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Hydroxylation of Phenol Catalyzed by Oxovanadium(IV) of Salen-Type Schiff Base Complexes with Hydrogen Peroxide

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Abstract Active and highly selective catalytic systems of oxovanadium(IV) salen-type have been prepared and characterized by various physico-chemical techniques. Substituted salen-type Schiff base ligands were prepared from 3-ethoxy salicylaldehyde with 1,2-diaminobenzene and 1,8-diaminonaphthalene abbreviated (EtOsalphen) and (EtOsalnaph), respectively. The catalytic activity of the complexes for hydroxylation of phenol to catechol and hydroquinone using H_2O_2 as an oxidant has been studied. The best suited reaction conditions were obtained by considering the effect of solvent, concentration of substrate, reaction time, concentration of catalyst and temperature. Under the optimized reaction conditions, VO-(EtOsalphen) catalyst shows high conversion (71%) at a short reaction time (2 h) with selectivity of 92.5% towards catechol, while VO-(EtOsalnaph) complex also shows higher conversion (76.6%) after longer reaction time (6 h) with almost similar selectivity to catechol (94.2%).

Keywords Phenol hydroxylation · Oxovanadium(IV) complexes · Salen-type Schiff base · Catalytic activity · Selectivity

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1 Introduction

Condensation reactions between carbonyl compounds and primary amines have provided one of the most important and widely studied classes of chelating ligand. A wide variety of ligand may be obtained via Schiff base condensation reaction which shows variations in flexibility and electronic properties.

The family of Schiff bases derived from aromatic or aliphatic diamine and phenolic aldehydes which are known as salen has proved to be the source of tetradentate ligands for many transition metals including vanadium(IV) [1–5]. Salen-type complexes show a great potential as catalysts for various reactions [6–16].

The selective and one-step hydroxylation of phenol by hydrogen peroxide is an attractive and challenging subject from economical and environmental point of view. The dihydroxybenzenes viz. catechol (CAT) and hydroquinone (HQ), are important intermediates for manufacturing of petrochemicals, agrochemicals and plastics [1]. They are widely used as photographic chemicals, antioxidants, pesticides, flavoring agents, and medicine. Catechol was also used as an organic sensitizer in a photoelectrochemical cell [4].

Vanadium salen-type complexes have attracted much interest as catalysts for various types of reactions. These vanadium complexes have attracted attention due to its interesting structural characteristics and biological properties [17, 18].

Oxovanadium complexes catalyzed various oxidation reactions such as oxidation of sulfides to sulfoxides [19, 20], epoxidation reaction of different olefins [21, 22], oxidation of alcohols [23] and hydroxylation of benzene and phenol to mono- and dihydroxybenzenes [24–28]. On the other hand vanadium Schiff bases complexes encapsulated in zeolite-Y were used as catalysts for hydroxylation reaction of phenols [24].

In continuation of our efforts to study the catalytic activity of oxovanadium(IV)-based catalyst, we report herein the preparation and characterization of two oxo-vanadium(IV) complexes abbreviated, VO-(EtOsalphen) and VO-(EtOsalnaph). These complexes are derived from tetradentate Schiff base ligand of type ONNO; *N,N′*-1,2-phenylenebis (3-ethoxysalicylideneaminate) (EtOsalphen) and *N,N′*-1, 8-naphthylene-bis(3-ethoxysalicylideneaminate) (EtOsalnaph). The catalytic activity of these complexes was tested for hydroxylation of phenol and the suitable reaction conditions have been optimized to get maximum hydroxylation.

2 Experimental Section

2.1 Materials

Vanadyl sulfate trihydrate was obtained from Fluka, 1,2-diamino benzene, 1,8-diaminonaphthaline and 3-ethoxysalicylaldehyde were obtained from Merck. Phenol and 28%, H_2O_2 were of AR grade and all other chemical reagents were used as such. Solvents were used after being purified according to the standard method.

2.2 Physical Methods and Analysis

Infrared spectra were recorded as KBr pellets on BUCK-500 FT-IR spectrometer. ^{1}H-NMR spectra were recorded on a Bruker 500 (500 MHz) using d6-DMSO or $CDCl_3$ as a solvent and TMS as internal standard. GC-Mass spectra were recorded on Hewlett Packard E1 at 70 eV. Elemental analysis was performed on Euro Vectro EA 3000A. All catalyzed reactions products were analyzed using Shimadzu gas chromatography (GC-14 B) fitted with FID detector.

2.3 Preparation

2.3.1 Preparation of the Ligands

2.3.1.1 A. N,N′-1,2-Phenylenebis(3-Ethoxysalicylideneaminate) (EtOsalphen) A mixture of 1,2-diaminobenzene (0.108 g, 0.001 mol) and 3-ethoxysalicylaldehyde (0.332 g, 0.002 mol) in 20 mL absolute ethanol were refluxed with stirring for 2 h. An orange solid was obtained which recrystallized from ethanol. Yield 68%; m.p. 122–124 °C; IR (KBr, cm^{-1}), 3343 *v*(OH), 1625 *v*(C=N), 1264 *v*(C–N), 1116 *v*(C–O), 3048–3094 *v*(C–H arom), 2890–2971 *v*(C–H aliph.). E1-mass (m/z), 405(12) [M + 1], 404(18) M$^+$, 254(51), 239(100), 197(72). ^{1}H-NMR δ ppm (500 MHz, $CDCl_3$): 1.56 (t, 6H, CH_3, $J = 7.0$ Hz), 4.20 (q, 4H, CH_2, $J = 6.95$), 6.82–7.31 (m, 10H, Ar–H), 8.68 (s, 2H, HC=N), 13.53 (s, 2H, OH).

2.3.1.2 B. N,N′-1,8-Naphthylenebis(3-Ethoxysalicylideneaminate) (EtOsalnaph) 1,8-Diaminonaphthaline (0.158 g), and 3-ethoxysalicylaldehyde (0.332 g) were dissolved in absolute ethanol (20 mL) and refluxed for 2 h. A brown solid obtained on recrystallization from cyclohexane. Yield 36%; m.p. 142–144 °C; IR (KBr, cm^{-1}), 3358 *v*(OH), 1614 *v*(C=N), 1269 *v*(C–N), 1114 *v*(C–O), 3044–3098 *v*(C–H arom), 2861–2990 *v*(C–H aliph.). E1-mass (m/z), 455 (66) [M + 1]$^+$, 454 (82) M$^+$, 436 (25), 391 (44), 304 (97), 290 (15), 247 (100); ^{1}H-NMR δ ppm (500 MHz, d$_6$-DMSO), 1.37 (t, 6H, CH_3, $J = 6.88$ Hz), 4.08 (q, 4H, CH_2, $J = 6.9$), 5.71 (s, 2H, OH), 6.54–7.19 (m, 12H, Ar–H), 8.80 (s, 2H, HC=N).

2.3.2 Preparation of the Oxavanadium(IV) Complexes

The two complexes were prepared according to the following procedure. An aqua solution (10 mL) of $VOSO_4 \cdot 3H_2O$ (0.217 g, 1 mmol), was added drop wise to the hot ethanolic solution (10 mL) of the Schiff base ligand (1 mmol). The mixture was heated under reflux for 5–6 h. The precipitated solid which was obtained, filtered, washed with hot water then ethanol and finally dried at 110 °C.

2.3.2.1 A. VO-(EtOsalphen) Green solid, m.p. > 300 °C, IR (KBr, cm^{-1}); 3064–3098 *v*(C–H arom), 2861–2980 *v*(C–H aliph.), 1602 *v*(C=N), 1600 and 1546 *v*(C=C), 1252 *v*(C=N), 1103 *v*(C–O), 987 *v*(V=O). ^{1}H-NMR (d$_6$-DMSO); 1.57 (t, 3H, CH_3), 4.52 (q, 2H, CH_2), 6.8 (m, 10H, Ar–H), 9.5 (s, 1H, HC=N). Anal. calc. for $C_{24}H_{22}N_2O_5V$: C, 61.4, H, 4.71, N, 5.96, found: C, 61.09, H, 4.48, N, 6.21.

2.3.2.2 B. VO-(EtOsalnaph) Green solid, m.p. > 300 °C, IR (KBr, cm^{-1}); 3041–3102 *v*(C–H arom), 2867–2988 *v*(C–H aliph.), 1604 *v*(C=N), 1600 and 1546 *v*(C=C), 1247 *v*(C–N), 1100 *v*(C–O), 976 *v*(V=O). 1H-NMR (d$_6$-DMSO); 1.37 (t, 3H, CH_3), 3.35 (q, 2H, CH_2), 6.9–7.26 (m, 12H, Ar–H), 10.1 (s, 1H, HC=N). Anal. calc. for $C_{28}H_{24}N_2O_5V$: C, 64.74, H, 4.65, N, 5.39. found: C, 64.02, H, 4.36, N, 5.82.

2.3.3 Catalytic Activity Study

The catalytic hydroxylation of phenol was carried out in a 50 mL flask fitted with a water condenser. In a typical reaction, an aqueous solution of 28% H_2O_2 (6.07 g, 0.05 mol) and phenol (4.7 g, 0.05 mol) were mixed in 2 mL of MeCN and the reaction mixture was heated at 70 °C with continuous stirring in an oil bath. An appropriate amount of catalyst (0.007 g) was added to the reaction mixture and the reaction was considered to begin. During the reaction, the products were analyzed after specific interval of time using a gas chromatograph by withdrawing small aliquot. The effects of various parameters, such as amounts of substrate, oxidant, catalyst and type of solvent as well as the temperature of the reaction were studied in order to study their effect on the reaction product pattern.

3 Result and Discussion

3.1 Synthesis and Characterizations

Condensation of 3-ethoxysalicylaldehyde with 1,2-diaminobenzene or 1,8-diaminonaphthalene in 2:1 molar ratio leads to the formation of the Schiff base ligands (EtOsalphen) and (EtOsalnaph), respectively. These ligands react with vanadyl sulfate to give the corresponding metal complexes (Structure 1). To enhance the catalytic activity of these complexes, the presence of strong electron rich metal centre is essential to facilitate the oxidation process. This is achieved by introducing an electron-donating group (ethoxy group) at the ortho positions of the phenyl groups. The ligands and their corresponding complexes were confirmed by elemental analysis FT-IR, mass and ^{1}H NMR spectroscopy.

The IR spectra data of the ligands show a strong absorption band around 3,343–3,358 cm^{-1} attributed the phenolic OH groups stretching vibration which disappeared on complexation indicating the coordination of the metal to the phenolic oxygen atom after deprotonation. A strong bands at 1,614–1,625 cm^{-1} in the ligands spectra are assigned to the azomethine (C=N) stretching vibration. This band shifted to lower frequency in the complexes due the coordination of nitrogen atom of the azomethine group to the central metal [29–32]. Unlike ν(C=N) stretching bands, the ν(C=C) stretching mode does not show any significant shift. The phenolic ν(C–O) band at 1,114–1,116 cm^{-1} in the free ligand is shifted by 10 ± 15 cm^{-1} towards lower wavenumbers in the complexes, consistent with coordination via the deprotonated phenolate oxygen. Both complexes show a strong band at 976–987 cm^{-1}, which is assigned to stretching vibration of V=O. The appearance of new two to three moderately intense bands in the low-frequency region of 350–500 cm^{-1} in the complexes are assigned to stretching frequencies of ν(M–O) and ν(M–N) bonds. These bands further indicates the coordination of nitrogen and oxygen to the metal. Thus, these ligands appear to be deprotonated at the phenolic OH group and behave as dibasic tetradentate ONNO donor ligands coordinating through the deprotonated phenolic oxygen and the azomethine nitrogen.

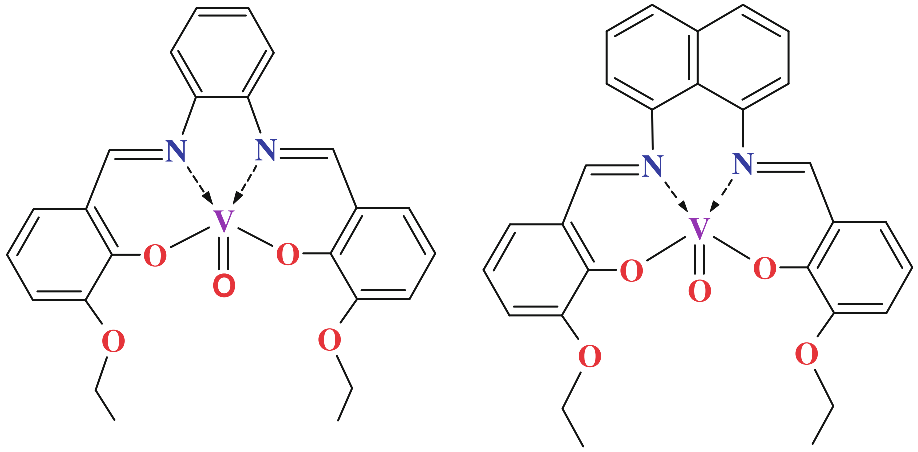
The elemental analysis of the complexes is in agreement with the formula. The result of GC-mass indicates that the ligands have 2:1 stiochiometry, where the molecular ions are in agreement with the suggested molecular weight of the proposed structure. The complexes were found nonvolatile and difficult to record the mass spectra by E1 methods of ionization.

As expected from ^{1}H-NMR spectra of the ligands only aromatic, –N=CH–, –CH$_2$, –CH$_3$ and –OH peaks are observed. The singlets at δ 8.68–8.8 in NMR spectra, indicating the presence of azomethine protons, substantiated the IR assignment.

3.2 Catalytic Activity Studies

In order to screen the catalytic oxidative potential of the prepared complexes, VO-(EtOsalphen) and VO-(EtOsalnaph) were tested as catalysts for hydroxylation of phenol using H_2O_2 as an oxidant under different reaction

Structure 1 Structures of the Schiff base ligands



VO-(EtOsalphen)

VO-(EtOsalnaph)

conditions as a function of time. The oxidation of phenol gave two major products, i.e. catechol and hydroquinone. A control reaction was made to test the non catalytic oxidation of phenol by H_2O_2 in the absence of a catalyst. Other products, if any, present as minor constituents could not be detected by the gas chromatography under the conditions used herein and were neglected.

In order to achieve suitable reaction conditions for a maximum oxidation of phenol, effect of various parameters, have been taken into consideration.

The effect of H_2O_2 concentration on the oxidation of phenol using both catalysts is illustrated in Fig. 1. Three different molar ratios of H_2O_2/phenol (mol H_2O_2) viz. 0.5:1 (25 mmol), 1:1 (50 mmol) and 2:1 (100 mmol), were considered while keeping a fixed amount of phenol (4.7 g, 0.05 mol) and catalyst (0.007 g) in 2 mL of MeCN at 70 °C. It is clear from the figure that the 1:1 molar ratio is the best to obtain maximum phenol conversion of 71 and 76% using VO-(EtOsalphen) and VO-(EtOsalnaph), respectively. Increasing the H_2O_2 concentration to 2:1 the % conversion and selectivity did not affected significantly. This clearly suggests that large concentration of oxidant is not an essential condition to maximize phenol transformation.

High selectivity towards catechol formation (84–94%) was obtained using all the molar ratios mentioned above. Such high selectivity has only been noticed with oxovanadium(IV) complexes of salen family [24] and VO–Y zeolite [33].

Similarly, three different concentrations of phenol (25, 50 and 100 mmol) were tested to study the effect of substrate to oxidant molar ratio on phenol hydroxylation. Figure 2 show that 0.5:1 molar ratio (25 mmol) gave minimum phenol conversion (63–68%) using both catalysts. increasing the molar ratio to 2:1 the reaction merely helped to achieve a phenol conversion of 49%. For both catalysts, the molar ratio 1:1 is found to be sufficient enough for the effective phenol conversion (71–76%) and high selectivity (>92%) towards the formation of catechol.

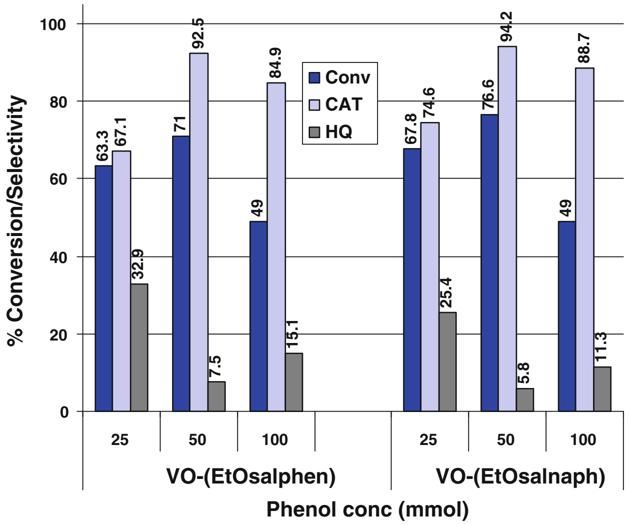


Fig. 2 Effect of phenol concentration on phenol oxidation using VO-(EtOsalphen) and VO-(EtOsalnaph)

To investigate the effect of amount of catalyst on phenol hydroxylation, three different amounts of catalysts (5, 7 and 9 mg) keeping all other parameters fixed. It was observed that increasing the amount of catalyst from 5 to 7 mg using VO-(EtOsalphen) as catalyst increases the % phenol conversion from ~63 to 71% within 2 h reaction time (Fig. 3). Increasing the amount of catalyst to 9 mg, did not improve the overall conversion, only a marginal decrease was detected. This may be due to the more H_2O_2

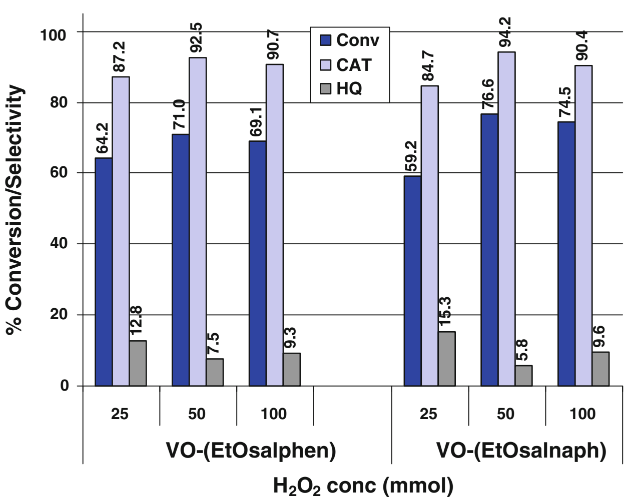


Fig. 1 Effect of H_2O_2 concentration on phenol oxidation using VO-(EtOsalphen) and VO-(EtOsalnaph)

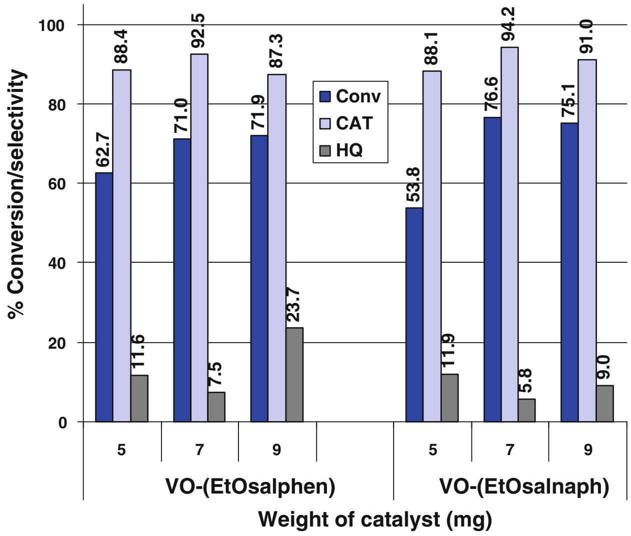


Fig. 3 Effect of amount of catalyst on phenol oxidation

decomposition by the catalyst. A similar result was obtained on using VO-(EtOsalnaph) as catalyst. The highest phenol conversion ~77% was obtained using 7 mg of catalyst after 6 h reaction time.

To determine the efficiency of the catalysts, the % phenol conversion, the % formation of catechol and hydroquinone were plotted as a function of time, are presented in Fig. 4. It was found that the overall percent phenol conversion increases with the increase in reaction time and attains a steady state giving a maximum phenol conversion of ~71% after 2 h for VO-(EtOsalphen) and 77% after 6 h for VO-(EtOsalnaph). On comparing these two catalysts it is clear that the VO-(EtOsalphen) attained larger phenol conversion in a shorter time than that with VO-(EtOsalnaph). The selectivity towards the products was changed slightly at different reaction time for both catalysts.

The performance of the catalysts were investigated at three different temperatures (45, 70 and 80 °C), while keeping other parameters fixed. The activity of these catalysts was found to increase as the temperature was raised from 45 to 80 °C (Fig. 5). From the results above it is clear that 70 °C is the best temperature as it gives high % conversion and selectivity towards catechol as well. With increasing temperature to 80 °C, a slight drop in the selectivity for the catechol formation was observed although it was still the predominant product.

Solvents may influence the reaction rate and the percentage of conversion of phenol. The effect of solvents on the rate of the hydroxylation of phenol was studied using five different solvents (C_6H_6, MeCN, DMSO, $C_2H_4Cl_2$ and CCl_4). While keeping other fixed. Results are shown in Figs. 6 and 7. The maximum percentage of phenol conversion obtained using both catalysts is in the following order: MeCN > DMSO > $C_2H_4Cl_2$ > C_6H_6 > CCl_4. From the above results it can be concluded that MeCN is the best solvent for the oxidation of phenol.

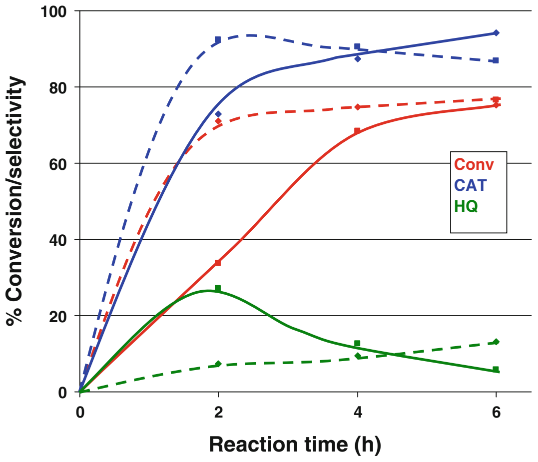


Fig. 4 Effect of reaction time on phenol oxidation using VO-(EtOsalphen) [—] and VO-(EtOsalnaph) [– –]

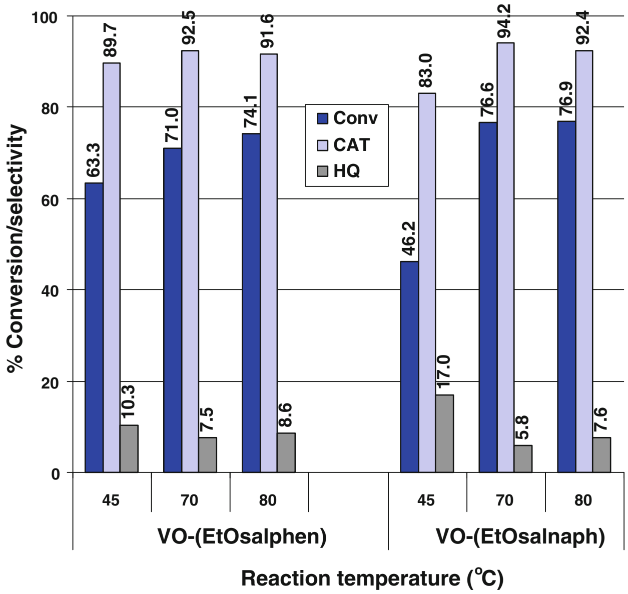
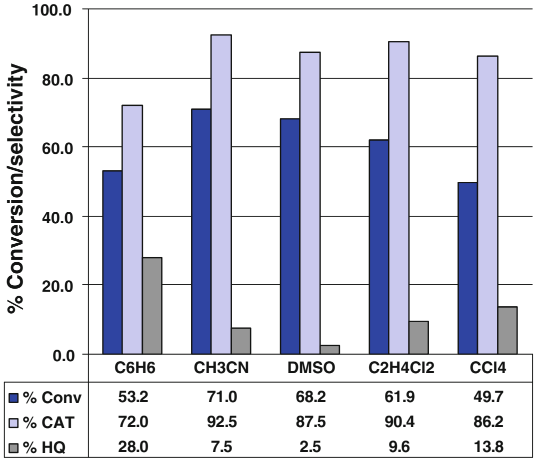


Fig. 5 Effect of reaction temperature on phenol oxidation using VO-(EtOsalphen) and VO-(EtOsalnaph)



	C6H6	CH3CN	DMSO	C2H4Cl2	CCl4
■ % Conv	53.2	71.0	68.2	61.9	49.7
□ % CAT	72.0	92.5	87.5	90.4	86.2
■ % HQ	28.0	7.5	2.5	9.6	13.8

Fig. 6 Effect of type of solvent on phenol oxidation with VO-(EtOsalphen)

4 Conclusion

Oxovanadium(IV) complexes of tetradentate Schiff bases obtained by condensation of 3-ethoxy salicyladehyde with two different diamines, have been prepared and characterized successfully.

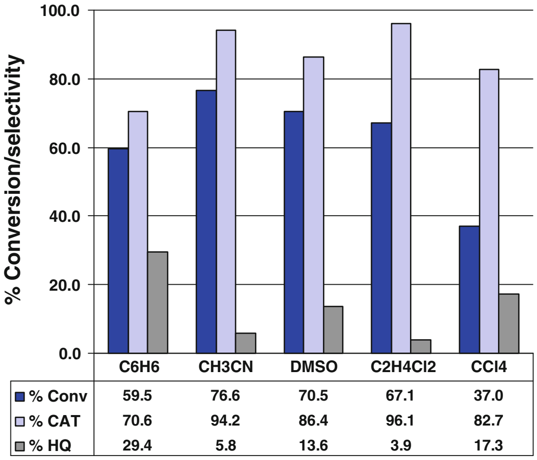


Fig. 7 Effect of type of solvent on phenol oxidation with VO-(EtOsalnaph)

These complexes were screened as catalysts for the oxidation of phenol using H_2O_2 as an oxidant. Several factors such as reaction time, amount of catalyst, phenol and H_2O_2 concentrations, type of solvents and temperature of the reaction mixture affect the performance of these catalysts.

The best-suited reaction condition is 4.7 g phenol, 0.007 g catalyst, 1:1 phenol/H_2O_2 molar ratio in 70 °C, reaction time 6 h in CH_3CN. Under optimum reaction condition, these catalysts show high phenol conversion and excellent selectivity toward catechol formation (>92%). Comparing the activity of our catalysts for hydroxylation of phenol to the literature data, our catalysts show a higher activity and show a very high degree of selectivity for the formation of catechol over hydroquinone.

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