Oxidation of benzoin with anchored vanadyl and molybdenyl catalysts

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Abstract

The organic polymer and alumina anchored vanadyl and molybdenyl complexes were found to be effective for the oxidation of benzoin with *tert*-butylhydroperoxide as oxidant. With some of the catalysts only benzil was formed, whereas with others three products, benzil, methyl benzoate and benzoic acid, were formed. The anchored molybdenum complexes were observed to be better catalysts than anchored vanadium complexes for the oxidation of benzoin. With the organic polymer anchored MoO_2(salphen) catalyst, 89% of benzoin to benzil was formed. The effect of ligand, metal and support on the catalytic activity for the oxidation of benzoin has been studied.

Keywords: Tert-butylhydroperoxide; Ligand effect; Benzoin; Benzil; *o*-phenylene-bis-salicylaldimine complexes; Salicylaldoxime complexes; Thenoyl-1,1,1-trifluoroacetylacetone complexes; Vanadium; Molybdenum; Alumina; Styrene-divinylbenzene

1. Introduction

Vanadyl and molybdenyl complexes are known to catalyse the epoxidation of allylic alcohols [1–4] with Bu^tO_2H in a highly regioselective manner. Though the oxidations of alcohol to ketones with Bu^tO_2H catalysed by vanadyl and molybdenyl complexes have been reported [5,6], the oxidation of α-ketol with Bu^tO_2H has not been studied. Most of the studies regarding the oxidation of benzoin, one of the most common α-ketol, have been concerned with the air oxidation of benzoin to benzil with Co^{II} [7], Cu^{II}, Ni^{II} [8], Mo^{VI} [9] complexes. The oxidation of benzoin with

Bu^tO_2H oxidant was of interest since Bu^tO_2H is one of the best sources of oxygen atoms from the point of view of economics, selectivity and safety. Bu^tO_2H is essentially inert to most organic molecules in the absence of catalysts and so catalysts can be used to push the oxidation reaction in pre-determined directions in a highly selective fashion. The oxidation of benzoin with Bu^tO_2H catalysed by chromium(VI) oxide has been reported by Muzart [10,11]. However, a very low yield of benzil (34%) was reported. Besides the chromium residues formed are toxic and thus not attractive.

As the anchored vanadyl and molybdenyl catalysts prepared by us proved to be effective for catalysing the oxidation of sulfoxides [12] to sulfones with Bu^tO_2H, these were also used in the oxidation of benzoin. To understand the

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effect of ligand, metal and support on the oxidation of benzoin with $Bu'O_2H$, the organic polymer and alumina anchored vanadyl complexes of salicylaldoxime (sal-H)$_2$, 3–2 (thenoyl-1,1,1-trifluoroacetylacetone) (TTA) and o-phenylene-bis-salicylaldimine (salphen) and molybdenum complexes of salicylaldoxime (sal-H)$_2$ and o-phenylene-bis-salicylaldimine (salphen) were again employed as catalysts.

In this paper we report studies on the variation in product yields and reaction time for the catalytic oxidation of benzoin with $Bu'O_2H$ as oxidant and anchored catalysts. To study the effect of support, ligand and metal on the oxidation of benzoin, the organic polymer anchored complexes of $VO(TTA)_2$, $VO(sal-H)_2$, $VO(salphen)$, $MoO_2(sal-H)_2$ and $MoO_2(salphen)$ and alumina anchored complexes of $VO(TTA)_2$, $VO(sal-H)_2$, $VO(salphen)$ were used. Chloromethylated polystyrene-divinylbenzene and polystyrene were used as organic supports and γ-alumina as inorganic support.

2. Experimental

Chloromethylated Merrifield's peptide resin (1% crosslinked, 200–400 mesh and having approximately 1 mequiv. Cl/g) was purchased from Aldrich. XAD-4 resin (polystyrene, 20–50 mesh) was purchased from Merck, Fluka. γ-alumina (Neutral-Beckmann grade 1 for chromatography) was purchased from BDH. *Tert*-butylhydroperoxide solution (70%) was purchased from Aldrich and used without further purification. Infrared spectra were recorded on a Nicolet DXFTIR instrument and thermograms on a Stanton Redcroft STA-780 thermal analyser. The metal-ion content in the polymer beads was determined by atomic absorption spectrometry after digestion of the beads with acid. HPLC was done on waters (501/810) instrument using a μ bondapack C_{18} column of 30 cm length and 3.9 mm diameter and a UV–visible detector (LC 481).

Table 1
Elemental analysis of metal complexes

Complex	Carbon (%)		Hydrogen (%)		Nitrogen (%)	
	calcd.	found	calcd.	found	calcd.	found
MoO$_2$(sal-H)$_2$	41.25	42.03	3.00	2.89	6.99	6.75
MoO$_2$(salphen)	54.20	53.98	3.20	3.15	6.30	6.23

The preparation of polymer and alumina anchored vanadyl complexes has been described in our previous communications [12,13]. Molybdenum complexes, $MoO_2(salphen)$ [14] and $MoO_2(sal-H)_2$ [15] were prepared according to the literature procedure and characterised by elemental analysis (Table 1).

2.1. Preparation of polymer supported $MoO_2(sal-H)_2$

The salicylaldoxime ligand was first anchored on to the chloromethylated Merrifield's resin by heating with stirring the polymeric beads (10 g) with the ligand (5 g) and sodium ethoxide (0.2 g) in tetrahydrofuran (150 ml) at 65°C for 24 h. The polymeric beads functionalised with the ligand were filtered out and then stirred with $MoO_2(sal-H)_2$ (3 g) in toluene (150 ml) at 110°C for 30 h. The polymeric beads were then filtered out and soxhlet extracted with acetonitrile (yield: 12 g).

2.2. Preparation of polymer supported $MoO_2(salphen)$

The anchoring of $MoO_2(salphen)$ on functionalised XAD-4 beads [12] was carried out in the same way as the anchoring of $MoO_2(sal-H)_2$ on chloromethylated polystyrene beads.

2.3. Oxidation of benzoin

1 g of the anchored catalyst was placed in 20 ml of methanol. To this 0.6 g (2.84 mmol) of benzoin and 4.5 ml (35 mmol) of $Bu'O_2H$ were added and the reaction mixture was stirred magnetically at a constant temperature of 60°C.

Small portions (0.5 ml) of the solution were periodically removed after 30 min by syringe and analysed by HPLC after suitable dilution. For HPLC analysis, μ bondapack C_{18} column (30 cm length and 3.9 mm diameter) was used. The mobile phase used was 80% methanol at a flow rate of 1 ml/min.

2.4. Recycling of the catalysts

The catalysts isolated by filtration after the oxidation of benzoin were used again for consecutive runs which were carried out in the same way as the first run.

2.5. Characterization of polymer supported metal complexes

The anchored complexes were characterised by infrared spectra and thermogravimetric analysis. Due to the small amount of metal complex
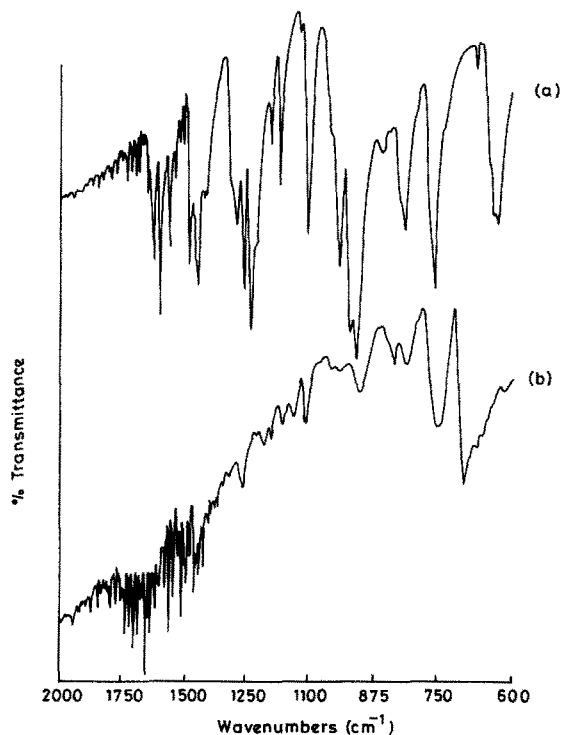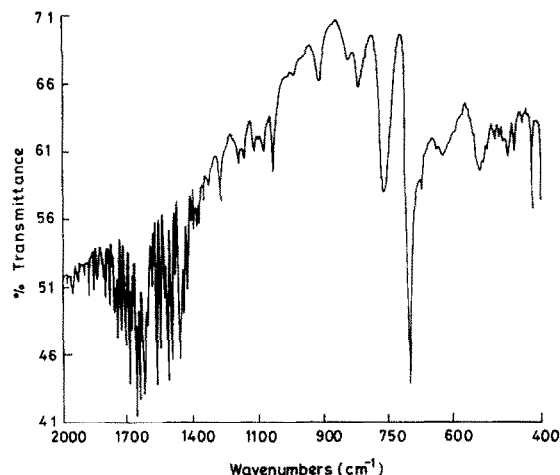

Fig. 2. Infrared spectrum of chloromethylated polymer.

anchored on the polymer, the infrared spectra could only be used qualitatively for confirming the presence of metal complex on the functionalised polymer. The characterization of polymer and alumina anchored vanadyl complexes using infrared and thermogravimetric data has been described in our previous communications [12,13].

The presence of the MoO_2 moiety on the polymer was confirmed by the presence of two bands at 850 cm^{-1} and 915 cm^{-1} assigned to the ν_{asym} and ν_{sym} (O=Mo=O) [16] in the infrared spectrum of P-MoO_2(sal-H)$_2$ (Fig. 1) but absent in the spectrum of chloromethylated polymer (Fig. 2) and P-salicylaldoximate.

Due to large overlapping of bands in the 1400–1700 cm^{-1} region in the infrared spectra of supported ligand and molybdenum complex, the $\nu_{C=N}$ vibration which is indicative of the mode of coordination does not impart any information.

The presence of molybdenum on the polymer (30.8 mg of Mo in 1 g of resin) was confirmed by quantitative determination of molybdenum by atomic absorption spectroscopy after acid digestion of the sample and this was supported by thermogravimetric analysis.

The thermogram of P-MoO_2(sal-H)$_2$ shows a residue (equal to 4% of sample weight taken) at

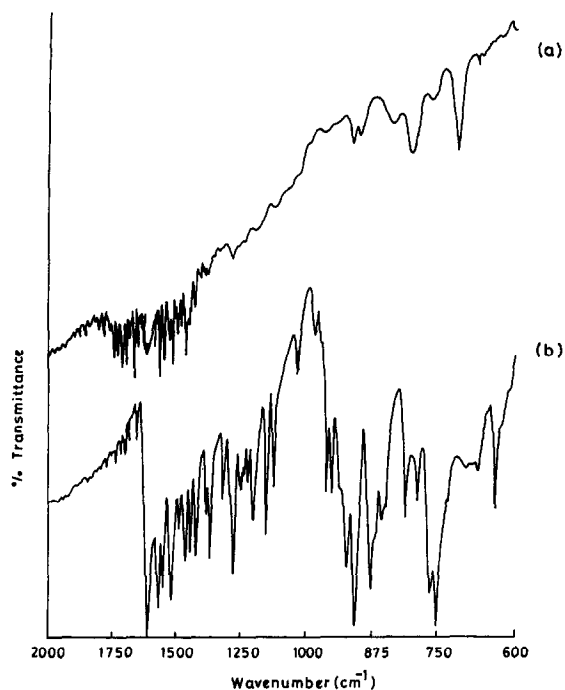Fig. 1. FTIR spectrum of (a) MoO_2(sal-H)$_2$ and (b) P-MoO_2(sal-H)$_2$.

Fig. 3. FTIR spectra of (a) P-MoO$_2$(salphen) and (b) MoO$_2$(salphen).

650°C. The residue was found to be Mo$_2$O$_3$ through analysis of molybdenum content and infrared spectra.

In the infrared spectrum of P-MoO$_2$(salphen) (Fig. 3), the presence of the MoO$_2$ moiety was indicated by the presence of two bands at 915 cm^{-1} and 903 cm^{-1} assigned to symmetric and asymmetric O=Mo=O vibrations. These bands were absent in the spectrum of P-salphen (Fig. 4).

The presence of molybdenum on the polymer (28.2 mg of Mo in 1 g of polymer) was confirmed by quantitative determination of molybdenum and supported by thermogravimetric analysis.

The thermogram of polymer supported MoO$_2$(salphen) shows a residue at 700°C. The residue was found to be Mo$_2$O$_3$ through chemical analysis and the infrared spectrum and corresponds to 30.1 mg of Mo in 1 g of resin and thus supports the atomic absorption spectroscopic data.
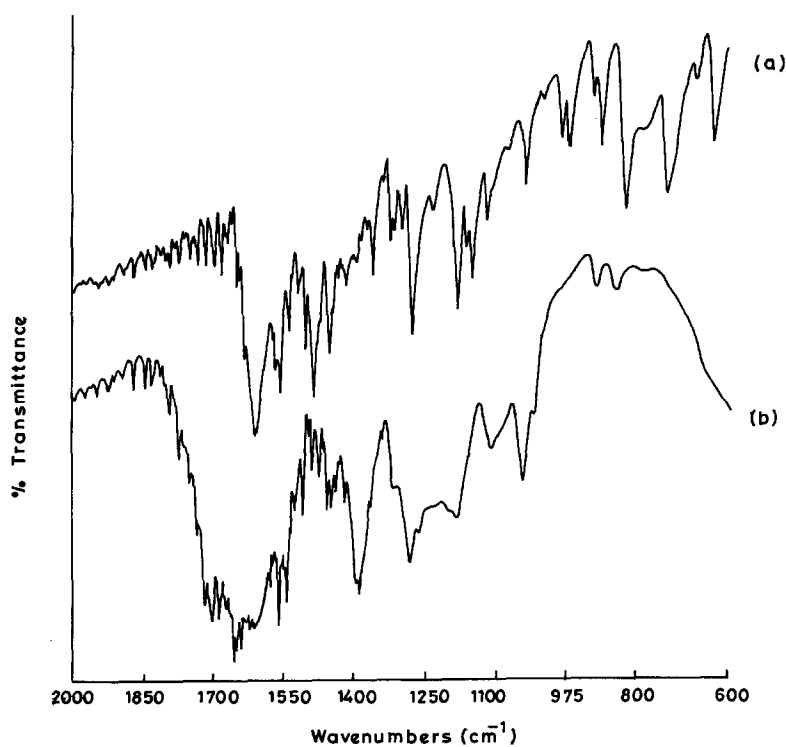

Fig. 4. Infrared spectra of (a) salphen and (b) P-salphen.

3. Results and discussion

The oxidation of benzoin with Bu^tO_2H, when carried out in the absence of catalyst, was very slow and low yields of benzil were obtained even when the reaction was allowed to proceed for a longer time (up to 32 h). Experiments were carried out using (i) the organic polymer without ligand and metal complex and (ii) the organic polymer functionalised with only the ligand. It was observed that neither of the above catalysed the oxidation of benzoin. However, alumina did catalyse the oxidation of benzoin to a very limited extent. With the anchored catalyst the reaction was faster. Thus, the oxidation of benzoin with all the polymer and alumina anchored catalysts using Bu^tO_2H oxidant was carried out under very similar conditions and the products analysed by HPLC. The metal-ion content of the supported catalysts and the yields of the product benzil obtained are given in Table 2. It was observed that with some of the catalysts, methyl benzoate and benzoic acid were also obtained along with benzil.

As three different products were obtained, the catalytic activity was compared on the basis of the amount of benzoin consumed in the reaction. Since the aim was to study the effect of ligand, metal and support on the variation of catalytic activity, the observations may be grouped as follows.

The order of catalytic activity is
1. $P\text{-}VO(TTA)_2 > P\text{-}VO(sal\text{-}H)_2 > P\text{-}VO(salphen)$
2. $P\text{-}MoO_2(salphen) > P\text{-}MoO_2(sal\text{-}H)_2$
3. $A\text{-}VO(TTA)_2 > A\text{-}VO(sal\text{-}H)_2 > A\text{-}VO(salphen)$
4. $A\text{-}MoO_2(salphen) > A\text{-}MoO_2(sal\text{-}H)_2$

Vanadyl and molybdenyl complexes catalyse the oxidation reactions with Bu^tO_2H by polarising the O–O bond in the hydroperoxides and thus facilitating its heterolysis. The oxidation products are then formed by transfer of electropositive oxygen from the metal activated hydroperoxide to the subtrate. The tendency of a metal complex to facilitate the heterolysis of the O–O bond in the hydroperoxide oxidation reaction is influenced by its Lewis acidity as the main function of the catalyst is to withdraw electrons from the peroxidic oxygen of the hydroperoxide and in doing so the catalyst is acting as a Lewis acid [17]. The Lewis acidity of the catalysts will be influenced by the metal present in the catalyst and also by nature of the ligands surrounding the metal-ion.

As in the present case there are three variables, support, metal and ligand, to study the effect of ligand, the metal and support were kept constant.

3.1. Catalytic activity of polymer anchored vanadyl complexes

The oxidation of benzoin with the polymer anchored vanadyl complexes of three different ligands TTA, salicylaldoxime and salphen was carried out for a fixed interval of time, i.e. 6 h, and the products were analysed by HPLC. With all the three catalysts, three products, benzil, methyl benzoate and benzoic acid, were formed. So the catalytic activity was compared on the basis of benzion consumed and can be grouped as follows: $P\text{-}VO(TTA)_2 > P\text{-}VO(sal\text{-}H)_2 > P\text{-}VO(salphen)$.

For the polymer anchored vanadyl complexes on the basis of Lewis acidity, the catalytic activity is expected to follow the order: $P\text{-}VO(TTA)_2 > P\text{-}VO(salphen) > P\text{-}VO(sal\text{-}H)_2$.

The lower catalytic activity of P-VO(salphen) as compared to $P\text{-}VO(sal\text{-}H)_2$ may be ascribed to the larger steric hindrance in P-VO(salphen). Similar trends were observed in the oxidation of dimethylsulfoxide to dimethylsulfone with Bu^tOOH oxidant and the polymer supported vanadyl complex catalysts [12].

3.2. Catalytic activity of alumina anchored vanadyl complexes

The vanadyl complexes supported on alumina showed the same order of catalytic activity

Table 2
Yields of the products with different catalysts

Catalyst	Metal ion content/g of support (mg)	Benzoin (%)	Benzil (%)	Methyl benzoate (%)	Benzoic acid (%)
P-VO(TTA)$_2$	39.2	41.2	6.5	30.7	21.6
P-VO(sal-H)$_2$	33.6	48.9	8.8	24.4	17.9
P-VO(salphen)	34.2	53.9	18.8	13.4	13.9
P-MoO$_2$(sal-H)$_2$	30.8	21.8	42.8	9.7	25.7
P-MoO$_2$(salphen)	28.2	10.4	89.6	—	—
A-VO(TTA)$_2$	23.3	37.1	61.9	1.0	—
A-VO(sal-H)$_2$	27.9	40.7	22.5	19.8	16.9
A-VO(salphen)	22.1	58.4	41.6	—	—
A-MoO$_2$(sal-H)$_2$	24.6	58.2	41.8	—	—
A-MoO$_2$(salphen)	26.0	28.4	71.4	—	—
Without catalyst	—	81.4	11.8	—	6.8
Polymer	—	81.1	11.9	—	7.0
Alumina	—	62.3	37.7	—	—
MoO$_2$(salphen)	—	7.8	79.6	3.4	9.2

P = organic polymer matrix, A = alumina, reaction time = 6 h.

as the polymer anchored vanadyl complexes, i.e., A-VO(TTA)$_2$ > A-VO(sal-H)$_2$ > A-VO(salphen).

The variation in catalytic activity from the order expected on the basis of Lewis acidity may be ascribed to the same reason as for the polymer anchored complexes.

3.3. Catalytic activity of polymer anchored molybdenyl complexes

In the polymer anchored molybdenyl complexes, the order of catalytic activity was that expected on the basis of increasing Lewis acidity of the coordinated ligand, i.e., P-MoO$_2$(salphen) > P-MoO$_2$(sal-H)$_2$.

The steric effects of the coordinated ligands did not seem to be equally important in the anchored molybdenyl complexes, as the anchored MoO$_2$(salphen) complex showed higher catalytic activity than the anchored MoO$_2$(sal-H)$_2$ complex. With the P-MoO$_2$(sal-H)$_2$ catalyst, all the three products diketone, ester and acid were formed.

As with the P-MoO$_2$(salphen) catalyst a very high conversion of benzion to benzil was observed, this oxidation reaction was monitored by HPLC. Samples were withdrawn after one hour and analysed by HPLC and the results are

reported in Table 3. It was observed that the reaction was over in 4 h and no further change was observed after that.

3.4. Catalytic activity of alumina anchored molybdenyl complexes

Among the A-MoO$_2$(salphen) and A-MoO$_2$(sal-H)$_2$ catalysts the A-MoO$_2$(salphen) catalyst was observed to be more effective for the oxidation of benzoin, thus supporting the ligand effect observed with the same complexes supported on organic polymer support.

3.5. 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 the vanadyl complexes with the

Table 3
Yields of benzil with P-MoO$_2$(salphen) in the first run

Time (h)	Benzoin (%)	Benzil (%)
1	24.7	75.3
2	19.8	80.2
3	13.5	86.5
4	10.8	89.2
5	10.4	89.6

same ligands. One reason for this could be the Lewis acidity and on this basis the molybdenum(VI) complexes are expected to be better catalysts than vanadium(V) complexes having the same ligands. Besides, the higher catalytic activity of the molybdenum complexes as compared to the corresponding vanadium complexes has also been reported by Sheldon and Van Doorn [18] for the epoxidation of olefins. Another reason for the lower catalytic activity of vanadyl complexes could be the greater oxidising ability of V(V) as compared to Mo(VI). Under similar environments, V(V) catalyses the unimolecular decomposition of hydroperoxides more effectively than Mo(VI) [19]. Besides, the autoretardation by the coproduct Bu^tOH formed in the oxidation reaction with *tert*-butyl hydroperoxide oxidant is more in reactions catalysed with vanadium complexes than molybdenum complexes.

3.6. Effect of support

The results of the oxidation of benzoin with the alumina anchored vanadyl complexes could not be compared directly with the polymer anchored complexes, as alumina itself catalysed the oxidation reaction and the amount of vanadium was less in the complexes anchored on alumina support. However the ligand effect was prevalent in alumina anchored complexes.

3.7. Catalytic activity of non-anchored $MoO_2(salphen)$ catalyst

As the anchored $MoO_2(salphen)$ was found to be very effective for the oxidation of benzoin, the same oxidation reaction with the non-anchored complex was carried out for comparison. The oxidation reaction was carried out under similar conditions and for the same amount of time.

It was observed that besides benzil (79.6%), methyl benzoate (3.4%) and benzoic acid (9.2%) were also formed. Though on the basis of amount of benzoin consumed, the non-anchored

Table 4
Yields of benzil with P-MoO$_2$(salphen) in the second run

Time (h)	Benzoin (%)	Benzil (%)
1	27.8	72.2
2	22.3	77.7
3	20.4	79.6
4	19.7	80.3
5	18.6	81.4

$MoO_2(salphen)$ complex showed higher catalytic activity than the anchored complex, it gave lesser yield for benzil and the methyl ester and acid products were also formed.

Thus for the oxidation of benzoin to benzil, the anchored $MoO_2(salphen)$ complex catalyst was observed to be more effective.

It is evident from the results in Table 2 that the best catalyst for the oxidation of benzoin to benzil is the $MoO_2(salphen)$ complex supported on the organic polymer support. Using the P-$MoO_2(salphen)$ catalyst, 89.6% of benzil was obtained after 6 h. This reaction was allowed to proceed for a longer time to see if it would go to completion, but no further change was observed in the amount of benzion consumed. The $MoO_2(salphen)$ complex anchored on alumina was also a good catalyst for oxidation of benzion to benzil and 71.4% of benzil was formed.

3.8. Recycling of catalyst

The P-$MoO_2(salphen)$ catalyst isolated at the end of the oxidation of benzoin was used for successive runs and the results are reported in Table 4.

It was observed that the catalytic activity decreased slightly in the second run (81.4%). This could be due to small extent of leaching of molybdenum metal from the catalyst.

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