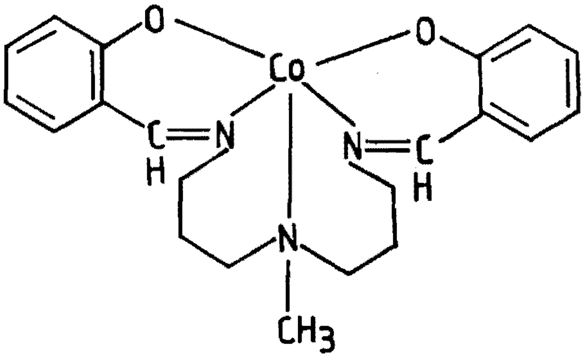
[c] Rest starting material was recovered



Co (Salen)	RR = $CH_2—CH_2$	X = Nil
Co(Salen)Py (I)	RR = $CH_2—CH_2$	X = Pyridine, quinoline, imidazole, 4-dimethylaminopyridine,
Co(Saloph) Py (II)	RR = o — C_6H_4	X = Pyridine
Co(SalMe) Py (IV)	R = Me	X = Pyridine
Co(Sal n-Bu) Py (V)	R = n-butyl	X = Pyridine
Co(Salcea) (VI)	R = CH_2CH_2CN	X = Nil



Co (SAP) Py (III)



Co (SalMDPT) (VII)

Fig. 1

e results in different geometries around metal ion and causes variation in the redox potential of the central metal ion. Co(Salen)Py has a tetragonal pyramidal geometry (13) and catalyses oxidation of 2,6-DTBP to give benzoquinone (89%), whereas Co(Saloph)Py with a similar geometry gives a mixture of benzoquinone (63%) and 3,3',5,5'-tetra-tert-butyl-4,4'- diphenoquinone, DPQ (25%). The fact that Co(Saloph)Py gave up to 25% yield of diphenoquinone indicates that inspite of having a similar geometry it is not as good an oxygen carrier as Co(Salen)Py. The presence of an aromatic ring in Co(Saloph)Py acts as an electron sink which presumably lowers the electron density at the metal atom by delocalization, reducing its oxygen carrying capacity (5). Square planar Co(SAP)Py (14), when used for oxidation of 2,6-DTBP gave only diphenoquinone (25%). Although no information is available on the effect of metal Shiff base complex geometry on its oxygen carrying ability. Our results seem to indicate that Co(SAP)Py having a square planar geometry is a poorer oxygen carrier. Oxidation using Co(SalMe)Py, Co(Sal n-Bu)Py and Co(Salcea) as catalysts resulted in exclusive formation of diphenoquinone, a phenoxy radical coupling product in high yields. In contrast to our present observation, two patent reports describe use of Co(SAP)Py (15) and Co(SalMe)Py (16) in the presence of molecular oxygen for the conversion of alkyl phenols to corresponding 1,4-benzoquinones.

Effect of Metal Ions

The effect of central metal ion (Co, Mn, Ni) on oxidation of 2,6-DTBP using Schiff base complexes was studied in methanol as solvent. In these cases complexes had no axial donor. The results are shown in table 2.

TABLE 2

Effect of metal ion in Schiff base chelates on oxidation of 2,6-DTBP[a]

Catalyst	Product Yield %	
	BQ	DPQ
Co(Salen)	57.7	38.7
Mn(Salen)	-	92.9
Ni(Salen)[b]	-	-
Fe(Salen)[c]	-	65.0

[a] Conditions same as in table 1

[b] Starting material recovered

[c] Conditions (19)

Co(Salen) gave benzoquinone (58%) and diphenoquinone (39%), whereas Mn(S gave exclusively diphenoquinone in 39% yield. Mn(Salen) is known (17) to form polymeric μ-oxo complex $[(Salen)Mn\text{-}O\text{-}]_n$ with dioxygen in an irreversible manner and does not form monomeric metal dioxygen complex ($M\text{-}O_2$) required for quinone formation. Ni(Salen)) did not show any catalytic activity. Our results are in contradiction to that of Vogt et al. (2) who have reported that Mn(Salen), Ni(Salen), Cu(Salen) and Fe(Salen) when used as catalyst for oxidation of 2,6-dimethylphenol resulted in complete recovery of starting material and only Co(Salen) gave mixture of benzoquinone and diphenoquinone. Our observation, however, is in accordance with Mitsuo et al. (18) who have shown that catalytic oxidation of 2,6-dimethylphenol in presence of Fe(Salen) gave diphenoquinone in 65% yield.

Effect of Axial Ligands

The effect of various axial ligands such as pyridine, quinoline, imidazole and 4-dimethylaminopyridine in Co(Salen) were evaluated for the oxidation of 2,6-DTBP. A complex having intramolecular axial donor Co(SalMDPT), was also examined. The results are shown in table 3. Incorporation of pyridine in Co(Salen) increased its oxygen carrying capability and gave benzoquinone in 89% yield. In the absence of pyridine, benzoquinone was formed only in 58% yield and appreciable amount of diphenoquinone (39%) was also formed. Introduction of quinoline as axial ligand gave benzoquinone (86%) and diphenoquinone (5%). In general, a donor molecule complexed to central

TABLE 3

Effect of axial ligand in Co(Salen) on oxidation of 2,6-DTBP[a]

Catalyst	Products Yield %	
	BQ	DPQ
Co(Salen)	57.7	38.7
Co(Salen)Py	89.0	-
Co(Salen)Q	85.8	5.0
Co(Salen)DMAP[b]	100	-
Co(Salen)Im[b]	100	-
Co(SalMDPT)	96.0	2.4

Py = Pyridine, Q = Quinoline, DMAP = 4-Dimethylaminopyridine, Im = Imidazole

[a] Conditions as in table 1

[b] DMF was used as solvent

metal atom is known to enhance the reversible oxygen binding capacity of the chelate. In a related study (6) on dioxygen binding ability of cobalt porphyrin complexes with different 4-substituted pyridines as axial donors, it was found that oxygen carrying capacity increased with donor basicity. In agreement with this it is observed that when pyridine (pKa 5.22) was replaced with DMAP (pKa 9.70) as an axial ligand, conversion and selectivity towards benzoquinone increased (100%) (table 3). Imidazole is less basic (pKa 6.65) than DMAP; however it was as effective presumably because of its better π donor capacity. Cobalt complex with intramolecular axial donor Co(SalMDPT), when used for oxidation of 2,6-DTBP under identical conditions gave benzoquinone (96%) and diphenoquinone (2.5%).

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