

Catalytic activities of a Mononuclear Vanadium(V) Complex with Phenol based Ligands

Mainak Debnath^{1*}, Indrajit Bhattacharyya¹, Sreyasree Basu¹,

¹Department of Applied Science & Humanities, Guru Nanak Institute of Technology, West Bengal, India

ABSTRACT

The present article describes the effective catalytic activities of a known mononuclear Vanadium(V) complex towards oxidative bromination of salicylaldehyde and oxidation of aromatic hydrocarbon, namely, toluene to give 5-Br-salicylaldehyde and benzoic acid respectively as major products.

Keywords: Vanadium(V) complex, Catalytic bromination, Catalytic oxidation of aromatic hydrocarbon

INTRODUCTION

The research on the coordination chemistry of vanadium has incepted from the discovery of vanadium(V) in the active site of vanadate dependent haloperoxidases (V-HalPO) [1] and its importance in catalytic reactions [2-9]. Haloperoxidases are enzymes that are well known to catalyze the oxidation of halides to the corresponding hypohalous acids or to a related two-electron oxidized halogenating intermediate such as OX^- , X_3^- and X^+ , using hydrogen peroxide as the oxidant. Halogenated compounds are generally formed in the presence of suitable nucleophilic acceptors [10,11]. These products probably are formed because of the biocidal effects of HOBr and some of the organohalogens. Kinetic studies suggest the formation of peroxido-vanadium intermediate, which ultimately facilitates the halogenation possibly via HOBr, Br_2 or Br_3^- formation [12-14]. Existences of peroxido as well as hypobromite-like vanadium intermediate in solution have been demonstrated in earlier literatures [15,16]. Moreover, evidences on peroxide binding to the active centre of bromoperoxidase isolated from *Ascophyllum nodosum* has been presented by Căsnýet. Al [17].

A variety of vanadium compounds have been studied as functional models for V-haloperoxidases to get a better understanding of the working mechanism of the vanadium haloperoxidase enzyme and to determine the role of vanadium. A lot of interests towards the exploration of chemical and electrochemical reactivity of oxidovanadium(V) complexes, and dioxygen activation along with the ability to form oxido-peroxido vanadium(V) species - an important reactive intermediate in the *in-vivo* enzymatic processes [18,19-21] is now apparent. Oxidoperoxido-vanadium(V) complexes are also known to exist in some catalytic cycles in the oxidation of various organic substrates [22-24]. Due to their high charge/radius ratio, vanadium(V) centres are usually strong Lewis acids, which lead them to activate the peroxidic reagents like H_2O_2 , molecular O_2 , peroxyacetic acid etc. [25] which make them to act as catalyst precursors in various oxidation reactions like bromination, epoxidations of alkenes and allylic alcohols, hydroxylations of alkanes and arenes, and oxidations of primary and secondary alcohols to the corresponding aldehydes and ketones [26,27].

Bio-degradation of hydrocarbons (aromatic and aliphatic) is catalyzed by some bacteria and yeast [28,29]. Catalytic oxidation of hydrocarbons to their alcoholic, phenolic, carbonyl, or carboxylic acid functions [30-32] finds a wide range of applications in many synthetic organic reactions as well as in the industry. The first catalytic hydrocarbon oxidation using oxidovanadium(V) compounds was furnished by Walter et al. [33] Many vanadium compounds, in combination with H_2O_2 or O_2 have also been used as catalyst for the oxidation of hydrocarbons, [28,29, 31-33] but so far the yields and TON (turn over number) obtained are not remarkable. Recently, vanadium(V) as well as group-4 transition metal complexes of *tri*- (ONO) and *tetra*- (ONNO) dentate ethylenediamine-*bis*(phenolate) ligands have proven to be highly active olefin polymerization catalysts [34-36]. All the above findings motivated us to design and synthesize the structural and functional models of biomolecules with potential ability to catalyze hydrocarbon oxidation and oxidative bromination. The model complexes, described here, are found to catalyze the oxidation of aromatic hydrocarbons and bromination of salicylaldehyde.

EXPERIMENTAL SECTION

A. Physical Measurement

Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyser. Infrared spectra ($400\text{--}4000\text{ cm}^{-1}$) were recorded from KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer. Mass spectra were recorded on a JEOL GCMATE II GC-MS instrument. GC analyses were carried out in a Agilent 7890A GC instrument with FID detector.

B. Materials

Starting materials for the synthesis of the ligand and complex (**1**) namely, 2,4-di-*tert*-butylphenol (Aldrich), trans-1,2-diaminocyclohexane (Aldrich), formaldehyde (Merck India), [VO(acac)₂] (Loba India), trimethylamine (TEA) (Merck India) were of reagent grade and used as received. Solvents like methanol, ethanol, acetonitrile (Merck India) were of reagent grade and dried by standard methods before use. Substrate, namely, salicylaldehyde (Loba, India) used in the catalytic reactions is of reagent grade and used as received. Another substrate, toluene (Merck India) used in the catalytic reactions was of spectroscopic grade and used as received. 30% H₂O₂ (Merck India), KBr (Merck India) and 70% of HClO₄ (Aldrich) were used in the catalytic bromination reactions.

C. Syntheses of the ligand and complex

Syntheses of the ligand and the complex were described in our earlier work [37].

D. Experimental set up for catalytic bromination

The substrate, namely salicylaldehyde (20 mmol), was dissolved in a mixed solvent (H₂O: MeOH: THF = 4: 3: 2) [38] and the resulting solution was taken in a 50 mL capacity round bottom flask. To the above solution was then added KBr (40 mmol) followed by 2 ml (67 mmol) of 30% H₂O₂. An appropriate catalyst (complex) (0.025 g, 0.04 mmol) and 70% HClO₄ (0.10 ml) were added to it and the reaction was considered to begin with stirring. After 2 h of stirring at ambient temperature 0.1 ml of 70% HClO₄ was further added and stirring was continued for next 12 h. The separated white product was filtered, washed with water followed by diethyl ether and dried in air. The crude mass was dissolved in CH₂Cl₂ and insoluble material was separated by filtration. After evaporation of the solvent to *ca.* 5 ml it was loaded over column packed with silica gel. The fast moving band on elution with CH₂Cl₂ was collected and evaporated to dryness to give 5-bromo-salicylaldehyde as major product.

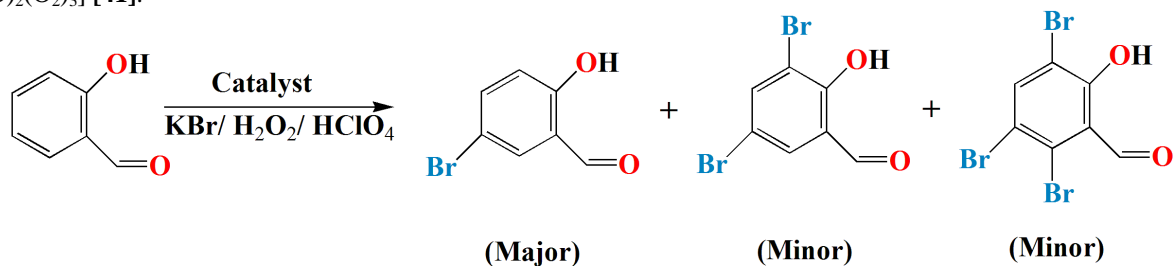
E. Experimental set up for the oxidation of aromatic hydrocarbon (toluene)

A mixture of the complex (the catalyst) (0.012 g, 0.02 mmol) and the substrate, namely toluene (5 mmol), were dissolved in 10 ml MeCN solvent and the resulting solution was taken into a 50 mL capacity two necks round bottom flask, one of which was closed with a rubber septum and the other was fitted with a condenser. To the above solution was then added 2 ml (67 mmol) of 30% H₂O₂ and the resulting solution immediately turned yellow. The solution was then heated upto 50 °C on an oil bath for 24 h and 0.5 ml (17 mmol) of H₂O₂ was added intermittently at a time interval of 60 min. When required, an aliquot (0.1 mL) of the reaction solution was withdrawn with the help of long a needle syringe and was subjected to multiple ether extraction and 1 μL of concentrated ether extract was injected to the GC port with the help of 10 μL syringe. The retention time of the peaks was compared with those of commercial standards.

RESULTS AND DISCUSSIONS

Catalytic study of the complex VO(L¹)(L²)

Oxidative bromination: Vanadium(V) complexes catalyze the oxidative bromination of organic substrates in the presence of H₂O₂ and bromide ion [39,40] where vanadium were claimed to coordinate with 1 or 2 equivalents of H₂O₂, forming oxo-monoperoxo, [VO(O₂)]⁺ and oxo-diperoxo, [VO(O₂)₂]⁻ species which further giving rise the actual oxidant [(VO)₂(O₂)₃] [41].



Scheme 1: Catalytic bromination of salicylaldehyde with KBr/H₂O₂ in presence of HClO₄

Then it oxidizes bromide species (most likely to be HOBr) and brominates the substrate. Here also, the complex is found to be able to catalyze the oxidative bromination of salicylaldehyde to give 5-bromosalicylaldehyde as major product along with 3,5-dibromosalicylaldehyde and 2,3,5-tribromosalicylaldehyde as a minor products, using H₂O₂/KBr in the

presence of HClO_4 in mixed solvents ($\text{H}_2\text{O}:\text{MeOH}:\text{THF}=4:3:2$) [33,38] (Scheme 1 and Figure 1). Presence of acid is found to be essential during catalytic reaction to facilitate the bromination but excess of HClO_4 (>80 mmol) causes decomposition of the catalysts as well as lowering of selectivity of the reaction. In absence of acid no catalysis is observed. Under the reaction conditions, a maximum of 76% is achieved (Table 1). In the absence of the catalyst, the reaction mixture gives only 4% conversion of salicylaldehyde to 5-bromosalicylaldehyde.

Catalytic oxidation of aromatic hydrocarbon (toluene)

The described complex $\text{VO}(\text{L}^1)(\text{L}^2)$ is also found to be effective catalyst for the oxidation of aromatic hydrocarbon, namely toluene. The major products for the oxidation of toluene are benzoic acid (~65%), benzyl alcohol and benzaldehyde (~10%) in MeCN solvent in presence of H_2O_2 with substrate:catalyst = 250:1 at 50°C with TON 188 (Table 2). The temperature 50°C was found to be the optimum temperature for these catalytic reactions and at above or below this temperature the % yield of products were found to be less.

Figures and Tables

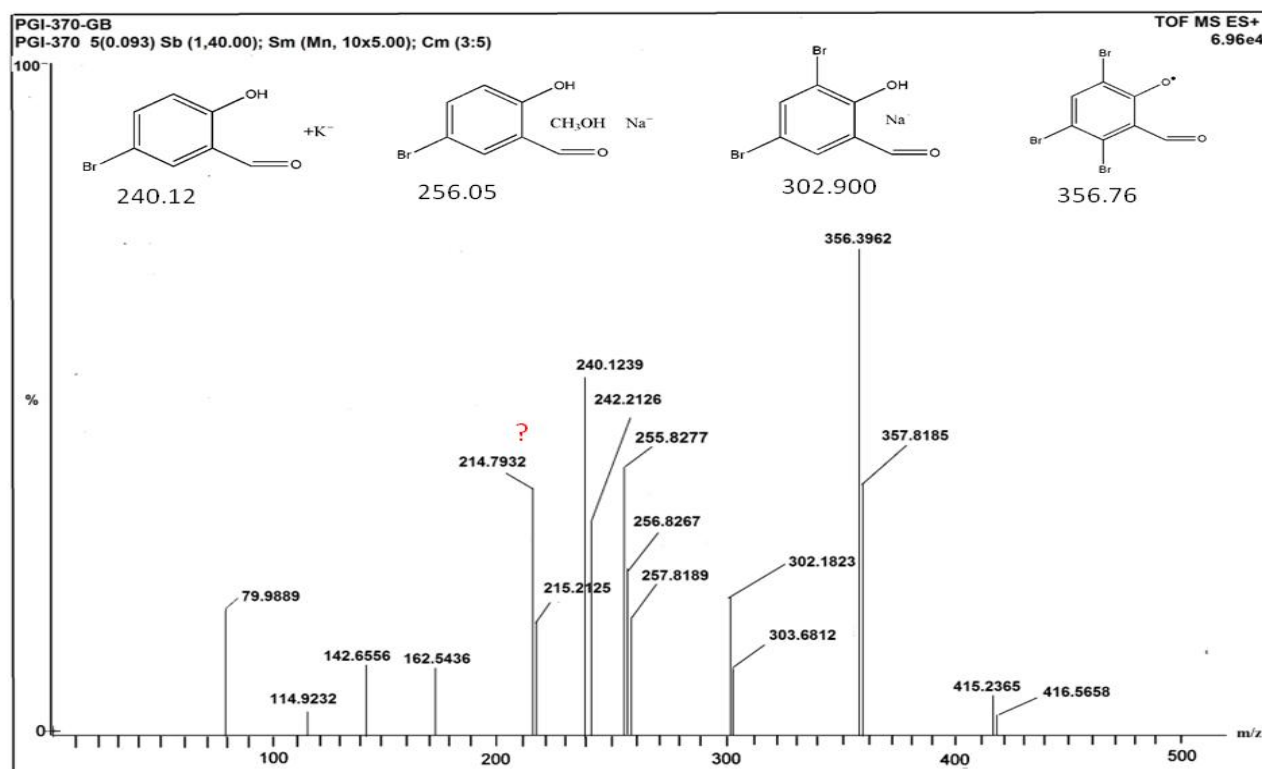


Figure 1: Products of catalytic bromination of salicylaldehyde by the complex

Table 1: Catalytic parameters for the bromination of salicylaldehyde by $\text{KBr}/\text{H}_2\text{O}_2$ ($\text{KBr} = 40$ mmol, $\text{H}_2\text{O}_2 = 2$ ml i.e. 67 mmol) using the complex as catalyst (0.04mmol) in mixed solvents $\text{H}_2\text{O}:\text{MeOH}:\text{THF} = 4:3:2$ at room temperature (25°C) in presence of 0.2 ml HClO_4 .

Catalyst	Substrate (Salicylaldehyde)	Reaction time (hr.)	Conversion (%)	Yield (%)		Selectivity	TON †
				5-Br-sal (major)	3,5-di-Br-sal and 2,3,5-tri-Br-sal (minor)		
Complex $\text{VO}(\text{L}^1)(\text{L}^2)$	20 mmol	03	09	08	01	88.88	
		06	30	26	04	86.67	
		09	56	49	07	87.50	
		12	76	65	11	85.52	380

†TON (turn over number) is determined by the ratio of no. of moles of substrate converted to product and the number of moles of catalyst (0.04 mmol) used.

Table 2: Catalytic parameters for the oxidation of aromatic hydrocarbons by H₂O₂ using complex VO(L¹)(L²) as catalysts (0.02 mmol) with substrate:catalyst = 250:1 and H₂O₂:substrate= 13:1 at 50 °C.

Catalyst	Substrate (toluene)	Reaction time (hr.)	Conversion (%)	Yield		Selectivity	TON†
				Benzoic acid (major)	Benzyl alcohol and benzaldehyde (minor)		
Complex VO(L ¹)(L ²)	5 mmol	24	75	65	10	86.67	188

†TON (turn over number) is determined by the ratio of no. of moles of substrate converted to product and the number of moles of catalyst (0.02mmol) used.

CONCLUSION

The complex described here, is found to catalyze the oxidative bromination of salicylaldehyde with 5-Br-sal as the major product using H₂O₂/KBr in the presence of HClO₄ in mixed solvents (H₂O:MeOH: THF= 4: 3: 2) as well as oxidation of toluene (aromatic hydrocarbon) to give benzoic acid as major product in presence of H₂O₂ at 50 °C..

ACKNOWLEDGMENT

This paper has been written with all coordination of all the writers, and help of all the writers mentioned in the reference. We would also like to thank our Principal Sir of Guru Nanak Institute of Technology, Prof. (Dr.) Swarup Kumar Mitra, for giving us this opportunity.

REFERENCES

- [1]. Maurya, M. R. *Coord. Chem. Rev.* **2003**, 237, 163.
- [2]. (a) Butler, A. *Coord. Chem. Rev.* **1999**, 187, 17 (b) Butler, A. in *Bioinorganic Catalysis*, ed. Reedijk, J.; Bouwman, E.; Dekker, M. New York, 2nd edn, **1999**, ch. 5.
- [3]. Weyand, M.; Hecht, H. J.; Kieb, M.; Liaud, M. F.; Vilter, H.; Schomburg, D. *J. Mol. Biol.* **1999**, 293, 595.
- [4]. Isupov, M. I.; Dalby, A. R.; Brindley, A. A.; Izumi, Y.; Tanabe, T.; Murshudov, G. N.; Littlechild, J. A. *J. Mol. Biol.* **2000**, 299, 1035.
- [5]. Colpas, G. J.; Hamstra, B. J.; Kampf, J. W.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1996**, 118, 3469.
- [6]. Hamstra, B. J.; Colpas, G. J.; Pecoraro, V. L. *Inorg. Chem.* **1998**, 37, 949.
- [7]. Littlechild, J. A.; Garcia-Rodriguez, E. *Coord. Chem. Rev.* **2003**, 237, 65.
- [8]. Macedo-Ribeiro, S.; Hemrika, W.; Renirie, R.; Wever, R.; Messerschmidt, A. *J. Biol. Inorg. Chem.* **1999**, 209, 209.
- [9]. Messerschmidt, A.; Wever, R. *Proc. Natl. Acad. Sci. USA*, **1996**, 93, 392.
- [10]. Geschwend, P.M.; MacFarlane, J.K.; Newman, K.A. *Science*, **1985**, 227, 1033.
- [11]. Gribble, G.W. *Chem. Soc. Rev.* **1999**, 28, 335.
- [12]. Butler, A. in *Bioinorganic Catalysis*, 2nd edn., Reedijk, J.; Bouwman, E.; Dekker, M. (Eds.), New York, **1999**, pp. 55–77.
- [13]. Pecoraro, V.L.; Slebodnick, C.; Hamstra, B. in: Crans, D.C.; Tracy, A.S. (Eds.), *Vanadium Compounds: Chemistry, Biochemistry and Therapeutic Applications*, ACS Symposium Series, **1998**, pp. 711 (Chapter 12).
- [14]. Butler, A. *Coord. Chem. Rev.* **1999**, 187, 17.
- [15]. Conte, V.; Bortolini, O.; Carraro, M.; Moro, S. *J. Inorg. Biochem.* **2000**, 80, 41.
- [16]. Bortolini, O.; Carraro, M.; Conte, V.; Moro, S. *Eur. J. Inorg. Chem.* **2003**, 1, 42.
- [17]. Čásný, M.; Rehder, D.; Schmidt, H.; Vilter, Conte, V. *J. Inorg. Biochem.* **2000**, 80, 157.
- [18]. "Vanadium and its Role in Life", 'Metal Ions in Biological Systems', Eds. Sigel, H.; Sigel, A.; Dekker, M. New York, **1995**, 31, 543.
- [19]. Rehder, D.; Santoni, G.; Licini, G.M.; Schuzke, V.; Meier, B. *Coord. Chem. Rev.* **2003**, 237, 53.
- [20]. Carter-Franklin, R.A.; Little, R.D.; Butler, A. *J. Am. Chem. Soc.* **2003**, 125, 3688.
- [21]. Thompson, K. H.; Mcweill, J. H.; Orvig, C. *Chem. Rev.* **1999**, 99, 2561.
- [22]. Remias, J.E.; Pavlosky, J.A.; Sen, A. *J. Mol. Catal. A: Chem.* **2003**, 203, 179.
- [23]. Battistel, E.; Tassinari, R.; Fornaroli, M.; Bonoldi, L. *J. Mol. Catal. A: Chem.* **2003**, 202, 107.
- [24]. (a) Mohebbiand, S.; Sererstini, A.H.; *Trans. Met. Chem.* **2006**, 31, 749 (b) Justino, L. L. G.; Ramos, M. L.; Nogueira, F.; Sobral, A. J. F. N.; Geraldés, C. F. G. C.; Kaupp, M.; Burrows, H. D.; Fiolhais, C.; Gil, V. M.

- S. *Inorg. Chem.* **2008**, 47, 7317 (c) Justino, L. L.; Ramos, M. L.; Kaupp, M.; Burrows, H. D.; Fiolhais, C.; Gil, V. M. *Dalton Trans.* **2009**, 28, 9735.
- [25]. (a) Conte, V.; Di Furia, F.; Moro, S. *J. Phys. Org. Chem.* **1996**, 9, 329 (b) Cuervo, L.G.; Kozlov, Y.N.; Süß-Fink, G.; Shul'pin, G.B. *J. Mol. Catal. A: Chem.* **2004**, 218, 171.
- [26]. (a) Butler, A.; Clague, M.J.; Meister, G.E. *Chem. Rev.* **1994**, 94, 625 (b) IMPRIMATUR POUR LA THESE, Iron and Vanadium complexes for the catalytic oxidation of hydrocarbons: Chemical catalyst and biomimetic models, by Cuervo, M. L.G. October, **2003** (c) Fernández, T.L.; Souza, E. T.; Visentin, L.C.; Santos, J.V.; Mangrich, A.S.; Faria, R.B.; Antunes, O.A.C.; Scarpellini, M.J. *Inorg. Biochem.* **2009**, 103, 474.
- [27]. Süß-Fink, G.; Cuervo, L.G.; Therrien, B.; Stoeckli-Evans, H.; Shul'pin, G.B.; *Inorg. Chim. Acta*, **2004**, 357, 475.
- [28]. Cheng, Q.; Thomas, S. M.; Rouvière, P.; *Appl. Biochem. Microbiol.* **2002**, 58, 704.
- [29]. Mimoun, H.; Saussine, L.; doire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, 105, 3101.
- [30]. Shul'pin, G. B.; Süß-Fink, G.; Shul'pin, L.S. *Chem. Commun.* **2000**, 13, 1131.
- [31]. Walter, J.; *J. Prakt. Chem.* **1895**, 51, 107.
- [32]. (a) Elemeans, J.A.A.W.; Bijsterveld, E.J.A.; Rowan, A. E.; Nolte, R.J.M. *Chem. Commun.* **2000**, 24, 2443 and references cited therein (b) Periana, R.A.; Mironov, D.; Taube, D.; Bhalla, G.; Jones, C. J. *Science*, **2003**, 301, 814 and references cited therein.
- [33]. Tshuva, E.Y.; Goldberg I.; Kol, M. *J. Am. Chem. Soc.* **2000**, 122, 10706.
- [34]. Das, S.; Bhowmick, T.; Punniyamurthy, T.; Dey, D.; Nath, J.; Choudhuri, M. K. *Tetrahedron Lett.* **2003**, 44, 4915.
- [35]. (a) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, 118, 10008 (b) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1996**, 119, 3830.
- [36]. Lorber, C.; Wolff, F.; Choukroun, R.; Vendier, L. *Eur. J. Inorg. Chem.* **2005**, 14, 2850.
- [37]. Debnath, M.; Bhattacharyya, I.; Basu, S., *Int. J. Enhanced Research in Sc. Tech. & Engg.*, 2024, 13, 4, 154.
- [38]. B.F. Sels, D. E. De Vos, M. P. Buntinx, A. Jacobs, *J. Catal.*, 2003, **216**, 288-297.
- [39]. Martinez-Perez, J.A.; Pickel, M.A.; Caroff, E.; Woggon, W.D. *Synlett.* **1999**, 12, 1875.
- [40]. Perrin, C.L.; Dwyer, T.J. *Chem. Rev.* **1990**, 90, 935.
- [41]. Ligtenberg, A.G.J.; Hage, R.; Feringa, B.L. *Coord. Chem. Rev.*, **2003**, 237, 89.