

Oxidation of 2,6-di-*tert*-butylphenol with polymer anchored molybdenyl and vanadyl complexes

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Abstract

The oxidation of 2,6-di-*tert*-butylphenol with *tert*-butylhydroperoxide ($\text{Bu}^t\text{O}_2\text{H}$) has been studied using polymer (XAD₄) anchored salicylaldoxime, 1,3-propylene-bis-salicylaldimine and *o*-phenylene-bis-salicylaldimine complexes of molybdenum and vanadium in acetonitrile. The predominant products formed in the oxidation reactions were 2,6-di-*tert*-butylbenzoquinone (BQ) and 3,3'-5,5'-tetra-*tert*-butyldiphenoquinone (dPQ), whereas with some only 2,6-di-*tert*-butylbenzoquinone was formed. This is the first reported use of polymer anchored molybdenyl and vanadyl complexes in selective oxidation of 2,6-di-*tert*-butylphenol. Solvent plays an important role in this reaction. The effects of varying the ligand, metal and the support on the catalytic activity in the oxidation of 2,6-di-*tert*-butylphenol have been studied. With polymer anchored $\text{MoO}_2(\text{salpen})$, 81% of 2,6-di-*tert*-butylbenzoquinone was formed from 2,6-di-*tert*-butylphenol. © 1998 Elsevier Science B.V.

Keywords: *tert*-Butylhydroperoxide; 2,6-di-*tert*-Butylphenol; 2,6-di-*tert*-Butylbenzoquinone; 3,3'-5,5'-tetra-*tert*-Butyldiphenoquinone; Salicylaldoxime; 1,3-Propylene-bis-salicylaldimine; *o*-Phenylene-bis-salicylaldimine; Vanadium; Molybdenum; Styrene-divinylbenzene

1. Introduction

Oxidation of hindered phenols is of considerable synthetic importance and can be accomplished with many oxidants [1–6]. In the absence of any catalyst, the oxidation of hindered phenols results in the formation of a mixture of products. However, the presence of a metal catalyst can influence the course of the reaction and several synthetically useful oxidative transformations can be accomplished using different catalysts.

Several catalytic systems have been used for these oxidations. These include transition metal salts of Fe, Cu, Co, Ru, Mo, etc., [7–9] and Schiff base complexes of Co, Mn, and Cu [10–13]. Heteropolyacids have been used in the oxidation of substituted phenols with *tert*-butylhydroperoxide and H_2O_2 [14–16]. Drago et al. have used polymer anchored chelating amine and Schiff base complexes [17]. They observed that polymer attachment of the catalyst offers considerable potential for enhancing selectivity along with the usual advantages of heterogenizing homogeneous catalysts.

Complexes of Co(II), Mn(II), Fe(II) and Cu(II) have been extensively used for the oxida-

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tion of hindered phenols. Vanadium(IV) and Mo(VI) complexes are known to act as efficient oxygen transfer catalysts for reactions involving organic hydroperoxide and alcohols [18,19]. However, use of such complexes in the oxidation of hindered phenols has not been reported so far.

In this paper we report studies on the variation of product yield in the oxidation of 2,6-di-*tert*-butylphenol with *tert*-butylhydroperoxide as oxidant, and polymer anchored vanadyl and molybdenyl complexes of salicylaldehyde, salpen (1,3-propylene-bis-salicylaldehyde) and salphen (*o*-phenylene-bis-salicylaldehyde) as catalysts. These catalysts are effective in catalyzing the oxidation of sulfoxides to sulfones [20] and benzoin to benzil [21] with Bu'O₂H.

2. Experimental

XAD-4 resin (polystyrene-di-vinylbenzene, 20–50 mesh) was purchased from Merck. *tert*-Butylhydroperoxide solution (70%) and 2,6-di-*tert*-butylphenol were purchased from Aldrich and used without further purification. Infrared spectra were recorded on a Nicolet 5DX-FTIR instrument and thermograms on a Stanton Redcroft STA-780 thermal analyzer. The metal ion content in the polymer beads was determined by atomic absorption spectrometry after digestion of the beads with acid. HPLC was carried out on Waters (50/810) instrument using a μ bondapak C₁₈ column of 30 cm length and 3.9 mm diameter and ultraviolet–visible detector (LC481).

Preparation of polymer anchored molybdenyl and vanadyl complexes has been described in our previous communications [20,21].

2.1. Oxidation of 2,6-di-*tert*-butylphenol

To the anchored catalyst (0.2 g) placed in 30 ml of acetonitrile 0.41 g (2 mmol) of 2,6-di-*tert*-butylphenol and 6 ml (47 mmol) of Bu'O₂H

were added and the reaction mixture was stirred magnetically at desired temperature for six hours. Small portions (0.5 ml) of the reaction mixture were removed by syringe and analyzed by HPLC after suitable dilution. The mobile phase used was hexane:benzene (3:1) at a flow rate of 1 ml/min.

The corresponding homogeneous reactions were carried out in a similar way by taking an equivalent amount of metal complex catalyst.

To ascertain the identity of the products formed in the oxidation of 2,6-di-*tert*-butylphenol catalyzed by vanadyl or molybdenyl complexes, the reaction mixture catalyzed by P-VO(Sal-H)₂ was filtered and concentrated. The concentrated reaction mixture was analyzed by thin layer chromatography (solid phase-silica gel for TLC, eluent hexane:benzene (1:1)). The products formed were separated by column chromatography (solid phase-silica gel for column, eluent hexane:benzene (3:1)) and characterized by NMR spectra and melting points. The products formed were (a) 2,6-di-*tert*-butylbenzoquinone and (b) 3,3'-5,5'-tetra-*tert*-butyl-diphenoquinone. To get an idea of the number of products formed in each reaction, the reaction mixtures were analyzed by thin layer chromatography before subjecting to HPLC.

2.2. Effect of temperature

To study the effect of temperature on the percentage conversion of 2,6-di-*tert*-butylphenol and selectivity of the reaction, the reaction was carried out at different temperatures, viz. 35, 50 and 70°C under similar conditions as mentioned in Section 2.1.

2.3. Recycling of the catalysts

The catalysts isolated by filtration after the oxidation of 2,6-di-*tert*-butylphenol were used again for consecutive runs which were carried out in the same way as the first run.

2.4. Characterization of polymer anchored metal complexes

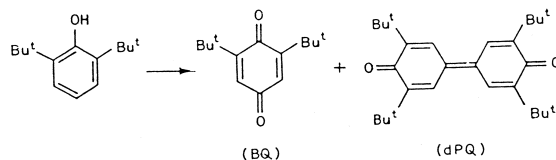
The characterization of polymer anchored vanadyl and molybdenyl complexes using infrared and thermogravimetric data has been described in our previous communications [20,21].

3. Results and discussion

Results of the catalytic oxidation of 2,6-di-*tert*-butylphenol with various polymer anchored and non-anchored vanadyl and molybdenyl complexes using $\text{Bu}^t\text{O}_2\text{H}$ as oxidant under identical conditions are reported in Table 1.

Examination of Table 1 shows that both homogeneous and heterogeneous catalyzed oxidations of 2,6-di-*tert*-butylphenol with $\text{Bu}^t\text{O}_2\text{H}$ yield 2,6-di-*tert*-butylbenzoquinone (BQ) and 3,3'-5,5'-tetra-*tert*-butyldiphenoquinone (dPQ) as the major products. Although oxidation of the phenol proceeded without catalyst or in the presence of the organic polymer functionalized with only the ligand (salpen), but the yield was

very low. Among the various catalysts tried, P-MoO₂(salpen) showed the highest activity.



Several points of Table 1 are noteworthy. As in the oxidation of 2,6-di-*tert*-butylphenol with oxygen employing Co complexes with tetraimidazolyl substituted pyridyl chelates as catalysts [22], use of polar solvents such as acetonitrile and methanol gave rise to better yields. Thus acetonitrile appears to be the most effective and efficient solvent for oxidation of 2,6-di-*tert*-butylphenol to its corresponding *p*-benzoquinone. Oxidation of 2,6-di-*tert*-butylphenol with $\text{Bu}^t\text{O}_2\text{H}$ catalyzed by metal complexes can proceed either via a radical pathway including a phenoxy radical or via an ionic pathway involving the phenolato peroxometal complexed intermediate [22]. It has been suggested by Sheldon

Table 1
Oxidation of 2,6-di-*tert*-butylphenol with different catalysts

Catalyst	Metal ion content	Solvent	Temp. (°C)	Phenol conversion (%)	Selectivity	
					BQ (%)	dPQ (%)
P-MoO ₂ (sal-H) ₂)	0.32 mmol of Mo/g of resin	CH ₃ CN	50	52.8	71.5	28.5
P-MoO ₂ (salpen)	0.32 mmol of Mo/g of resin	hexane	35	30.6	44.5	55.5
		CHCl ₃	35	43.5	51.0	49.0
		CH ₃ OH	50	78.3	77.0	23.0
		CH ₃ CN	50	80.6	100.0	0.0
P-MoO ₂ (salphen)	0.29 mmol of Mo/g of resin	CH ₃ CN	50	75.3	99.0	1.0
P-VO(Sal-H) ₂	0.66 mmol of V/g of resin	CH ₃ CN	50	68.5	22.1	77.9
P-VO(salpen)	0.73 mmol of V/g of resin	CH ₃ CN	50	63.7	20.3	79.7
P-VO(salphen)	0.67 mmol of V/g of resin	CH ₃ CN	50	46.9	8.5	91.5
Without catalysts	—	CH ₃ CN	40	20.0	81.0	19.0
Polymer functionalized with salpen	—	CH ₃ CN	40	21.6	78.0	22.0
MoO ₂ (Sal-H) ₂		CH ₃ CN	50	51.0	32.2	67.8
MoO ₂ (salpen)		CH ₃ CN	50	75.1	63.0	37.0
MoO ₂ (salphen)		CH ₃ CN	50	77.3	56.0	44.0
VO(Sal-H) ₂		CH ₃ CN	50	68.8	17.4	82.6
VO(salpen)		CH ₃ CN	50	69.0	10.0	90.0
VO(salphen)		CH ₃ CN	50	69.6	6.8	94.2

Reaction conditions: time, 6 h; amount of 2,6-di-*tert*-butylphenol, ~ 0.4 g; amount of catalyst, 0.2 g; amount of $\text{Bu}^t\text{O}_2\text{H}$, 4 ml.

and Kochi [23] that vanadyl and molybdenyl complexes catalyze oxidation reactions involving the oxidant $\text{Bu}'\text{O}_2\text{H}$, preferably by its heterolysis. The ionic pathway is thus facilitated. Increase in the total yield of the reaction with increase in the polarity of the solvent (Table 1) lends further support to this suggestion. Polarity of the solvents increases in the order hexane < chloroform < acetonitrile. An increase in the yield of the product is expected as the production of metal complexed phenolate intermediate is enhanced with increase in polarity of the solvent.

Metal complexed phenolate intermediate further gives 2,6-di-*tert*-butylbenzoquinone. The Phenoxy radical is produced through the minor pathway of the reaction, metal catalyzed homolytic decomposition of the hydroperoxide. Formation of 3,3'-5,5'-tetra-*tert*-butyldiphenoquinone can be explained by the coupling of a phenoxy radical with another phenoxy radical [22].

The catalyst has to be a good Lewis acid for the formation of the metal complexed phenolate intermediate and to polarize the O–O bond in $\text{Bu}'\text{O}_2\text{H}$ and thus, for facilitating its heterolysis (major reaction pathway—ionic pathway). The Lewis acidity of the catalyst is influenced by the metal present in the catalyst and also by the electronic properties of the ligand surrounding the metal ion.

As two different products were obtained, the catalytic activity was compared on the basis of the amount of 2,6-di-*tert*-butylphenol consumed in the reaction.

3.1. Catalytic activity of polymer anchored molybdenyl complexes

For the oxidation of 2,6-di-*tert*-butylphenol with the polymer anchored molybdenyl complexes of three different ligands, salicylaldoxime, salpen and salphen (Table 1), the catalytic activity can be grouped as follows:

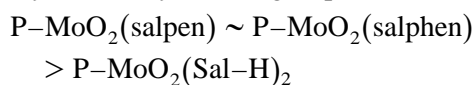


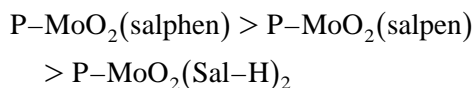
Table 2

Yields of 2,6-di-*tert*-butylbenzoquinone with P-MoO₂(salpen) in 1st run

Time (in h)	2,6-di- <i>tert</i> -Butylbenzoquinone (%)
1	57.9
2	69.6
3	78.2
4	80.6
24	80.6

Reaction conditions: amount of 2,6-di-*tert*-butylphenol, 0.4 g; amount of catalyst, 0.2 g; amount of $\text{Bu}'\text{O}_2\text{H}$, 4 ml; temperature, 50°C; solvent, CH_3CN .

The amount of molybdenum present in the catalysts is approximately the same in all the three catalysts and so the difference in catalytic activity should be due to the coordinated ligands. On the basis of Lewis acidity, the catalytic activity is expected to follow the order given below:

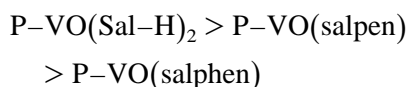


Both P-MoO₂(salpen) and P-MoO₂(salphen) are showing higher catalytic activity compared to P-MoO₂(sal-H)₂, as expected on the basis of Lewis acidity, showing the steric effect of the coordinated ligand is being compensated by the increase in Lewis acidity.

With the P-MoO₂(salpen) catalyst, highest catalytic activity was observed. Therefore, this oxidation reaction was monitored by HPLC. Samples were withdrawn after one hour and analyzed by HPLC and the results are reported in Table 2. It was observed that the reaction was finished after 4 h and no further change was observed after that.

3.2. Catalytic activity of polymer anchored vanadyl complexes

In the polymer anchored vanadyl complexes, the order of catalytic activity is as follows:



which is just the reverse of the catalytic activity expected on the basis of Lewis acidity.

The size of the coordinated ligand affect the complex formation between the $\text{Bu}'\text{O}_2\text{H}$, metal catalyst and the reactant, i.e. formation of metal complexed phenolate intermediate and hence, affect the catalytic activity. The *o*-phenylene and 1,3-propylene backbones of (salphen) and (salpen) ligand decrease the complex formation due to steric effect, more compared to $(\text{sal-H})_2$, thus leading to their lower catalytic activity. Decrease in catalytic activity increases the contribution of the competing free radical pathway to the total reaction, resulting in increase in percentage yield of diphenoquinone. Therefore, the bulkier the ligand of vanadyl complexes $(\text{salphen} > \text{salpen} > (\text{Sal-H})_2)$, the higher the percentage yield of diphenoquinone is and the smaller the percentage conversion of hindered phenol. The steric effect of the coordinated ligand seems to be important in the anchored vanadyl complexes compared to molybdenyl complexes.

3.3. Effect of metal

Regarding the effect of variation of metal on the catalytic activity, it was observed that anchored molybdenyl complexes were much better catalysts than vanadyl complexes with the same

ligands. One reason for this could be the Lewis acidity and on this basis the molybdenum(VI) complexes are expected to be better than vanadium(V) complexes having the same ligand. Besides, the autoretardation by the coproduct $\text{Bu}'\text{OH}$, formed in the oxidation reaction with $\text{Bu}'\text{O}_2\text{H}$ oxidant, is more in reactions catalyzed with vanadium complexes than molybdenum complexes. The higher catalytic activity of the molybdenum complexes as compared to the corresponding vanadium complexes has also been reported by Sheldon and Van Doorn [24] for the oxidation of olefins. Because of the greater oxidizing ability of V(V) as compared to Mo(VI), V(V) catalyzes the unimolecular decomposition of hydroperoxide more effectively than Mo(VI) under a similar environment [25]. Therefore, a higher percentage yield of 3,3'-5,5'-tetra-*tert*-butyldiphenoquinone is obtained with V(V) catalyst than with Mo(VI) catalysts.

3.4. Effect of support

The results of the oxidation of 2,6-di-*tert*-butylphenol with $\text{Bu}'\text{O}_2\text{H}$ catalyzed by anchored molybdenyl and vanadyl complexes were compared with that of non-anchored molybdenyl and vanadyl complexes, respectively. It was observed that on anchoring the metal complexes to polymer, the catalytic activity was

Table 3
Effect of temperature on conversion of 2,6-di-*tert*-butylphenol

Catalyst	Temperature	Conversion of 2,6-di- <i>tert</i> -butylphenol (%)	Selectivity	
			BQ (%)	dPQ (%)
P-MoO ₂ (Sal-H) ₂	35	51.8	71.0	29.0
P-MoO ₂ (Sal-H) ₂	70	55.0	60.6	39.4
P-MoO ₂ (salpen)	35	79.3	100	—
P-MoO ₂ (salpen)	70	81.5	74.1	25.9
P-VO(Sal-H) ₂	35	67.9	22.0	78.0
P-VO(Sal-H) ₂	70	69.0	15.1	84.9
P-VO(salphen)	35	46.5	8.5	91.5
P-VO(salphen)	70	49.9	3.9	96.1

Reaction conditions: amount of 2,6-di-*tert*-butylphenol, 0.4 g; amount of $\text{Bu}'\text{O}_2\text{H}$, 4 ml; amount of catalyst, 0.2 g; solvent, CH_3CN (30 ml); time, 6 h.

lowered by a small value, but the selectivity was enhanced towards *p*-benzoquinone. A similar effect was observed by Drago et al. in the oxidation of 2,6-dimethyl phenol with polymer anchored cobalt complexes [17]. The reason for the increase in selectivity towards benzoquinone, on anchoring the metal complexes to polymer, could be the increase in Lewis acidity of anchored vanadyl and molybdenyl complexes compared to their homogeneous counterpart (as metal complexes are anchored by ester linkages) [23] and dispersed catalytic sites on the polymeric resin.

3.5. Effect of temperature

Table 3 shows that there is not much difference in phenol conversion on increasing the temperature from 35 to 70°C, but the selectivity towards 3,3'-5,5'-tetra-*tert*-butyldiphenoquinone increases.

The P-MoO₂(salpen) catalyst isolated at the end of the oxidation of 2,6-di-*tert*-butylphenol was used for successive runs. It was observed that the catalytic activity decreased slightly by about 5% during three subsequent runs, which could be attributed to the small extent of leaching of molybdenum metal from the catalyst.

Thus the present studies show that 2,6-di-*tert*-butylphenol is smoothly oxidized to *p*-benzoquinone and diphenoquinone by Bu'^tO₂H in the presence of various anchored vanadyl and molybdenyl complexes. By controlling the reaction conditions (solvent and temperature) and by using the appropriate catalyst, 2,6-di-*tert*-butylphenol can be selectively oxidized to BQ or dPQ. Oxidation of 2,6-di-*tert*-butylphenol with polymer anchored MoO₂(salpen) gave BQ with 100% selectivity. On the other hand poly-

mer anchored vanadium complexes yielded dPQ to a larger extent than BQ.

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