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FULL PAPER

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Peroxidative catalytic oxidation of alcohols catalyzed by heterobinuclear vanadium(V) complexes using H_2O_2 as terminal oxidizing agents

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Here we report the catalytic oxidation of benzylic alcohol, hetero-aryl alcohols and propargylic alcohols to their corresponding carbonyl compound using heterobimetallic sodium-dioxidovanadium(V) complexes. The present catalytic oxidation studies proceed at 70 °C using H_2O_2 as terminal oxidant. During the whole process, the complexes react with hydrogen peroxide to form peroxo-vanadium(V) species. The present study shows the heterogeneity of pre-catalyst which could be easily recovered and moreover isolation of product is very simple.

KEYWORDS
bimetallic vanadium (V), catalysis, oxidation, peroxidative

1 | INTRODUCTION

Selective oxidation of alcohols to corresponding aldehydes and ketones have seen a tremendous growth in the field of aerobic oxidation catalysis and a wide variety of efficient methodologies have been developed for this organic transformations.[1–4] Aldehydes and ketones are important starting materials for the preparation of more complex organic compounds.[5,6] Conventionally, there are several methods that have been reported in the literature for the transformation of alcohols to carbonyl compounds which include the use of metal like chromium[7] and manganese.[8] Implementing these methods generate a large quantity of effluents, such as $KMnO_4$, MnO_2 and CrO_3 which are environmentally toxic and hazardous.

In many cases, the use of noble metal catalysts such as ruthenium,[9] gold,[10] palladium[11] and platinum,[12] shows excellent activities and selectivity's for this chemical process. However, the use of these novel metals find many drawbacks and limited services because of their expensive nature, hence, in order to reduce their usage, some non-noble transitional metals are required. In particular, vanadium complexes are well known as an attractive class of catalysts.[13–15]

In terms of economy and environmental friendliness, vanadium complexes catalyzed the aerobic oxidation of benzylic, allylic, and propargylic alcohols. Vanadium complex of the composition $(HQ)_2VO(OiPr)$ (HQ = 8-quinolinate) reported by Hanson and coworkers, efficiently catalyzed the oxidation of benzylic, allylic, and propargylic alcohols in the presence of triethylamine in air.[16] With regard to safety hazard associated with heating organic solvents at elevated O_2 pressure using air instead of pure oxygen are more advantageous.[12] Recent studies have focused on the development of vanadium catalysts for the oxidation of alcohols with air, few reports are known to exist of an efficient vanadium catalytic system for aerobic oxidation of alcohols under atmospheric conditions. Herein, we report the aerobic oxidation of benzylic, allylic, and propargylic alcohols by heterobimetallic dioxido-vanadium(V) complexes.

2 | RESULTS AND DISCUSSION

Vanadium(V) complexes 1 and 2 were synthesized and characterized in previous reported article.[17] Molecular structures of the complexes are given in Figure 1. The

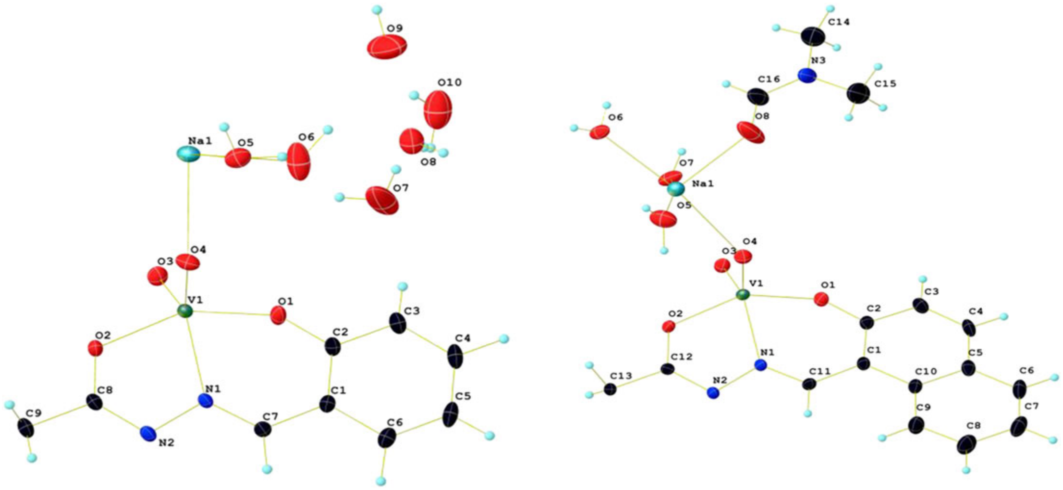
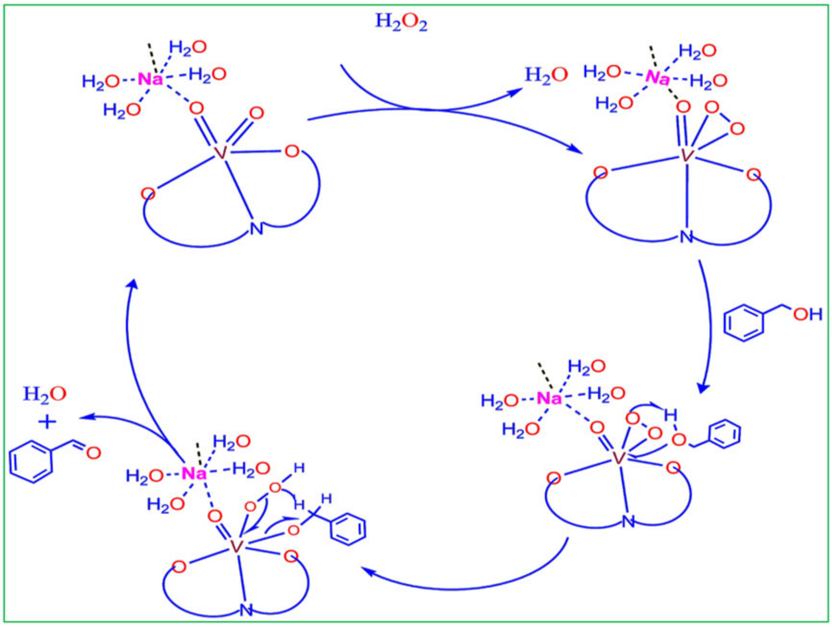


FIGURE 1 Molecular structure of the complexes 1 and 2 (only one asymmetric unit are shown)

heterobimetallic complexes 1 and 2, are of interest as a precatalyst for oxidation of organic substrates (Scheme 1).

In order to achieve the optimum condition, we carried out the oxidation of benzyl alcohol leading to the formation of benzaldehyde as a model reaction. Using complex 1, the reaction was carried out using different amount of catalyst and found that 0.01 mmol of complex gave the best yield (Figure 2) at 70 °C (Figure 3). The reaction was also tested using different organic solvents, but it was found that acetonitrile gave the best yield (Figure 4). Using the catalytic amount of catalyst (0.01 mmol), temperature (70 °C) and acetonitrile as solvent, we studied the effect of additive/base for the oxidation of benzyl alcohol and it was found that the use of base reduces the rate of oxidation. We also performed the oxidation of benzyl alcohol by using different sources of vanadium V_2O_5, $VOSO_4$, Vanadyl acetylacetonate and $NaVO_3$, but it was found that the complex gave better yield compare to these vanadium sources. The catalytic activity of the complex 2 were also tested using the same reaction condition and it was found that complex 2 can be used as catalyst for oxidation of benzylic, allylic and propargylic alcohols but its yield is slightly less (<5) compared to complex 1. When the reaction was carried out under dinitrogen atmosphere, the percentage conversion of benzyl alcohol to benzaldehyde was unchanged. This proved that air does not participate in oxidation. Using the above standardized method, we carried out the catalytic oxidation of various benzylic, allylic and propargylic alcohols (Table 1).

Primary benzyl alcohols bearing electron donating groups such as, p-methoxy benzyl alcohol gave 91%



SCHEME 1 Plausible mechanism for the catalytic oxidation alcohols (only one unit of complex is shown)

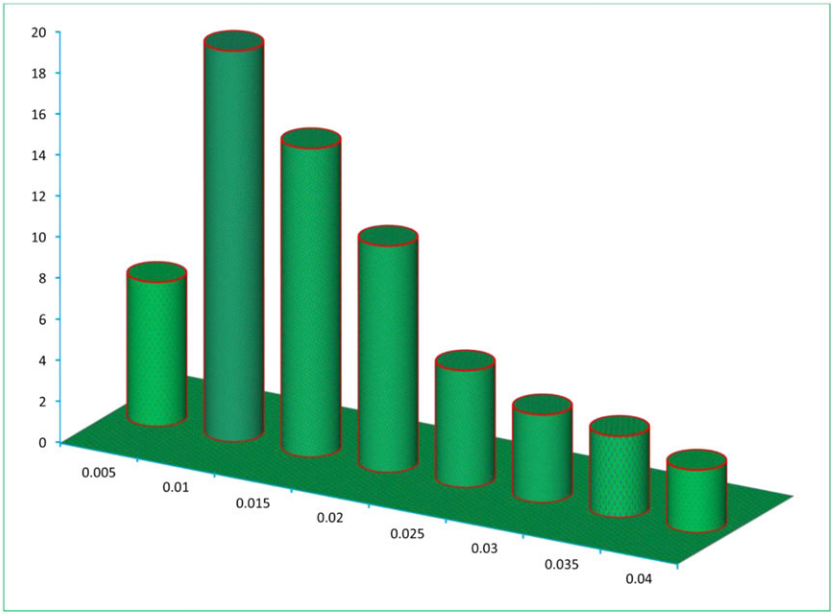


FIGURE 2 Effect of concentration of catalyst on oxidation of benzyl alcohol

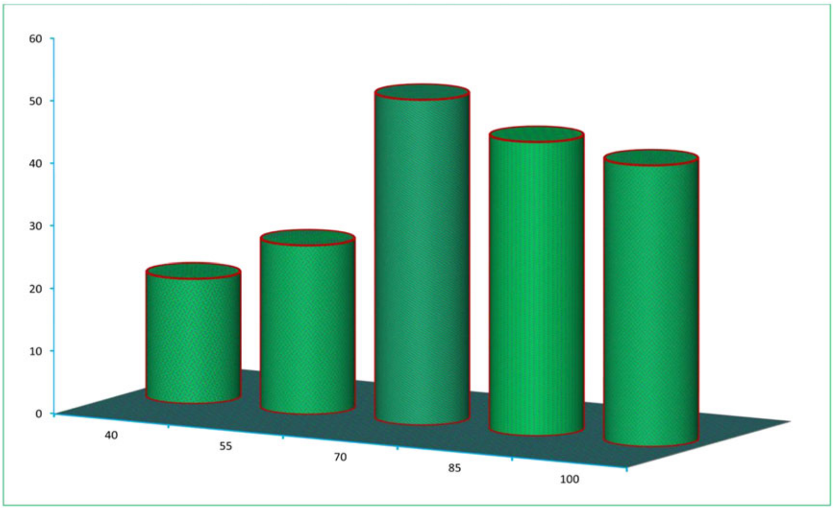


FIGURE 3 Effect of temperature on oxidation of benzyl alcohol

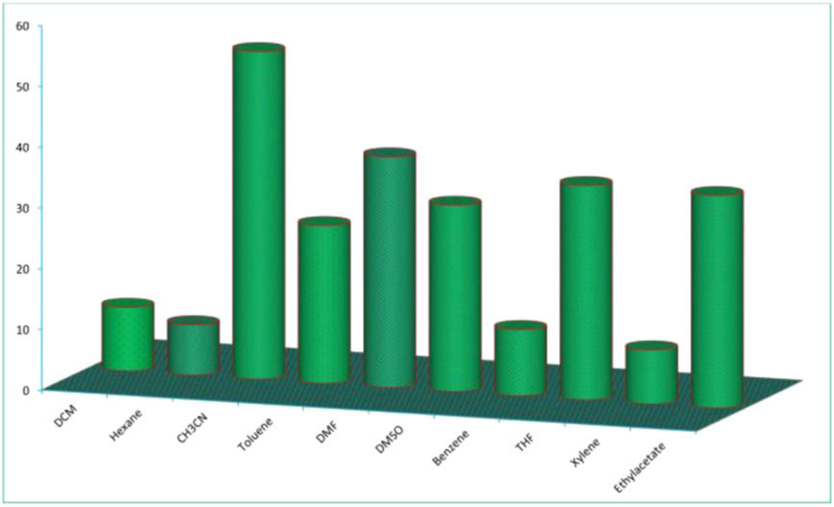
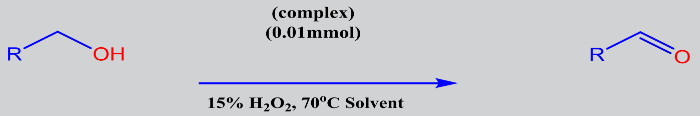
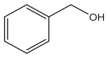
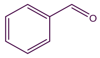
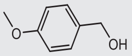
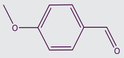
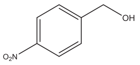
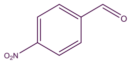
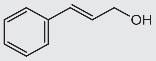
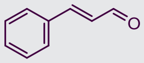
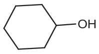
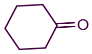
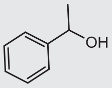
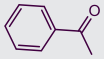
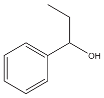
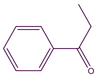
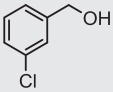
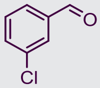
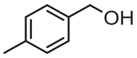
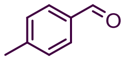
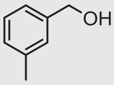
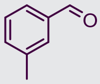
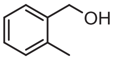
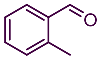
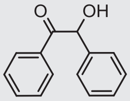
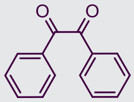
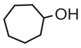
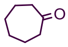
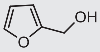
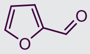
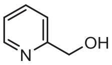
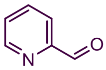
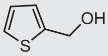
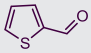
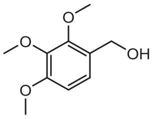
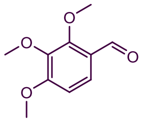


FIGURE 4 Effect of solvent on oxidation of benzyl alcohol

TABLE 1 Catalytic oxidation of alcohols by heterobimetallic vanadium(V) complexes

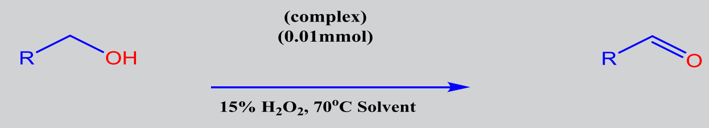


R=aryl, alkyl, heteroaryl

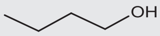
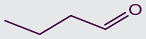
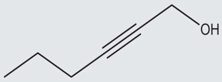
Sl. No	Alcohol	Product	Time (h)	Yield (%) (isolated)^b R-CHO	TON	TOF (h^{-1})	Yield (%) (GC %)^c R-CHO
1			3.4	89	445	130.88	93
2			4	91	455	113.75	94
3			4.3	80	400	93.02	87
4			7.5	88	440	58.67	76
5			3	No reaction	-	-	-
6			6	No reaction	-	-	-
7			7.2	No reaction	-	-	-
8			4.5	74	370	82.22	79
9			4.5	88	400	97.78	90
10			5	86	430	86	88
11			5	84	420	84	86
12			4	86	430	107.5	88
13			3	No reaction	-	-	-
14			3	85	425	141.67	89
15			4	89	445	111.25	92
16			2.3	78	390	169.57	82
17			3.5	94	470	134.29	96

(Continues)

TABLE 1 (Continued)



R=aryl, alkyl, heteroaryl

Sl. No	Alcohol	Product	Time (h)	Yield (%) (isolated)[b] R-CHO	TON	TOF (h^{-1})	Yield (%) (GC %)[c] R-CHO
18			48	80	400	8.33	82.4
19			48	34	170	3.54	37
20			24	17	85	3.54	21

[a]Reaction condition: catalyst (0.01 mmol); 15% H_2O_2 (4.85 mmol); alcohol (4.84 mmol). [b]yield; [c]GC Yield.

isolated yield of p-methoxy benzaldehyde (GC: 94%) (Table 1, entry 2), p-methyl benzyl alcohol gave 88% p-methyl benzaldehyde (Table 1, entry 9), whereas 3,4,5-trimethoxy benzyl alcohol gave 94 % of isolated yield within 3.5 h (GC: 96%) (Table 1, entry 17). Electron donating group present at the ortho and meta position of the benzene ring such as o-methyl benzyl alcohol gave 84% of o-methyl benzaldehyde and m-methyl benzyl alcohol give 86% of isolated m-methyl benzaldehyde (Table 1, entry 10, 11). Benzyl alcohol containing electron withdrawing group such as p-nitro benzyl alcohol and m-chloro benzyl alcohol gave 80% (Table 1, Entry 3) and 74% (Table 1, Entry 8) of the isolated yield of corresponding aldehyde lower to that of electron donation groups present in para position of the benzene ring. Benzyl alcohol containing double bond functional groups, such as cinnamyl alcohol was oxidized selectively with 88% conversion without oxidation of double bond and 75% (Table 1, entry 4) selectivity for aldehyde. 2-Hydroxy-1,2-diphenylethan-1-one was also oxidized to benzil with 86% yield within 2 h. Secondary benzyl alcohols such as phenyl ethanol (entry 6), phenyl propanol (entry 7), cyclohexanol (entry 5) and cycloheptanol (entry 13) were also subjected to oxidation but did not react at all. Further, hetero-aryl alcohols such as furan-2-yl-methanol, pyridine-2-yl methanol and thiophene methanol (entries 14, 15, 16) gave 85%, 89% and 78% of their corresponding aldehydes. In case of aliphatic alcohols such as n-butanol, and n-octanol were also oxidized for a period of 48 h, giving their yield of 80% and 34%. Propargylic alcohols such as 2-hexyne-1-ol, were also oxidized to 2-hexyne-1-al with lower yield 12% (entry 19).

At the end of each reaction, the catalyst was separated out using separating funnel, washed three times with acetonitrile and dried at 60 °C. In the consecutive cycles, the catalyst was recovered and reused again. The studies confirmed that during the oxidation process, dissociation of the ligand from the metal ions doesn't occur.

3 | CONCLUSION

In conclusion, we have reported an efficient practical method for the catalytic oxidation of benzyl alcohol, hetero-aryl alcohols and propargylic alcohols using H_2O_2 as terminal oxidant under mild conditions using available heterobimetallic vanadium(V) complexes and cheap available starting materials. The process is simple, efficient and the catalyst can be easily recovered without any lost during the whole conversion process.

4 | MATERIALS AND METHODS

4.1 | Materials and instruments

All alcohols such as benzyl alcohol, aliphatic alcohols, propargylic alcohols and solvents were reagent grade and used as received. The ^{1}H NMR were recorded with a Bruker Avance II 400 MHz in DMSO solution using TMS as an internal standard.

4.2 | Procedure for oxidation of alcohols

In 50 ml round bottom flask containing benzyl alcohol (0.05 g, 0.5 mmol), 15% H_2O_2 (0.3 g, 8.83 mmol), complexes 1 and 2 (0.01 mmol) were added. The reaction mixture was first stirred at ambient temperature for 20 min and then temperature was raised to 70 °C for 2 h. The reaction mixture containing crude product was extracted and dried over anhydrous sodium sulfate. The oxidized product was purified by column chromatography to afford the corresponding aldehyde. The NMR spectra of the oxidized products are given in the supporting information.

4.3 | Characterization data

4.3.1 | Benzaldehyde

Colourless liquid; yield, 89%; ^{1}H (400 MHz, $CDCl_3$): 9.96 (s, 1H), 7.87-7.4 (m, 5H); ^{13}C (100 MHz, CDCl3): 192.5, 136.2, 134.4, 129.8, 128.9; IR (KBr): 1702 cm^{-1}.

4.3.2 | p-Methoxybenzaldehyde

Colourless liquid; yield: 91%; ^{1}H (400 MHz, $CDCl_3$): 9.78 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H); 13C (100 MHz, $CDCl_3$): 190.83, 164.5, 131.9, 129.8, 114.3, 55.4; IR (KBr): 1699 cm^{-1}.

4.3.3 | p-Nitrobenzaldehyde

Pale yellow solid; yield: 80%; ^{1}H (400 MHz, $CDCl_3$): 10.17 (s, 1H), 8.41 (d, J = 8.0 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H); 13C (100 MHz, CDCl3): _ 190.2, 140.0, 130.4, 124.3; IR (KBr): 1677 cm^{-1}.

4.3.4 | Cinnamaldehyde

Yellow liquid; yield: 88%; ^{1}H (400 MHz, $CDCl_3$): 9.57 (d, J = 7.5 Hz, 1H), 7.31-7.18 (m, 6H), 6.55-6.24 (m, 1H); ^{13}C (100 MHz, CDCl3): 194.4, 153.5, 136.8, 130.8, 129.1, 128.3; IR (KBr): 1677 cm^{-1}.

4.3.5 | m-Chlorobenzaldehyde

Light yellow liquid; yield: 74%; ^{1}H (400 MHz, $CDCl_3$): 9.99 (s, 1H), 8.00 (s, 1H), 7.84 (m, 1H), 7.46 (m, 1H); 13C (100 MHz, CDCl3): 190.9, 128.8, 129.4, 130.9, 131.5; IR (KBr): 1702 cm^{-1}.

4.3.6 | p-Methylbenzaldehyde

Colourless liquid; yield: 88%; ^{1}H (400 MHz, $CDCl_3$): 9.84 (s, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C (100 MHz, $CDCl_3$): 190.7, 132.0, 129.4, 128.3, 18.8; IR (KBr): 1685 cm^{-1}.

4.3.7 | Furfural

Light yellow liquid; yield: 85%; ^{1}H (400 MHz, $CDCl_3$): 9.66 (s, 1H), 7.32-7.31 (d, J = 4.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$): 177.8, 152.7, 148.1, 121.4, 112.5; IR (KBr): 1680 cm^{-1}.

4.3.8 | Pyridine-2 Cabaldehyde

Colourless liquid; yield: 89%: ^{1}H (400 MHz, $CDCl_3$): 9.66 (s, 1H), 7.32 (d, J = 3.6 Hz, 1H), 6.64-6.63 (m, 1H); ^{13}C (100 MHz, $CDCl_3$): 191.2, 152.7, 151.3, 137., 124.3, 121.8; IR (KBr): 1680 cm^{-1}.

4.3.9 | Thiophene-2-carbaldehyde

Light yellow liquid; yield: 78; ^{1}H (400 MHz, $CDCl_3$): 9.95 (s, 1H), 7.72-7.79 (m, 2H), 7.22 (m, 2H); ^{13}C (100 MHz, $CDCl_3$): 183.8, 144.0, 136.8, 135.3, 128.1; IR (KBr): 1676 cm^{-1}.

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