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Structural and Functional Models of Vanadate-Dependent Haloperoxidases (VHPO)†

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The active center of vanadate-dependent haloperoxidases (VHPO) is constituted by vanadate(V) covalently linked to the imidazole moiety of a histitine side-chain of the protein. Vanadium in these enzymes is in a trigonal-bipyramidal environment, with the imidazole-N and an OH^- in the axial positions. We have prepared vanadium(V) complexes with ONO and ONN donor ligands that partly model active site structure of vanadate-dependent haloperoxidases. Generally, KVO_3 reacts with sodium/potassium salt of ligands in aqueous medium at pH *ca*. 7.0 to give dioxovanadium(V) complexes with these ligands. Reaction of $[V^{IV}O(acac)_2]$ with these ligands followed by aerial oxidation also provides dioxovanadium(V) complexes. The catalytic potential of these dioxidovanadium(V) complexes as mimics for the activity of vanadate-dependent haloperoxidases and oxidation of other organic substrates are also studied.

Key Words: Vanadium complexes, Haloperoxidases, Structural models, Functional models, Catalysts.

INTRODUCTION

Vanadate-dependent haloperoxidases enzymes *e.g. Ascophyllum nodosum* (isolated from brown algae)[1], *Carallina officinalis* (from red algae)[2] and *Curvularia inaequalis* (from fungi)[3] have been structurally characterized and all of these show a close similarity in their active centers. A representative structure considering *Ascophyllum nodosum* as an example is presented in Fig. 1.

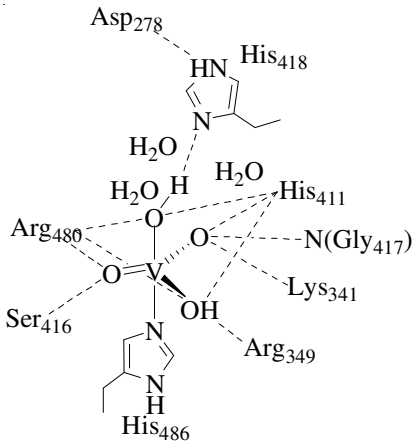

Fig. 1. Active site structure of vanadate-dependent haloperoxidase from *Ascophyllum nodosum*

In these enzymes, the overall geometry around vanadium is trigonal bypyramidal with O_4N coordination. The peroxo form $\{VO(O_2)(OH)(his)\}$, where peroxo ligand occupies two equatorial positions, has also been structurally characterized for the fungal *Curvularia inaequalis* and has a tetragonal pyramid structure[4].

These enzymes catalyze the oxidation of halides (X^-) to hypohalous acid (HOX, along with other oxidized halogen species) according to eqn. (1) using H_2O_2 as an oxidant followed by non-enzymatically halogenation of organic compounds, eqn. (2)[5-8].

$$X^- + H_2O_2 + H^+ \rightarrow HOX + H_2O \quad (1)$$

($X^- = Cl^-$, Br^- and I^-)

$$HOX + RH \rightarrow RX + H_2O \quad (2)$$

(RH = organic substrate, RX = halogenated organic product)

Oxidation of (prochiral) sulfides to (chiral) sulfoxides, eq. (3)[9,10] has also been observed frequently.

$$RSR' + H_2O_2 \rightarrow RS(O)R' + H_2O \quad (3)$$

Vanadium (V) complexes provide suitable structural and/or functional models for these enzymes[11-15] as they are stable under aerobic conditions. Model experiments show that intermediate species having $\{VO(H_2O)\}$, $\{VO_2\}$, $\{VO(OH)\}$ and $\{VO(O_2)\}$ cores form during catalytic turnover.

Recently, we have started work on the coordination chemistry of oxovanadium(V) and dioxovanadium(V) in order

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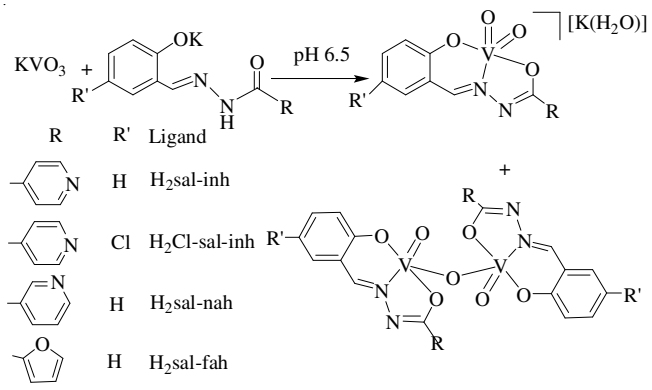
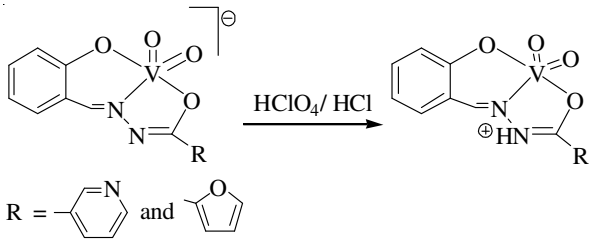
to provide suitable structural and functional models of haloperoxidases. In this report, results of our efforts are discussed. Reactivity of the resulting complexes with various substrates is also presented.

Structural models of haloperoxidases: Several groups worldwide have prepared structural models[11-15], we started our work with simple ligands derived from salicylaldehyde, substituted salicylaldehyde and isonicotinic acid hydrazide (H_2R'-sal-inh, I). Thus, the dioxovanadium(V) complexes $[K(H_2O)][V^VO_2(sal\text{-}inh)]$ and $[K(H_2O)][V^VO_2(Cl\text{-}sal\text{-}inh)]$ have been isolated by the reaction of potassium vanadate and potassium salt of the corresponding ligands at pH *ca*. 7.5. Lowering the pH of the reaction mixture to *ca*. 6.5 causes the formation of oxo-bridged binuclear complexes $[\{V^VO(sal\text{-}inh)\}_2\mu\text{-}O]$ and $[\{V^VO(Cl\text{-}sal\text{-}inh)\}_2\mu\text{-}O]$, respectively, along with the respective expected anionic species; **Scheme-I**. The mixture of anionic and neutral complexes could be separated easily by fractional crystallization from methanol[16]. Using NH_4VO_3 in place of KVO_3 results in the formation of the corresponding ammonium salt $NH_4[V^VO_2(sal\text{-}inh)(H_2O)]$ and the neutral species $[\{V^VO(sal\text{-}inh)\}_2\mu\text{-}O]$[16]. Aanionic and neutral μ-oxo binuclear complexes of the types $[V^VO_2L]^-$ and $[(VOL)_2\mu\text{-}O]$ (H_2L = ligands) with ligands H_2sal-nah and H_2sal-fah have also been isolated similarly as reported above[17].



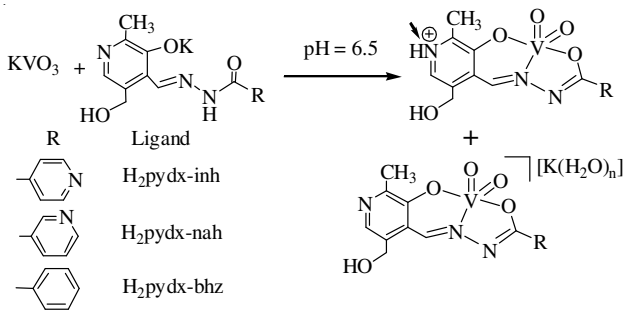
Scheme-I: Synthetic procedure for vanadium(V) complexes

Reaction of aqueous solution of $[V^VO_2(sal\text{-}nah)]^-$ and $[V^VO_2(sal\text{-}fah)]^-$ with $HClO_4$ or HCl yields the neutral complexes $[V^VO_2(Hsal\text{-}nah)]$ and $[V^VO_2(Hsal\text{-}fah)]$, respectively in which one of the nitrogens of the -N=N- group is protonated (**Scheme-II**). Isolation and structural characterization of such complexes, *e.g.* $[V^VO_2(Hsal\text{-}bhz)]$ has been reported by Plass *et al.*[18].



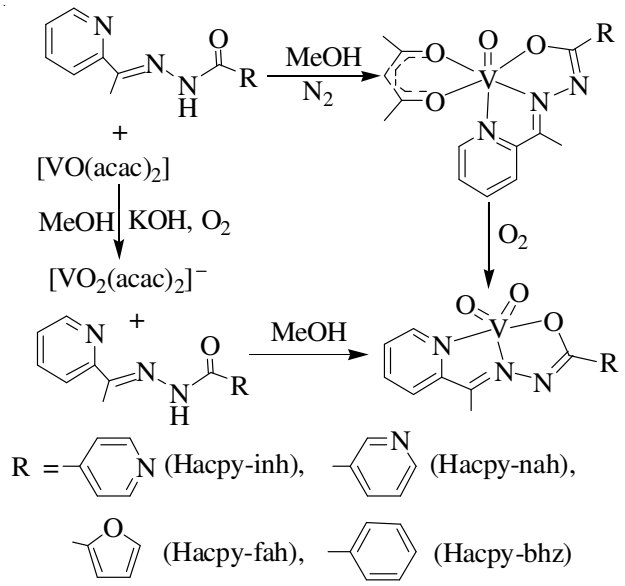
Scheme-II: Synthesis of neutral dioxovanadium(V) complexes

Reaction of equimolar amounts of potassium salt of ligands H_2pydx-inh, H_2pydx-nah and H_2pydx-bhz with KVO_3 at pH *ca*. 6.5 produces $[K(H_2O)_3][VO_2(pydx\text{-}inh)]$, $[K(H_2O)_2][V^VO_2(pydx\text{-}nah)]$ and $[K(H_2O)_2][V^VO_2(pydx\text{-}bhz)]$, respectively, along with neutral species $[V^VO_2(Hpydx\text{-}inh)]$, $[V^VO_2(Hpydx\text{-}nah)]$ and $[V^VO_2(Hpydx\text{-}bhz)]$ (**Scheme-III**). All these complexes are good structural models of VHPO. IR spectroscopy suggests protonation of pyridine's nitrogen to stabilize these complexes as neutral species[19].



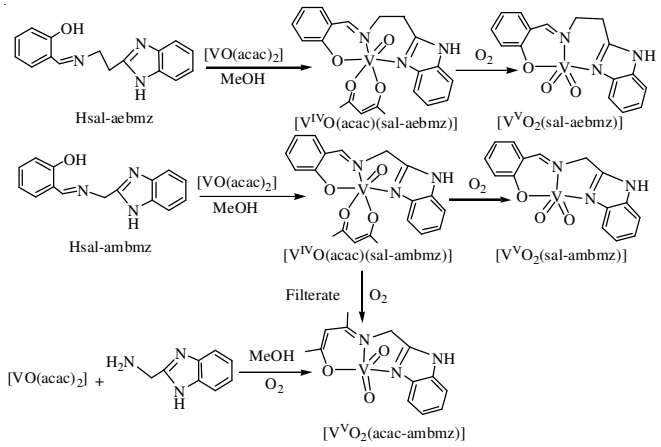
Scheme-III: Synthetic procedure for pyridixal based vanadium(V) complexes

Ligands having a monobasic tridentate ONN donor systems, *e.g*. Hacpy-inh and Hacpy-bhz also provide dioxovanadium(V) complexes. These complexes were prepared by the reaction of $[V^{IV}O(acac)_2]$ with ligands followed by aerial oxidation. Aerially oxidized $[V^{IV}O(acac)_2]$ (*i.e*. $[V^VO_2(acac)_2]^-$) directly give dioxovanadium(V) complexes on reaction with these ligands. **Scheme-IV** represents the synthetic procedure[20]. The coordination geometry around vanadium in $[V^VO_2(acpy\text{-}inh)]$ and $[V^VO_2(acpy\text{-}bhz)]$ can be described as distorted square-pyramidal, distortion towards a trigonal bipyramid, where one of the doubly bonded oxo groups, the pyridine-N, imine-N and the amide-O of the monobasic tridentate ligands form the base. Very similar ligands Hacpy-nah and Hacpy-fah gave binuclear complexes $[\{V^VO(acpy\text{-}nah)\}_2(\mu\text{-}O)_2]$ and $[\{V^VO(acpy\text{-}fah)\}_2(\mu\text{-}O)_2]$, respectively where one of the V-O distances is longer than the expected and their solution behaviours are similar to that shown by $[V^VO_2(acpy\text{-}inh)]$ and $[V^VO_2(acpy\text{-}bhz)]$, confirming their monomeric nature in solution[21]. The monomeric $[V^VO_2(acpy\text{-}fah)]$ has also been isolated and characterized by single crystal X-ray method[22].



Scheme-IV: Dioxovanadium(V) complexes with monobasic tridentate ONN donor ligand

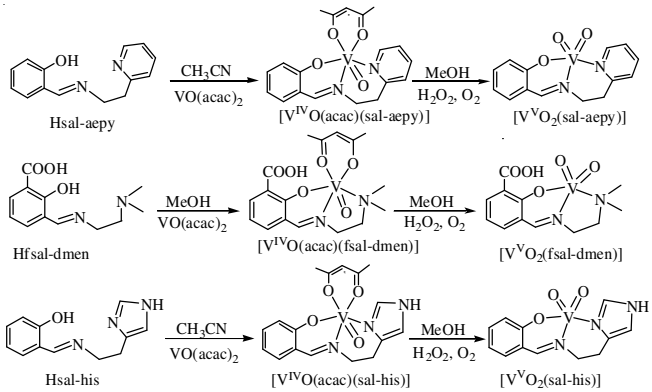
Complex $[V^{V}O_2(acac\text{-}ambmz)]$ along with minor amount of $[V^{IV}O(sal\text{-}phen)]$ has been isolated from the filtrate obtained after isolating $[V^{IV}O(acac)(sal\text{-}ambmz)]$ from the reaction of equimolar amounts of $[V^{IV}O(acac)_2]$ and Hsal-ambmz in refluxing methanol; **Scheme-V**. Complex $[V^{V}O_2(acac\text{-}ambmz)]$ can also be prepared directly by reacting $[V^{IV}O(acac)_2]$ with ambmz followed by aerial oxidation. Aerial oxidation of $[V^{IV}O(acac)(sal\text{-}ambmz)]$ and $[V^{IV}O(acac)(sal\text{-}aebmz)]$ gives the corresponding dioxovanadium(V) complexes $[V^{V}O_2(sal\text{-}ambmz)]$ and $[V^{V}O_2(sal\text{-}aebmz)]$, respectively. These complexes can also be obtained from the reaction of aerially oxidized solutions of $[V^{IV}O(acac)_2]$ with the respective ligand in methanol. These complexes can be considered to be structural models of VHPO as they attain the geometry of a trigonal bipyramid, distorted toward the square pyramid. The τ-parameters for $[V^{V}O_2(acac\text{-}ambmz)]$ and $[V^{V}O_2(sal\text{-}ambmz)]$ amount to 0.71 and 0.60, respectively[23].



Scheme-V: Synthesis of vanadium complexes with benzimidazole based ligands

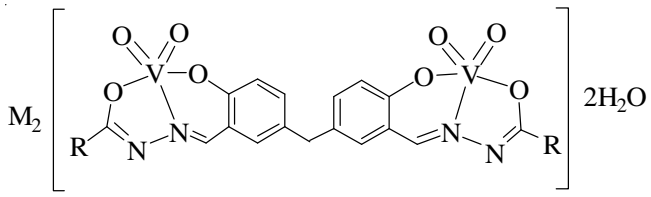
Similarly, the reaction of $[V^{IV}O(acac)_2]$ with equimolar amount of Hsal-aepy, Hfsal-dmen and Hsal-his in solvent yield the oxovanadium(IV) complexes $[V^{IV}O(acac)(sal\text{-}aepy)]$, $[V^{IV}O(acac)(fsal\text{-}dmen)]$ and $[V^{IV}O(acac)(sal\text{-}his)]$, respectively. Dioxovanadium(V) complexes $[V^{V}O_2(sal\text{-}aepy)]$, $[V^{V}O_2(fsal\text{-}dmen)]$ and $[V^{V}O_2(sal\text{-}his)]$ were obtained by the aerobic oxidation of respective oxovanadium(IV) complexes in solvent in the presence of a small amount of H_2O_2; **Scheme-VI**[24-26]. Single crystal X-ray diffraction study of $[V^{V}O_2(sal\text{-}dmen)]$ confirms the distorted square pyramidal structure[25]. The structure of this compound was also previously reported[27].

Complex $[V^{V}O_2(sal\text{-}aepy)]$ exhibits two resonances at δ = -517 and -491 ppm in DMSO-d_6[24]. These chemical shifts are within the values expected for dioxovanadium(V) complexes containing a O/N donor set[28]. The first major signal at δ = -517 ppm (92 %) is due to authentic complex *i.e.* $[V^{V}O_2(sal\text{-}aepy)]$. The resonance at -491 ppm gains intensity with time in DMSO (24 h) and therefore is assignable to $[V^{V}O_2(sal\text{-}aepy)(DMSO)]$. Addition of methanol to $[V^{V}O_2(sal\text{-}aepy)]$ in DMSO results in the appearance of a single signal at -542 ppm, identical to what is obtained by recording ^{51}V NMR of $[V^{V}O_2(sal\text{-}aepy)]$ directly in MeOH only. The signal at -515 ppm is, therefore, assigned to $[V^{V}O_2(sal\text{-}aepy)(MeOH)]$. A very similar ^{51}V NMR spectrum with a strong resonance at δ = –503 ppm (92.0 %) and a minor resonance at –490 ppm (8.0 %) for $[V^{V}O_2(fsal\text{-}dmen)]$ (*ca.* 4 mM) dissolved in DMSO-d_6 has also been obtained. Addition of methanol (50 % v/v) to a 4 mM solution of $[V^{V}O_2(fsal\text{-}dmen)]$ in DMSO shifts the -503 ppm resonances to -515 ppm, identical to the spectrum of $[V^{V}O_2(fsal\text{-}dmen)]$ in MeOH only.



Scheme-VI: Design of dioxovanadium(V) complexes.

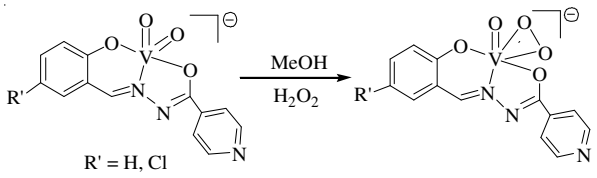
The reaction of $CH_2(H_2sal\text{-}bhz)_2$, $CH_2(H_2sal\text{-}fah)_2$, $CH_2(H_2sal\text{-}inh)_2$ and $CH_2(H_2sal\text{-}nah)_2$ (ligands derived from 5,5'-methylenebis(salicylaldehyde) and hydrazides) with $[V^{IV}O(acac)_2]$ in 1:2 molar ratio in refluxing methanol followed by aerial oxidation in the presence of KOH or $CsOH.H_2O$ yield the corresponding salt of dioxovanadium(V) species $[CH_2\{V^{V}O_2(sal\text{-}bhz)\}2]^{2-}$, $[CH_2\{V^{V}O_2(sal\text{-}fah)\}_2]^{2-}$, $[CH_2\{V^{V}O_2(sal\text{-}inh)\}_2]^{2-}$ and $[CH_2\{V^{V}O_2(sal\text{-}nah)\}_2]^{2-}$; **Scheme-VII**. In these complexes, two independent dioxovanadium(V) units do not interact with each other[29,30].



M^+	R	Complex
K^+		$K_2[CH_2\{V^{V}O_2(sal\text{-}bhz)\}_2]\cdot 2H_2O$
Cs^+		$Cs_2[CH_2\{V^{V}O_2(sal\text{-}bhz)\}_2]\cdot 2H_2O$
K^+		$K_2[CH_2\{V^{V}O_2(sal\text{-}fah)\}_2]\cdot 2H_2O$
Cs^+		$Cs_2[CH_2\{VO_2(sal\text{-}fah)\}_2]\cdot 2H_2O$
K^+		$K_2[CH_2\{V^{V}O_2(sal\text{-}inh)\}_2]\cdot 2H_2O$
Cs^+		$Cs_2[CH_2\{V^{V}O_2(sal\text{-}inh)\}_2]\cdot 2H_2O$
K^+		$K_2[CH_2\{V^{V}O_2(sal\text{-}nah)\}_2]\cdot 2H_2O$
Cs^+		$Cs_2[CH_2\{V^{V}O_2(sal\text{-}nah)\}_2]\cdot 2H_2O$

Scheme-VII: Structure of dinuclear dioxovanadium(V) complexes

Characterization of intermediate species: As η^2-peroxo vanadium(V) species is one of the important intermediate form during catalytic turn over of haloperoxidases, the isolation and/or generation of such peroxo species in solution and their characterization spectroscopically have been attempted. Thus, complexes $[V^{V}O(O_2)(sal\text{-}inh)(H_2O)]^-$ and $[V^{V}O(O_2)(Cl\text{-}sal\text{-}inh)(H_2O)]^-$, isolated by the treatment of methanolic solution of $[V^{V}O_2(sal\text{-}inh)]^-$ or $[V^{V}O_2(Cl\text{-}sal\text{-}inh)]^-$ with aqueous 30 % H_2O_2 (**Scheme-VIII**), show three IR active vibrational modes associated with the $[V(O_2)]^{2+}$ moiety, namely the symmetric $V(O_2)$ stretch (ν_2) at *ca.* 580 cm^{-1}, the antisymmetric $V(O_2)$ stretch (ν_3) at *ca.* 740 cm^{-1} and the O-O(ν_1) stretch at *ca.* 895 cm^{-1}, characteristic of η^2-coordination of the peroxo group[16]. In addition, they display the ν(V=O) mode at *ca.* 950 cm^{-1}. These complexes are unstable and lose oxygen even at ambient temperature within a day. Such poor stability is an important characteristic of complexes to transfer peroxo oxygen to substrate during catalytic activity.



Scheme-VIII: Formation of oxoperoxovanadium(V) complexes

Similarly, isolated peroxo complex $[V^{V}O(O_2)(sal\text{-}aebmz)]$ is poor stable and characterized only partially by IR and UV-VIS spectroscopy while complex $[V^{V}O(O_2)(sal\text{-}ambmz)]$ could not be isolated in the solid state[23]. The formation of the peroxo complex $[V^{V}O(O_2)(sal\text{-}aebmz)]$ in methanol has also been established by electronic absorption spectroscopy (Fig. 2) by treating $[V^{V}O_2(sal\text{-}aebmz)]$ with H_2O_2 in methanol[23]. The charge transfer band for $[V^{V}O_2(sal\text{-}aebmz)]$ appearing at 405 nm slowly broadens (Fig. 2) and the band at 313 nm shifts to 321 nm along with a decrease in intensity. At the same time, the bands at 273 and 281 nm split into three bands (at 269, 276 and 279 nm) along with just a marginal decrease in intensity. The 252 nm band shifts marginally to 256 nm while the 212 nm band remains constant but both losses intensity considerably. The final spectrum is similar to that recorded for the isolated peroxo complex.

Solution of oxovanadium(IV) complex $[V^{IV}O(acac)(sal\text{-}his)]$ in methanol is also sensitive towards the addition of H_2O_2, as monitored by electronic absorption spectroscopy, yielding oxoperoxo species. The spectral changes obtained is presented in Fig. 3. The disappearance of d-d bands is in accordance with the oxidation of the $V^{IV}O$-complex to an oxoperoxovanadium(V) and the appearance of a new band at *ca.* 425 nm of weak intensity is probably due to a LMCT band of the monoperoxo complex. The spectral changes due to addition of H_2O_2 to $[V^{V}O_2(sal\text{-}his)]$ (both taken in methanol) also demonstrate the formation of same oxoperoxovanadium(V) species[26].

^{51}V NMR study also provides useful information on the formation of peroxo or other intermediates. Thus, addition of 1.0 equivalent 30 % aqueous H_2O_2 to a methanolic solution of $[V^{V}O_2(fsal\text{-}dmen)]$ results in the appearance of resonances at -559 and -576 ppm. These signals were assigned due to

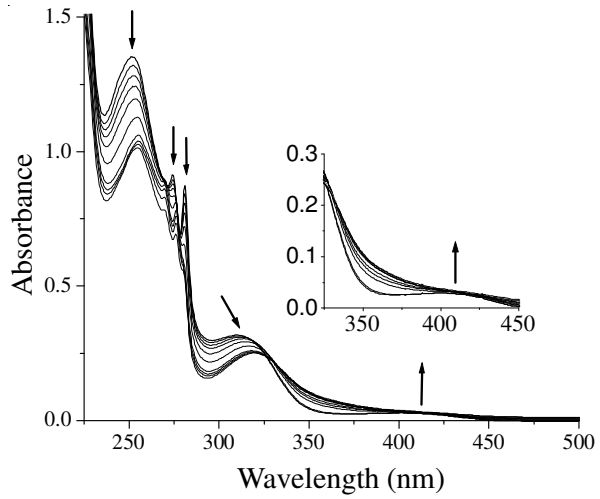


Fig. 2. Titration of $[V^{V}O_2(sal\text{-}aebmz)]$ with 30 % H_2O_2 in MeOH. The spectra were recorded after successive addition of 1-drop portions of H_2O_2 dissolved in MeOH to 10 mL of a *ca.* 1×10^{-4} M solution of $[V^{V}O_2(sal\text{-}aebmz)]$

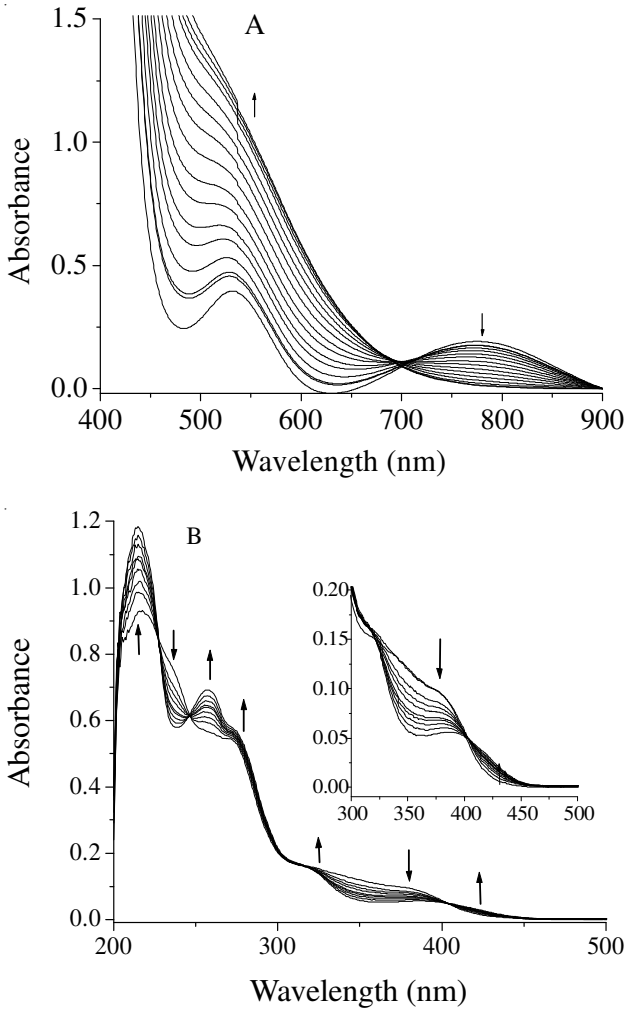


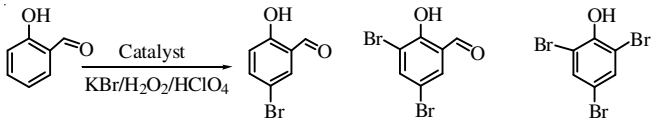
Fig. 3. UV-VIS spectral changes observed during titration of $[V^{IV}O(acac)(sal\text{-}his)]$ with H_2O_2. (A) The spectra were recorded after successive additions of one drop portions of H_2O_2 (6.6×10^{-4} mmol of 30 % H_2O_2 dissolved in 10 mL of methanol) to 50 mL of *ca.* 10^{-3} M solution of $[V^{IV}O(acac)(sal\text{-}his)]$ in methanol. (B) The equivalent titration, but with lower concentrations of a $[V^{IV}O(acac)(sal\text{-}his)]$ solution (*ca.* 10-4 M); the inset shows an enlargement of the 300-500 nm region.

$[V^{V}O(O_2)(fsal\text{-}dmenH^{+})]$ (protonation of nitrogen of dimethylamine residue) and $[V^{V}O(O_2)(fsal\text{-}dmen)]$, respectively. Further addition of 30 % aqueous H_2O_2 causes the increase in relative intensities of these peaks[25].

Catalytic activities of model complexes

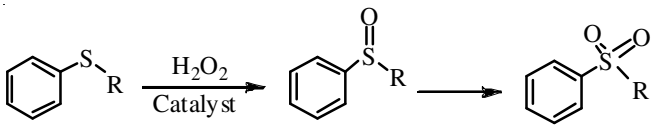
Oxidative bromination: Vanadium(V) complexes can also act as functional models of vanadate dependent haloperoxidases catalyzing the oxidative bromination of organic substrates in the presence of H_2O_2 and bromide ion in aqueous acidic medium[7,31,32]. Oxidative bromination of salicylaldehyde catalzsed by the complexes $[K(H_2O)][V^{V}O_2(sal\text{-}nah)]$ and $[K(H_2O)][V^{V}O_2(sal\text{-}fah)]$, using aqueous H_2O_2/KBr in the presence of $HClO_4$, has been carried out successfully. During this process vanadium reacts with one or two equivalents of H_2O_2, forming monoperoxo $\{VO(O_2)^{+}\}$ or *bis*-(peroxo) $\{VO(O^2)^{-}\}$ species, which ultimately oxidise bromide, possibly *via* a hydroperoxo intermediate. The oxidised bromine species (Br^2, Br^{3-} and/or HOBr) then brominates the substrate[33-35]. A maximum of *ca.* 51 % conversion of salicylaldehyde was achieved with 4 mmol of $HClO_4$, 2 mmol of substrate, 15 mmol of H_2O_2, 0.020 g (*ca*. 0.05 mmol) of catalyst and 0.476 g (4 mmol) of KBr. The selectivity of obtained products varied in the order: 5-bromosalicylaldehyde (85.8 %) > 3,5-dibromosalicylaldehyde (9.0 %) > unidentified (5.2 %). Under similar conditions, $[K(H_2O)_3][V^{V}O_2(pydx\text{-}inh)]$ gave only 46 % conversion of salicylaldehyde with almost similar selectivity of products as obtained for above complexes[19]. Other non-oxidizing acids such as H_2SO_4 were also tested successfully giving comparable results.

Dinuclear dioxovanadium(V) complexes, $[CH_2\{V^{V}O_2(sal\text{-}bhz)\}_2]^{2-}$, $[CH_2\{V^{V}O_2(sal\text{-}fah)\}_2]^{2-}$, $[CH_2\{V^{V}O_2(sal\text{-}inh)\}_2]^{2-}$ and $[CH_2\{V^{V}O_2(sal\text{-}nah)\}_2]^{2-}$ have also been used as catalyst for the oxidative bromination of salicylaldehyde. A maximum of *ca*. 90 % conversion of salicylaldehyde was achieved under optimized conditions but the addition of $HClO_4$ in four equal portions during the first 2 h of reaction time was necessary to improve the conversion of the substrate and to avoid decomposition of catalyst. At least three products, 5-bromosalicylaldehyde, 3,5-dibromosalicylaldehyde and 2,4,6-tribromophenol were identified; **Scheme-IX**[29,30]. Increasing the amount of oxidant improves the conversion of salicylaldehyde but the selectivity of 5-bromosalicylaldehyde decreases considerably, while that of 3,5-dibromosalicylaldehyde and 2,4,6-tribromophenol increase. The presence of excess H_2O_2 facilitates the formation of more and more HOBr, which ultimately helps in the further oxidative bromination of salicylaldehyde to other position(s).



Scheme-IX: Oxidation products of salicylaldehyde.

Oxidation of organic sulfides: Vanadium complexes also catalyze the oxidation of organic sulfides to sulfoxides, a reaction also promoted by haloperoxidase enzymes. Organic sulfides have electron-rich sulfur atoms which undergo electrophilic oxidation giving sulfoxide; upon further oxidation sulfones are formed; **Scheme-X**.



Scheme-X: Oxidation of organic sulfides. R = CH_3 : methyl phenyl sulfide (mps), R = C_6H_5: diphenyl sulfide (dps)

Most vanadium catalysts are good/excellent for the oxidation of sulfide conversion with high turn over frequency (TOF) along with good selectivity towards sulfoxide. Complexes $[K(H_2O)][V^{V}O_2(sal\text{-}inh)]$ and $[K(H_2O)][V^{V}O_2(sal\text{-}bhz)]$, under optimized reaction conditions, exhibit 54.8 % and 57.3 % conversion of methyl phenyl sulfide, respectively[36]. The turn over frequencies of these catalysts are 60 and 70 respectively and the formation of sulfoxide is always higher than sulfone. A maximum of 91 % (with $[V^{V}O_2(sal\text{-}ambmz)]$), 81 % (with $[V^{V}O_2(sal\text{-}aebmz)]$) and 68 % (with $[V^{V}O_2(acac\text{-}ambmz)]$) conversion of methyl phenyl sulfide has been obtained where a selectivity with respect to the major product (the sulfoxide) of 98, 93 and 88 %, respectively, has been achieved (Fig. 4). About 3 h were required to acquire the steady state with all the complexes. Complex $[V^{V}O_2(sal\text{-}his)]$ also catalyses the sulfoxidation of methyl phenyl sulfide and diphenyl sulfide with 84.8 and 70.7 % conversion, respectively. The selectivity of sulfoxide formation for these two catalysts are 61 and 68 %, respectively[26].

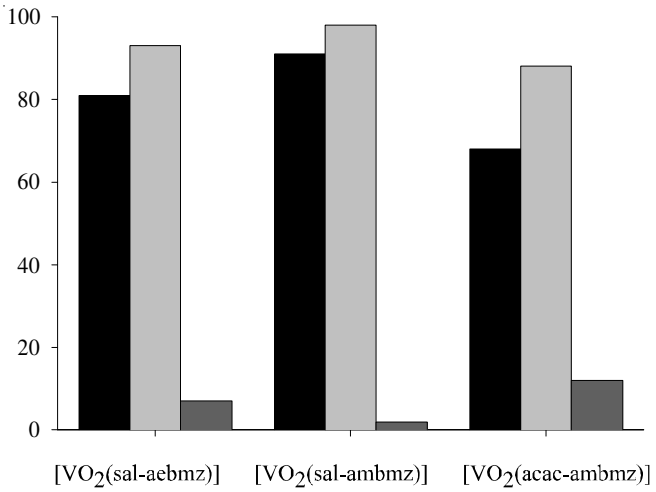


Fig. 4. Bar diagram, showing the percent conversion (black) of methyl phenyl sulfide and the selectivity with respect to sulfoxide (light grey) and sulfone (dark grey)

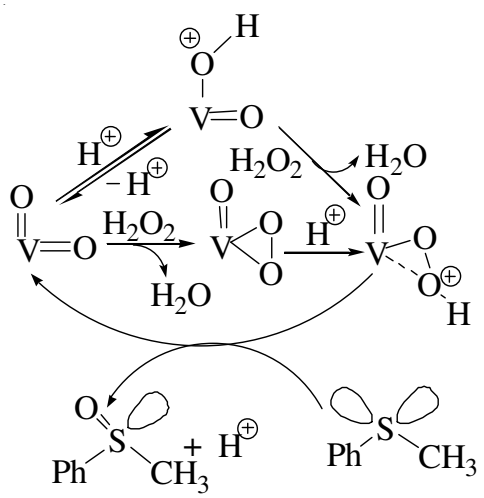
As the dioxovanadium(V) complexes are able to generate peroxo species $[V^{V}O(O_2)(L)]$ on treatment with H_2O_2, an intermediate peroxo complex is likely to form, followed by a hydroperoxovanadium(V) complex in the presence of H^{+}, enhancing the electrophilicity of the peroxo intermediate[10,37]. The peroxide thus activated is subjected to a nucleophilic attack by the sulfide as shown in the catalytic cycle proposed in **Scheme-XI**.

The removal of sulfur compounds from petroleum products has attracted attention of many researchers to fulfill the demand

TABLE-1
DESULFURIZATION AND REACTION PRODUCTS USING THE DIOXOVANADIUM COMPLEX [$V^{V}O_2$(fsal-dmen)] (0.050 g), 30 % H_2O_2 (OXIDANT:SUBSTRATE MOLAR RATIO OF 3:1) AT 60 ºC

Catalyst	Sulfur containing compound	Sulfur content (ppm)		Sulfur removal (%)
		Initial amount	After desulfurization	
[$V^{V}O_2$(fsal-dmen)]	Thiophene	500	113	77.4
[$V^{V}O_2$(fsal-dmen)]	Benzothiophene	500	110	78.1
[$V^{V}O_2$(fsal-dmen)]	Dibenzothiophene	500	112	77.7
[$V^{V}O_2$(fsal-dmen)]	2-Methylthiophene	500	108	78.4

of environment friendly fuels. The oxidation of model organosulfur compounds with sulfur concentrations of 500 ppm was tested in *n*-heptane using [$V^{V}O_2$(fsal-dmen)] as catalysts in presence of 30 % H_2O_2. The results are summarized in Table-1. It is clear from the table that [$V^{V}O_2$(fsal-dmen)] is significantly effective in oxidizing organic sulfur.



Scheme-XI: Proposed reaction mechanism of sulfoxidation

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