

Vanadium peroxocomplexes as oxidation catalysts of sulfur organic compounds by hydrogen peroxide in bi-phase systems

Alexander V. Anisimov*, Elena V. Fedorova, Andrey Z. Lesnugin,
Vladimir M. Senyavin, Leonid A. Aslanov, Viktor B. Rybakov, Alla V. Tarakanova

Department of Chemistry, Moscow State University, Moscow 119899, Russia

Abstract

New vanadium oxodiperoxocomplexes $\text{Bu}_4\text{N}^+[\text{VO}(\text{O}_2)_2\text{L}_2]^-$ were synthesized, where L = pyridine (**1**), 2-methylpyridine (**2**), 4-methylpyridine (**3**), 2-oxymethylpyridine (**4**). All complexes were characterized by NMR (^1H , ^{51}V) and IR spectroscopy. The oxidation of sulfur organic compounds and diesel fuel desulfurization catalyzed by vanadium peroxocomplexes in bi-phase system was investigated in various solvents. The complexes manifested high catalytic activity and selectivity in oxidation of sulfides.

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1. Introduction

The bi-phase catalysis principle [1] is one of the most perspective ways of homogeneous catalysis in industry. This concept is a combination of phase transfer and metal complex catalysis. So, the substrate and reaction products are dissolved in organic phase and catalyst is presented in water phase. After the reaction proceeds to completion, the water phase can be easily removed and can be repeatedly used with the activity retention of catalyst.

During the past decades the chemistry of vanadium peroxocomplexes has attracted considerable attention due to possible applications of these compounds as catalysts for the oxidation of various organic compounds [2–13]. Vanadium peroxocomplexes are soluble both in polar organic solvents and in water, thus

giving the possibility to use these catalysts in bi-phase systems. In the last few years, we studied the oxidation of thiols and sulfides in the presence of tungsten and molybdenum peroxocomplexes in bi-phase systems containing basically the phosphate anions as ligands [14]. Those complexes show good selectivity in thiol–disulfide transformations and disulfide oxidation [15]. Following our recent work, we report herein a study of new vanadium peroxocomplexes and their usage as catalysts for oxidation of various sulfur organic compounds.

2. Experimental

2.1. General procedures

All reactions were proceeded in thermostat reactor under argon atmosphere. Beforehand, the solvents were dried and distilled under nitrogen using standard

* Corresponding author.

methods. Elementary analyses of H, C and N were performed with a Carlo Erba microanalyzer. ^1H -NMR spectra at 400 MHz were recorded on Varian XR-400 instrument, ^{51}V -NMR spectra at 52.6 MHz were recorded on Tesia Bruker AL-200 instrument, mass spectra were obtained on a Finnigan MAT 112S spectrometer.

IR spectra were obtained on a Specord M80 (Carl Zeiss) spectrophotometer within the spectral range of 400–4000 cm^{-1} under resolution of 2.5–4 cm^{-1} . Spectra of the solutions in CH_2Cl_2 or CHCl_3 were shown to represent pure solvents; the films were obtained on a KBr substrate by evaporation of the solvent. Reference spectra of the initial substances (ligands and TBAB) were also registered.

2.2. Preparation of vanadium peroxocomplexes

Vanadium peroxocomplexes **1–4** are synthesized using following general procedure outlined below for compound **1**.

To fivefold excess of 50% H_2O_2 dissolved in 20 ml of water was added an equivalent amount of the pyridine ligand to sodium metavanadate $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$, then 20 mmol $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ and 20 ml of water. The mixture was stirred for 5 min at room temperature and then was cooled up to 0 °C. After cooling the solution of 9 mmol TBAB in CH_2Cl_2 (20 ml) was added dropwise for 15 min to the reaction mixture and this mixture was stirred for 15 min at 0 °C. Water phase was separated from organic phase and vanadium peroxocomplex was salted out from CH_2Cl_2 by pentane and finally dried and recrystallized.

2.3. Oxidation experiments

The reaction mixture which contained 10 mmol sulfur organic compound in 10 ml CH_2Cl_2 , H_2O_2 (31 mmol), $\text{NaVO}_3 \cdot \text{H}_2\text{O}$ (0.03 mmol) in H_2O , 2×10^{-4} mmol TBAB in 20 ml CH_2Cl_2 , and 15 mmol corresponding ligand was stirred for 2 h at 30 °C under nitrogen atmosphere. The organic and the aqueous layers were separated and the aqueous layer was extracted twice with 25 ml portions of ether. The combined organic layers were washed with water and dried over magnesium sulfate. After removing the solvent under reduced pressure, the reaction product was purified by chromatography on silica gel.

3. Results and discussions

Active forms of the used catalytic system are peroxovanadate ion $[\text{V}(\text{O}_2)\text{O}]^+$ and oxodiperoxovanadate ion $[\text{V}(\text{O}_2)_2\text{O}]^-$ formed by reaction of NaVO_3 and hydrogen peroxide; they usually are in equilibrium. The first ion has strong electrophilic properties and is more kinetic effective oxidizing reagent. In the absence of phase-transfer catalyst, the equilibrium is shifted to the formation of the monoperoxovanadate ions. This is the strong evidence of the key role that the second ion plays in oxidative transformations.

The peroxovanadium complexes $\text{Bu}_4^+[\text{V}(\text{O}_2)_2\text{OL}_2]^-$ **1–4** were prepared by dissolving $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$, ligand L [L = pyridine (**1**), 4-methylpyridine (**2**), 2-methylpyridine (**3**), 2-oxymethylpyridine (**4**)], tetrabutylammonium bromide and 30% hydrogen peroxide in water in the molar ratio of 1:2:1:4. Those products were isolated by extraction from water solution by chloroform, subsequent precipitation by pentane and then vacuum pumping of solvent residues. The samples for the ^1H and ^{51}V -NMR studies were prepared by dissolving the complexes in CDCl_3 and CHCl_3 , respectively. As the vanadium peroxocomplexes are rather unstable, the samples for the NMR and IR studies should be prepared just before the experiments.

3.1. ^1H -NMR study

In the ^1H -NMR spectra of vanadium peroxocomplexes **1–4**, the H-atom marks of pyridine ring in bound ligands are noticeably displaced to the weak field as against their position in free ligands (Table 1). This phenomenon can be explained by the fact that the density of circular-type current in aromatic ring of ligand in negative-charged oxodiperoxovanadium ions is much higher than the same in uncharged ligand; thus, the general magnetic displacement vector is collinear to the external field vector.

3.2. ^{51}V -NMR study

In all ^{51}V -NMR spectra of complexes **1–4**, the legible singlets are observed relating to the bound anion (Table 2). The difference in chemical shifts is caused by difference in the electron-donating properties of ligands entering the internal coordination orbs of complexes. It is known [16] that the

Table 1
¹H-NMR data for bound and free pyridine ligands

Ligand	H atom	Bound ligand	Free ligand
Py (1)	α-	9.080 tt	8.601 tt
	β-	7.559 dd	7.321 dd
	γ-	8.001 tt	7.724 tt
γ-Pic (2)	α-	8.940 d	8.446 d
	β-	7.314 d	7.113 d
α-Pic (3)	α-	9.128 d	8.465 d
	β-	7.268 dd	7.097 dd
	γ-	7.805 m	7.589 m
	δ-	7.336 d	7.156 d
2-Oxymethylpyridine (4)	α-	9.046 M	8.650 M
	β-	7.768 M	7.402 M
	γ-	8.307 M	8.054 M
	δ-	7.995 M	7.750 M

electronic screening is amplified at magnification of electron-donating properties of ligands. Thus, one should expect beefing-up of a shielding characteristic in a series α-pic–Py–γ-pic–2-oxymethylpyridine, in which one of the least expressed donor properties α-pic are caused by the ligand methyl group position in an unprofitable α-position.

3.3. IR study

IR spectra of the complexes **1–4** under investigation can be referred as a superposition of those of the counter-ion, vanadium–oxygen skeleton and an appropriate ligand. Only the most intense bands of the ligands were observed in IR spectra of complexes. For example, in the case of complexes **1** and **4** they were found at 1594, 1296, 1152, 1002, 472 cm^{−1}, and at 1152 and 1060 cm^{−1}, respectively. As compared to the pure substance spectra, they are shifted within several cm^{−1} and redistributed in intensity, thus evidencing the bonding of the fragments into the complexes. This is also true for the counter-ion bands which are generally most intense in the overall spectrum. In the

Table 3
 The stretching frequencies of VO(O₂)₂ group in the complexes **1–4**

Compound (ligand)	ν(V=O)	ν(O–O)	ν _{asym,sym} (V–O)
1 (Py)	943	868–886	528–624
2 (α-Pic)	943	876–885	528–618
3 (γ-Pic)	944	870–884	530–616
4 (2-Oxymethylpyridine)	926	882–890	538–680
Literature data [8]	925–1000	850–894	510–636

latter case, as compared to the pure TBAB spectrum, additional considerable broadening of the bands takes place. The phenomenon is most probably caused by the charging of the moiety and leads to the coalescence of some of them. Such broadening resulting from the three [Bu₄N]⁺ vibrations was observed at ca. 880 cm^{−1} in the range of the peroxo O–O stretching [9] interfering thus its observation. Hence, that drastic enhance of the band intensity against the spectra of the sole counter-ion serves the spectroscopy evidence of the presence of the peroxo-structure; the band exhibits well-defined wings and its contour varies from complex to complex. So, the corresponding frequencies in Table 3 should be considered arbitrary. At the same time the region of 920–990 cm^{−1} is free from the ligands and counter-ion vibrations and the medium intensity band of V=O stretching is clearly seen at 926–944 cm^{−1}, depending on the complex structure (Table 3).

At the same time, the range of 920–990 cm^{−1} is free from the ligands and counter-ion vibrations and the medium intensity band of V=O stretching is clearly seen at 926–944 cm^{−1}, depending on the complex constituents (Table 3). Broadening of the bands assigned to V–O_{peroxo} were also observed in the IR spectra. Their position is known to be most sensitive to the structure involved [9]. It is suggested that in diperoxo complexes, the monodentate ligand leads to the separation between symmetric and antisymmetric stretches of metal–oxygen bonds in each VOO triangle of about

Table 2
⁵¹V-NMR data for compounds **1–4** (CHCl₃, 21 °C, ppm)

Ligand	Py	γ-Pic	α-Pic	2-Oxymethylpyridine
δ (ppm) ^a	−655.837	−660.363	−642.598	−648.110

^a From VOCl₃.

100 cm^{-1} and that the bands should be observed at 630 and 530 cm^{-1} , respectively. This is exactly the fact for the complexes **1–3**: in their spectra, these bands are found at $624/528$, $616/530$, and $618/538\text{ cm}^{-1}$, respectively. Alternatively, in the spectra of complex **4**, a very broad band in the $500\text{--}640\text{ cm}^{-1}$ interval is observed with no clear structure showing possible overlapping of V–O bands in accordance with the known much less (about 40 cm^{-1} [9]) splitting of these modes for a bidentate bonding to the $\text{VO}(\text{O}_2)_2$ fragment.

3.4. X-ray study

More data on the structure of vanadium peroxo-complexes were obtained from the X-ray studies of the following complexes: $\text{Na}[\text{VO}(\text{O}_2)(\text{bipy})]\cdot 8\text{H}_2\text{O}$ (**5**) and $\text{Na}[\text{VO}(\text{O}_2)(\text{py})]\cdot 8\text{H}_2\text{O}$ (**6**). The vanadium atom in peroxocomplex **5** is surrounded by five oxygen atoms and two nitrogen atoms from bipyridine ligand (Scheme 1).

Four oxygen atoms originate from two peroxogroups and one more oxygen atom does not. This last oxygen atom belongs to the Na-atom coordinate sphere as well. The distances between vanadium and oxygen atoms are different, but in pairs they are practically the same: pyridine rings within the bipyridine ligand are practically flat and the angle along the $\text{C}_{16}\text{--C}_{17}$ bond equals 0.34° . Molecular structure of this complex is slightly distorted octahedron formed

by the oxygen atoms. One of those atoms serves as a bridge between the sodium and the vanadium atoms. One of the water molecule (the boundary one) is in *trans*-position to the O(1) atom. The O(4) and O(6) oxygen atoms from the water molecule are in *cis*-position to the O(1) and O(2) atoms and form equatorial plane with the O(4) and O(6) atoms. The water molecules form a widespread three-corner net of hydrogen bonds.

3.5. Oxidation of thiols

It is well known that oxidation of thiols and sulfides is one of the most important method of hydrocarbon feedstocks purification from sulfur compounds [17].

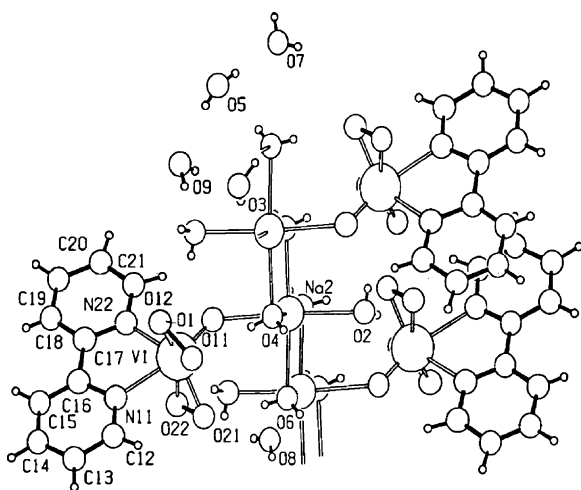
As oxidants, a wide variety of reagents were used: molecular oxygen in the presence of strong bases, hydrogen peroxide, peracids, metal oxides (MnO_2 , Fe_2O_3 , CuO , etc.) or their salts, aliphatic sulfoxides, N-oxides, or halogens. As other oxidizing agents used in the conversion of thiols to disulfides and sulfonic acids HNO_3 , KMnO_4 , $\text{Ba}(\text{MnO}_4)_2$ or BaCr_2O_7 should be noted, electrochemical oxidation was also practiced [14].

Thiols can be oxidized by hydrogen peroxide in the presence of peroxocomplexes of various transition metals as catalysts in bi-phase system. In this work, we investigated the oxidation of thiols and sulfides by hydrogen peroxide in bi-phase system using combined concepts of phase-transfer and metal complexes catalysis. The following metal complexes were used: vanadium, tungsten and molybdenum peroxo-complexes (Table 4).

The oxidation of benzenethiol in the presence of vanadium peroxocomplexes **1–4** as catalysts leads to the formation of diphenyldisulfide and benzenesulfonic acid. Small amounts of PhSSO_2Ph and PhSO_2Ph was detected in reaction mixture as well (Scheme 2).

The most active in benzenethiol oxidation is vanadium complex **1** with pyridine ligand and the lowest activity was obtained for the complex with water as ligand. This phenomenon can be explained by different lipophilicity of those oxodiperoxo anions.

The oxidation of *n*-butanethiol by hydrogen peroxide with phosphotungstate, phosphomolybdate, or phosphorovanadate peroxocomplexes as catalysts in the presence of quaternary ammonium base provided

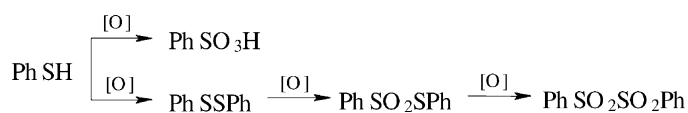


Scheme 1. Structure of complex $\text{Na}[\text{VO}(\text{O}_2)_2(\text{bipy})]\cdot 8\text{H}_2\text{O}$.

Table 4

Oxidation of benzenethiol by H₂O₂ in the presence of vanadium peroxocomplexes (1.5 h, CH₂Cl₂, r.t.)

PTC	Ligand	Products of reaction (%)				Residual of PhSH (%)
		PhSO ₃ H	PhSSPh	PhSO ₂ SPh	PhSO ₂ SO ₂ Ph	
TBAB	H ₂ O	15	62	4	2	14
	1-Leycin	17	67	4	2	9
	Bipy	18	67	4	2	8
	Py	19	72	4	2	4
Dodecyl-trimethyl ammonium bromide	H ₂ O	15	68	4	2	11
	1-Leycin	17	70	4	2	7
	Bipy	18	70	4	2	5
	Py	20	73	4	2	2

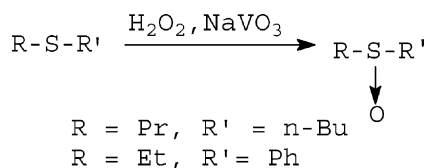


Scheme 2.

the two principal products: dibutylsulfide and butylbutanethiolsulfonate; the butanesulfonic acid was also detected. The yield of butanesulfonic acid in the presence of cetyltrimethylammonium bromide as a PTC was up to 95%.

3.6. Oxidation of sulfides

In order to obtain more information on the reactivity of vanadium peroxocomplexes we have tried to investigate catalytic activity complexes **1–4** in the oxidation of propylbutyl sulfide and ethylphenyl sulfide as model reactions. Propylbutyl sulfide and ethylphenyl sulfide were transformed to the respective sulfoxides. Very high selectivity of sulfides oxidation by hydrogen peroxide is the most important peculiarity of the used vanadium peroxocomplexes: only sulfoxides were produced from the sulfide oxidation and no sulfones are formed (Scheme 3).



Scheme 3.

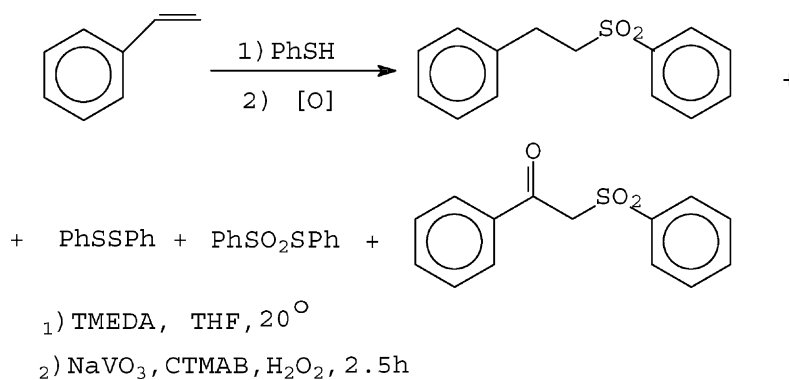
The most active catalyst for sulfide oxidation is the vanadium peroxocomplex **2** with the 4-methylpyridine ligand and the lowest activity has the peroxocomplex **4** with the 2-hydroxymethylpyridine ligand.

Such dependence can result from combination of the ligand lipophilicity and some bulky reasons which influence in opposite directions.

3.7. Oxidative addition of thiols to unsaturated compounds

Oxidative addition of thiols to olefins can lead to one-step formation of sulfoxide or sulfones from the starting materials available. To investigate this reaction in bi-phase system without intermediate isolation of sulfides, we used the peroxocomplexes of vanadium, molybdenum and tungsten. Water solutions of transition metal complex and hydrogen peroxide were added immediately to reaction mixture containing products of thiols added to unsaturated compound. The unsaturated compounds used were styrene, cyclohexene, allylphenyl ether, and methyl ester of acrylic acid.

Oxidative adds of benzenethiol to cyclohexene and allylphenyl ether leads mainly to the formation of diphenylsulfide and corresponding thiolsulfonate. The main cause of this phenomenon is the very low activity



Scheme 4.

of those compounds in nucleophilic addition to double bond.

The oxidative adds of benzenethiol to styrene leads to the formation of two compounds: phenacyl sulfone (52%) and phenyl(phenylethyl)sulfone. Diphenyldisulfide and PhSO₂SPh were also detected in the reaction mixture (Scheme 4).

Methyl ester of acrylic acid activates the double bond and thus oxidative addition to this compound was more successful. In reaction mixture, methyl ester of β -phenylthiopropionic acid, corresponding sulfone and small amount of diphenyldisulfide were detected. The most active catalyst in this reaction is the vanadium peroxocomplex (Scheme 5).

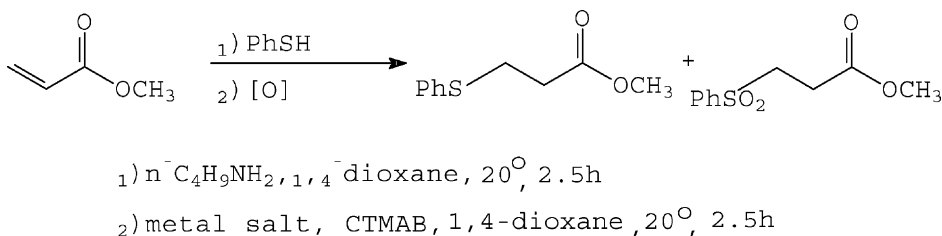
Oxidative adds of isobutane thiol to the methyl ester of β -phenylthiopropionic acid was less selective. Final reaction mixture consisted of β -isobutylsulfonylpropionic acid methyl ester, products of starting thiol oxidation and products of its splitting and rearrangements. The main cause of this phenomenon is low acidity of the isobutane thiol as compared to the benzenethiol.

3.8. Diesel fuel desulfurization

Sulfur organic compounds in fuels are a major source of environmental pollution. On combustion they are converted to sulfur oxides which in turn give arise to sulfur oxyacids contributing to acid rains. The requirement to produce diesel fuels with very low levels of sulfur has stimulated much work in the area of hydrodesulfurization. The heterogeneous desulfurization of oil fractions is aimed at the removal of sulfur compounds in the form of hydrogen sulfide, which usually proceeded to sulfuric acid.

This part of the present work is aimed at production of highly selective and recoverable homogeneous catalyst for oxidative desulfurization of diesel fuel. Recently, tungsten catalyst was used for such process of the dibenzothiophene oxidation [18].

Vanadium peroxocomplexes should be suitable catalysts for such process due to high activity and selectivity in oxidation of sulfur organic compounds and the bi-phase system should be a good technical procedure due to the very simple technique of oxidation



Scheme 5.

Table 5

Oxidation of sulfides in the presence of peroxocomplexes with pyridine ligands (30 °C, CHCl₃)

Ligand	Yield of RSOR' (%)	
	PrSBu	EtSPh
Pyridine	100	78
4-Methylpyridine	100	81
2-Methylpyridine	77	63
2-Oxymethylpyridine	65	60

Table 6

Desulfurization of diesel fuel by hydrogen peroxide in the presence of vanadium peroxocomplexes (3 h, r.t.)

Reagents ratio	Ligand (μmol)	S (% mass)
V:L = 1:2, V:TBAB = 1:1.25	γ-Pic (0.031)	0.21
	Py (0.037)	0.21
	Bipy (0.032)	0.23
	Pyr (0.030)	0.21

system removal from hydrocarbon phase. The above system of choice is similar to the Venturello epoxidation system employing a phase transfer agent, aqueous hydrogen peroxide as the oxidant and phosphotungstic acid as the catalyst [19].

The vanadium peroxocomplexes **1–4** were practically inactive in saturated hydrocarbon oxidation in bi-phase system. Only small amount of cyclohexanol and benzene were detected in cyclohexane oxidation by hydrogen peroxide. Under the same conditions, no conversion of cyclohexanol to benzene was detected.

To test the catalytic activity of vanadium peroxocomplexes in desulfurization, a diesel fuel (fraction 180–350 °C) with total sulfur amount 0.86% was taken. According to the Russian legislations, total sulfur amount in the diesel fuels must be within 0.2%. All vanadium complexes show high activity in oxidation of the two-model sulfides—diphenylsulfide and phenylbenzyl sulfide—to the corresponding sulfoxides.

The oxidation of diesel fuel with hydrogen peroxide and vanadium peroxocomplexes as catalysts reduces the total amount of sulfur in the fuel to 0.2% (Tables 5 and 6). These results are in good agreement with the requirements of the Russian legislations concerning total amount of sulfur in diesel fuels.

To demonstrate the recyclability of vanadium catalysts, the water phase with vanadium compound was used several times and a new portion of hydrogen peroxide was added after each oxidation experiment. Even after four cycles, sulfur amount detected in the diesel fuel was within 0.22%.

Acknowledgements

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