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ORIGINAL PAPER

Vanadium (IV) complexes with Schiff base ligands derived from 2,3-diaminopyridine as catalyst for the oxidation of sulfides to sulfoxides with H_2O_2

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Abstract

Sulfoxides are substances used in the synthesis of valuable complexes and as drugs in medicine. Sulfides were selectively oxidized to the corresponding sulfoxides in proper yields with (H_2O_2) hydrogen peroxide applying a vanadium (IV) Schiff base complex in the role of a catalyst in glacial acetic acid in the role of solvent beneath mild conditions. For the conversion of sulfides to sulfoxides of various catalysts are applied. It must be noted that in our previous article, the vanadyl complexes (VOY^1) synthesized were applied as a catalyst in the epoxidation of styrene (Zabardasti and Shangaie, J Iran Chem Soc 13:1875–1886, 2016) but in the new work, vanadium (IV) complexes with Schiff base ligands derived from 2,3-diaminopyridine were used to as catalyst for the oxidation of sulfides to sulfoxides with H_2O_2. To the most of our information, there is not any literature description on the selective oxidation of sulfides to sulfoxides by means of a vanadium (IV) Schiff base complex with N, O donor ligand derived from 2,3-diaminopyridine catalyst beneath these conditions. Dimethyl sulfide was chosen as a pattern substrate for optimization experiments. Oxidation of sulfides was functioned at 25 °C temperature in the attendance of a catalytic quantity of the vanadium (IV) complex or (VOY^1) utilizing 20% H_2O_2 in the role of the oxidant, Scheme 1 and glacial acetic acid in the role of the solvent.

Keywords Sulfide · Hydrogen peroxide · Selective oxidation · Catalyst · VO^{2+} Schiff base complex · 2,3-Diaminopyridine · Sulfoxide

Introduction

Schiff bases including N, O donor atom sets are renowned to match with different metal ions and this has fascinated lots of inventors. The Schiff base property of complex is affected on the catalytic ability of vanadium oxide. Not only the Schiff bases perform an important role in coordination chemistry, but also, their complexes have enough potentials for property of catalyst. Recently, one of the important ligand synthesis systems is tetradentate Schiff base from typical of N, O, especially, in relationship with unsymmetric and selective catalysis. By reason of coordination facility of N, O Schiff bases their transition metal complexes widely applied in the role of catalyst in production of biological materials. Additionally, complexes of transition metals which include of salicylaldehyde and diamine have gained substantial attentiveness. Complexes with N, O donor ligands have been planned for their dioxygen insight and oxidative catalysis. The consequences of tetradentate Schiff base obtained from 2-hydroxybenzaldehyde and diamine are the topic of a lot of investigation [1–4]. In the last era metallated Schiff bases have significant attention because of their broad application and in addition simply formation by the condensation between imines and aldehydes. In 1986, reported on the asymmetric oxidation of sulfides into the corresponding sulfoxides using organic hydroperoxides catalyzed by optically active Schiff base oxovanadium (IV) complexes. The complexes used for the asymmetric catalytic reactions involved tetradentate Schiff base ligands derived from optically active 1,2-diamines and salicylaldehyde. Such complexes are usually green and in the solid state have a monomeric five-coordinate square pyramidal structure. However, a few orange oxovanadium(IV) complexes have also been reported. The advantage of vanadium complexes

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as catalysts in comparison to other intermediate elements is that their CV curves are reversible and play a better catalytic role in reactions [5].

In recent years, dimethyl sulfoxide has been used to treat various diseases tested. Chiral sufoxides find application in specific drugs such as esomeparasole and armodafinil. In addition, sulfoxides in pharmaceuticals known as an aprotic polar solvent. DMSO is chiefly applied as a solvent in the laboratory. The rising emphasis and functions of sulfoxides have interested investigation into novel techniques for their synthesis. Organic sulfoxides are useful for the manufacture of an assortment of chemically and biologically effective molecules containing medicinal intermediates for example anti-painful (proton pump preventers), bladder diseases [6] anti-atherosclerosis, uncontaminated, syndrome palms and soles, antifungal [7] anti-hypertensive [8] and cardiotonic intermediaries [9] in addition to psychotropics [10] and vasodilators [11].

The oxidation of sulfides to sulfoxides is an uncomplicated artificial manner. There are numerous substances and oxidative processes accessible for this modification. Consequently, checking the reaction conditions, that is temperature, time and the essential quantity of oxidants, performs a significant function to prevent constructing oxidative side results, on the other hand, these necessities are frequently difficult to seem. Therefore, there is yet substantial attention in the improvement of selective oxidants for this modification [12–17].

Whereas the hydrogen peroxide oxidation of sulfides to sulfoxides catalyzed by means of many transition metal schiff base complexes has been described [18–21], however, the oxidation catalyzed via vanadium (IV) has obtained fewer consideration. H_2O_2 is investigated as a perfect ‘green’ oxidant because of its intensity and nonexistence of poisonous by-yields [22, 23].

In perpetuation of our effort on the discriminating oxidation of hydrocarbons, we describe a mainly appropriate and selective oxidation of sulfides to the corresponding sulfoxides consuming H_2O_2 catalyzed with VO^{2+} Schiff base complex.1 (VOY^1), beneath mild conditions (Fig. 1).

Preparation of the complex

The complex was designed by means of a process alike to that applied by Karmaker et al. [24]. 3 mmol of the $VO(acac)_2$ which was dissolved in 30–45 ml of warmed ethanol, added to an ethanolic assortment of 3 mmol of the *N,N′*-bis (5-fluoro-2-hydroxybenzaldehyde) pyridine Schiff base (H_2Y^1) in the 1:1 molar relative amount. The color of the mixture altered in a few seconds. The reaction mixture was refluxed for 4 h. The production was washed several times using distilled water, afterwards by ethanol and continue with crystallization in ethanol and drying at 50 °C. Then, the resulting crystals were prepared for X-ray diffraction.

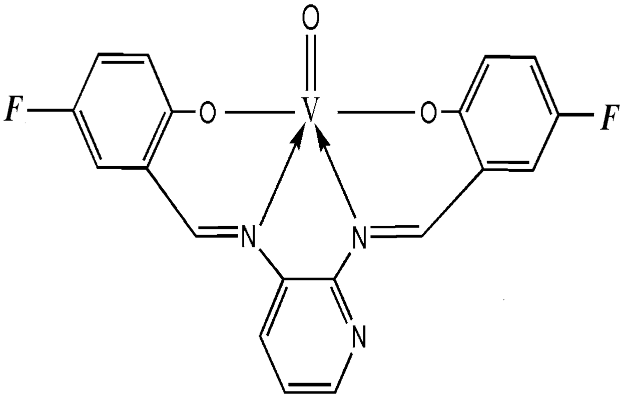


Fig. 1 Structural representation of the Schiff base complex.1 or VOY^1

X-ray crystallography

Crystals of complex.1 (VOY^1) appropriate for X-ray diffraction examination were acquired by crystallization from ethanol. For completely the complexes, the unit cell elements and the strength statistics were attained on a Bruker-Nonius SMART APEX CCD filtered crystal X-ray diffractometer, arranged with a graphite monochromator and a Mo Ka fine-focus closed pipe ($k = 0.71073$ Å) operated at 2.0 kW. The indicator was placed at a distance of 6.0 cm from the unit cell. Information were brought together at 298 K with an experiment length bond of 0.3 in *x* and an occurrence time of 5 s/frame. The SMART software was beneficial for programs attainment and the SAINT-PLUS software was useful for programs extraction [25]. The SADABS software [26] was valueble for the intensity modification. The complex were identified by application of straightforward techniques and purified on (F^2) by top matrix least-squares techniques.

Our investigation to appropriate single crystal of (VOY^1) for X-ray diffraction calculation have been successful. All non-hydrogen atoms were refined with anisotropic thermal parameters. Atom scattering factors were taken from the International Tables for Crystallography. Crystal data and structure refinement details:

Empirical formula, $C_{19}H_{11}N_3O_3F_2$ V; Formula weight, 417.92 g; Crystal color, green; Crystal dimensions (mm), 0.42, 0.35, 0.04; Crystal system, monoclinic; V (Å^3), 1795(4); Space group, P2(1)/c; F(000), 2625; Maximum and minimum peak in difference map (e Å^{-3}), 1.65 and – 1.22; Goodness-of-fit on F^2, 1.12.

An illustrative crystal and optimized configuration of complex 1 (VOY^1) are showed in Figs. 2 and 3. It should

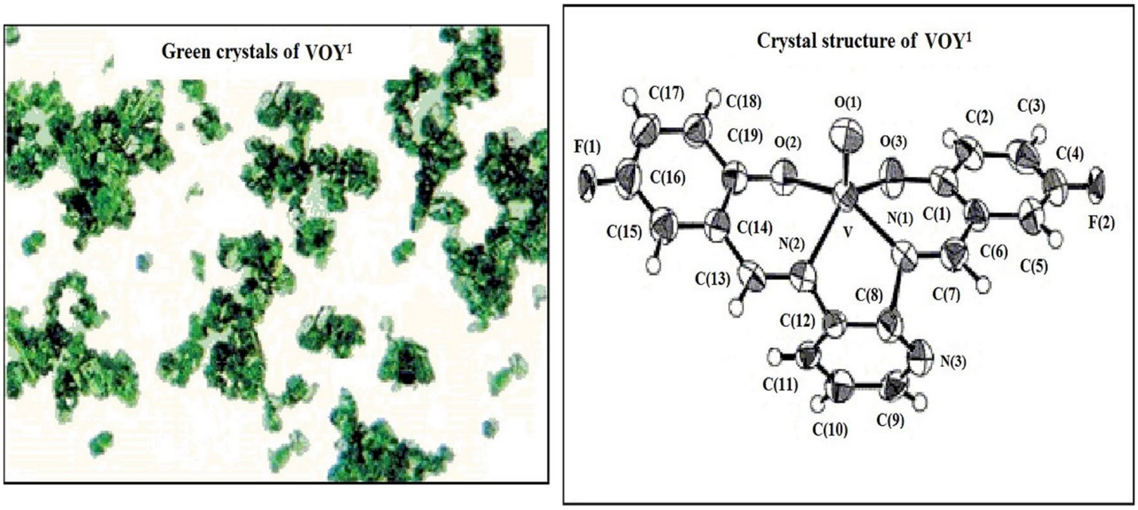


Fig. 2 Crystal structure of (VOY^1). Displacement ellipsoids are drawn at the 20% probability level

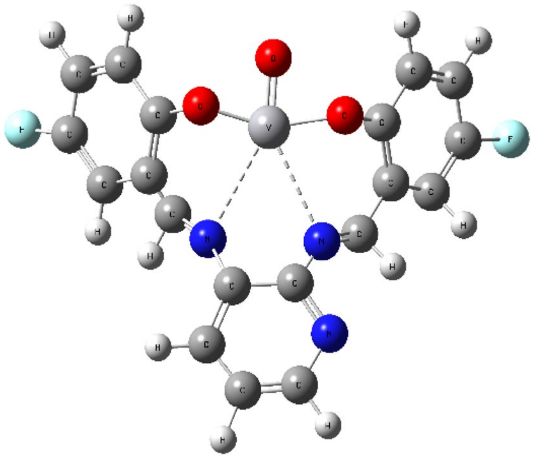


Fig. 3 Representative optimized structure of VOY^1 at MP2/6-311++G(2d,2p)

be noted that in former article of the vanadyl complexes (VOY^1) synthesized was used as a catalyst in the epoxidation of styrene [27].

Entirely non-hydrogen atoms were refined anisotropically. Transform ellipsoids are presented at the 20% possibility uniform. The statistics assortment and modification performances are review in Table 1. Chosen angles and bond distances are presented in Table 2.

The bright green crystal of complex.1 (VOY^1) (0.35, 0.04, 0.42 mm) was applied in the diffraction valuation at 298 °K. This compound was recrystallized from $CHCl_3$. The IR spectrum of crystal (VOY^1) displayed the stretching band (V=O) at 977 cm^{-1}, which is demonstrating of a monomeric arrangement.

The complex was confirmed by X-ray diffraction and the consequences designed whole confirmation that it is monomeric and the configuration close by each vanadium atom is a deformed square-pyamid with the oxo ligand in the axial locality.

The entire cis angles are in the situations 57.508(15)–88.336(15)° for VOY^1 crystal. The N (2)–V–O(3) 168.401(14)° is the maximum, whereas N(2)–V–O(1), 134.471(16)° is the minimum trans angle.

The corresponding bond distances in the crystal (VOY^1) for situation of vanadium atom are 1.537(6), 1.765(5), 1.798(4) Å for V–O(1), V–O(2) and V–O(3), respectively, and 2.342(6), 2.267(7)Å for V–N(1) and V–N(2), respectively. There is isolated oxygen atom attached to the vanadum atom to complete it one axial location (V=O).

The V–O (2) and V–O (3) bonds (1.765 and 1.798 Å) are longer than of V–O (1) bond (1.537 Å). As forecast, due to π-back bonding, the V–O bond distance (V–O (1) = 1.537 Å) containing vanadyl oxygen is smaller than the V–O(2), (1.765 Å) and V–O(3), (1.798 Å) and V–N(1), (2.342 Å) and V–N(2), (2.267 Å). The vanadium(IV) atom is (0.006 Å) outside plane of the plane described by O(2), O(3), N(1) and N(2).

IR-spectral studies and Electronic spectra (Uv–vis)

A practical list of IR spectral data is presented in Tables 3, 4. By comparing the IR spectrum of dimethyl sulfide and dimethyl sulfoxide, it can be seen that an extensive peak arose at almost 1050 cm^{-1} in the dimethyl sulfoxide (Fig. 4). This peak is allocated to the S=O streching vibrations.

The Schiff base ligand show an extensive band almost at 3360 cm^{-1} due to hydroxy O–H vibration. A strong band for Schiff base at almost 1285 cm^{-1} is allocated to OH in-plane bending vibration.

The phenolic streching vibrations (C–O), that arose at 1295 cm^{-1} in the Schiff base, undertake a alteration to greater frequence (28 cm^{-1}) in the complex. This alteration approves the share of oxygen in the (M–O) bond. Additionally, an extensive peak arised at almost 1640 cm^{-1} in the isolated ligand and their complex. This peak is allocated to the imine streching vibrations (C=N). An alteration to lesser frequency afterward complexation suggesting to matching of nitrogen in (C=N) to metal ion and consequently this is anticipated to decrease the electron density in the (C=N) bond.

In the short frequncy section the peak detected in the complex in the Section 480 and 585 cm^{-1} is allocated to ν(M–O) and ν(M–N), respectively, proffer that the metal ion is attached to the ligand via the imino nitrogen (C=N) and phenolic oxygen(C–O). In brief, the green compound VOY^1 whose ν(V = O) amount is at about 977 cm^{-1}, is monomeric penta-coordinated to display square-pyramidal geometries with the oxo ligand in the axial arrangement.

It looks electron-withdrawing effect of Schiff bases with: (R = F > H) replace on the metal core are convinced concluded π-accepting properties of imin (C = N) bond. Whereas the electron density of the metal core reduces by electron-withdrawing units as robust π-acceptors, it enhances by decreasing π-accepting property of electron giving Schiff base by way of imin (C = N) bond. Confirmation for this reality is likeness of imin (C = N) bond energy diminishing upon complex creation of Schiff bases, in another situation it has to be anticipated further declining. Our proposition, the electron-withdrawing effects of Schiff bases to inner metal have to be shifted through π bond not σ bond.

The electronic bands of the ligand show binary chief peaks at 309 nm. The initial peak in the Schiff base are ascribed to $\pi \rightarrow \pi$ ∗transition. Additional peak in the spectra of the Schiff base at (around 420 nm) is allocated to $n \rightarrow \pi *$ transition. This peak is transferred to lengthier wave length (about 20 nm) accompanied by enlarging in intensity. This alteration perhaps ascribed to the gift of the isolated pairs of the nitrogen atoms of the ligands to the metal ion (N→M).

The electronic bands of vanadyl compound, [VOY^1] in DMF solution displayed two peaks in the range 754 – 733 nm. The ground state of V (IV) are d_{xy} and earliest motivated dublet levels in the order of enhancing energy (d_{xz}, d_{yz}) and ($d_{x^2-y^2}$). Therefore, two peaks conforming to $d_{xy} \rightarrow d_{xz} - d_{yz}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ are imaginable. These transitions are in conformity with the arrangement of a square pyramid configuration.

Catalytic activity research

For the conversion of sulfides to sulfoxides of various catalysts are applied. It must be noted that in previous work of the vanadyl complexes synthesized (VOY^1) was applied as a catalyst in the epoxidation of styrene [27] but the new work on the conversion of sulfides to sulfoxides use of vanadyl complex (VOY^1). In recent years, various catalysts ([VO (sal-oaba)(H_2O)]-Y, [Cu(sal-oaba)(H_2O)]-Y and [Ni(sal-oaba)(H_2O)$_3$]-Y) have been used to convert sulfides to sulfoxides with conversion (88.7%), [28].

To the best of our knowledge, there is no literature report on the selective oxidation of sulfides to sulfoxides by means of a (VO^{2+} Schiff base complex with N, O donor ligand derived from 2,3-diaminopyridine) catalyst under these conditions. Oxidation of sulfides was functioned at room temperature in the attendance of a catalytic amount of the vanadium (IV) complex or (VOY^1) utilizing 20% H_2O_2 in the role of the oxidant, Scheme 1 and glacial acetic acid in the role of the solvent.

Sulfoxides are generally prepared by oxidation of sulfides [29]. Diaryl sulfoxides can be designed by Fridel-Crafts arylation of sulfur oxide applying acid catalyst. A particular experimental method is as follows:

To the complex 1 (VOY^1), (1 mmol) in glacial acetic acid was inserted the sulfide (2 mmol), then hydrogen peroxide (8 mmol, 20%) was inserted gradually. The reaction mixture was stirred at room temperature until TLC displayed the reaction was finished. The consequent solution was neutralized with aqueous NaOH (6 M) and the results was extorted with CH_2Cl_2. The organic level was dehydrated over anhydrous Na_2SO_4 and then focused under reduced pressure to yield a residue, which was passed through a small pad of silica gel by means of ethyl acetate and hexane (1:1) as eluent to provide analytically pure product. The produce remainder was then separated with ether (45–65 °C) and the activity and selectivity data were studied and measured by GC. Finally, sulfoxide and sulfone products were detected by GC. Dimethyl sulfide was chosen as a pattern substrate for optimization experiments.

The oxidation happen to afford dimethyl sulfoxide in 82% yield at the attendance of VOY^1 and 8 equiv of 20% H_2O_2 in 32 min, Table 3, item (1) The great extra of hydrogen peroxide needed was a result of its disintegration in the attendance of the VO^{2+} catalyst. The oxygen released during decomposition played little role in the oxidation of the sulfides. The oxidation take place, although in minor yield, by easily bubbling molecular oxygen among the reaction assortment under alike reaction conditions, Table 3, item (2) The oxidation of dimethyl sulfide in numerous solvents was investigated, Table 5, items 3–5. Between the solvents studied, glacial acetic acid was the greatest effective, Table 3, item 2.

On the other hand, the reaction was accomplished at various temperatures under the identical conditions. However, the oxidation was finished after 32 min at raised temperature, the selectivity diminished considerably, Table 3, items 6–8. Additional, when the oxidation of dimethyl

Scheme 1 Selective oxidation of sulfides to the matching sulfoxides applying H_2O_2 catalyzed by VO^{2+} Schiff base complex (VOY^1)

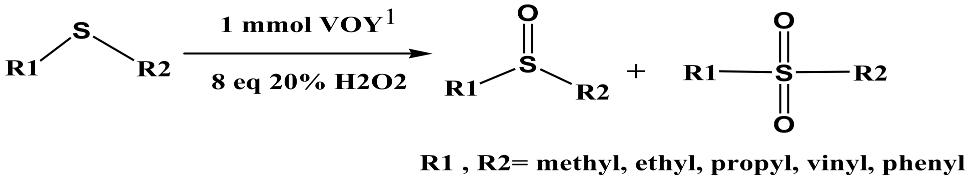


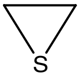
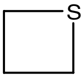
Table 1 Crystallographic and structure refinements data for complex (VOY^1)

Complex	VOY^1
Empirical formula	$C_{19}H_{11}N_3O_3F_2$ V
Formula weight	417.92
Crystal color	Green
Crystal dimensions (mm)	0.42, 0.35, 0.04
Crystal system	Monoclinic
a (Å)	12.958(2)
b (Å)	7.643(2)
c (Å)	15.234(10)
α (°)	90
β (°)	107.825(4)
γ (°)	90
V ($Å^3$)	1795(4)
Space group	P2(1)/c
Z	4
Temperature	298
T_{max}, T_{min}	0.654, 0.201
F(000)	2625
Index ranges	$-16 \leq h \leq 16$ $-17 \leq k \leq 17$ $-20 \leq l \leq 20$
Data/restraints/parameters	3595/0/242
R1; Rw	0.045, 0.145
R_{int}	0.081
Maximum and minimum peak in difference map (e $Å^{-3}$)	1.65 and − 1.22
Goodness-of-fit on F^2	1.12

Table 2 Selected bond distances (Å) and bond angles (°) for complex (VOY^1)

Bond distances (Å)	Bond angles (°)		
V–O(1)	1.537(6)	O(1)–V–O(2)	57.508(15)
V–O(2)	1.765(5)	O(1)–V–O(3)	57.128(14)
V–O(3)	1.798(4)	O(2)–V–N(2)	76.96(14)
V–N(1)	2.342(6)	O(3)–V–N(1)	80.064(16)
V–N(2)	2.267(7)	N(1)–V–N(2)	88.336(15)
		O(3)–V–N(2)	168.401(14)
		O(1)–V–N(1)	137.193(14)
		O(1)–V–N(2)	134.471(16)
		O(2)–V–N(1)	165.298(14)

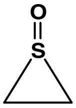
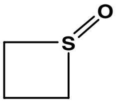
Table 3 Table unscaled vibrational frequencies (cm^{-1}) of sulfides

Compound	^{v}C–S	^{v}C–H	^{v}C–C	^{v}C=C
Me–S–Me	1010	2950, 1375	–	–
CH_3–CH_2–S–CH_3	1005	2850, 1375	950	–
$(CH_3$–$CH_2)_2S$	1000	2820, 1375	995	–
CH_3–CH_2–CH_2–S–CH_3	995	2810, 1375	990	–
CH_2=CH–S–CH_3	1043	3125, 1450	–	1650
$(CH_2$=$CH)_2S$	1100	3200, 1425	–	1660
Ph–S–CH_3	1120	3215, 1375	–	1450
Ph–S–Ph	1135	3220, 1420	–	1490
 S	990	2800, 1400	980	–
 S	995	2910, 1300	990	–

sulfide was accomplished by means of various concentrations of hydrogen peroxide (H_2O_2), the reaction did not reach achievement when applying fewer than 8 mmol of hydrogen peroxide (H_2O_2). Although, when a greater concentration was used, neither the conversion nor selectivity of the reaction was enhanced, Table 3, items 9–11. The oxidation take place in inadequate yield when the reaction was accomplished under identical reaction conditions, however, in the nonexistence of complex 1, Table 3, item 12 or when applying other VO salts, for example $VO(acac)_2$ as the catalyst, Table 3, item 13.

The oxidation of other sulfides such as ethyl methyl, diethyl, methyl propyl, methyl vinyl, divinyl, phenyl methyl, diphenyl and cyclic sulfides were then examined using the optimized reaction conditions, Table 4. For aliphatic sulfides, the conversion (98%) is greater than unsaturated, aromatic and cyclic sulfides (less than 93%). In the case of vinyl sulfides, Table 4, items 5 and 6, no oxidation was observed at the C–H bonds. Similarly, the carbon–carbon double bonds in vinyl sulfides remained intact during the oxidation, Table 4, items 5 and 6. This procedure can also be applied to the oxidation of cyclic sulfides, Table 6, items 9 and 10. The deactivation of C–H and C–C bonds has also been proven by manganese complexes [Mn(III)] [23]. As can be seen, the selectivity of converting sulfides to sulfoxides for aliphatic and aromatic compounds with similar conditions is slightly different.

Table 4 Table unscaled vibrational frequencies (cm^{-1}) of sulfoxides

Compound	^{v}C–S	^{v}C–H	^{v}C–C	^{v}C=C	^{v}S=O	^{v}V=O
$(Me)_2S{=}O$	890	3050, 1375	–	–	1050	–
$(C_2H_5)(CH_3)S{=}O$	885	3020, 1375	930	–	1048	–
$(CH_3\text{-}CH_2)_2S{=}O$	880	3010, 1375	1000	–	1035	–
$(C_3H_7)(CH_3)S{=}O$	875	3007, 1375	995	–	1030	–
$(CH_2{=}CH)(CH_3)S{=}O$	1049	3135, 1375	–	1655	1045	–
$(CH_2{=}CH)_2S{=}O$	1105	3210, 1430	–	1670	1042	–
$(Ph)(CH_3)S{=}O$	1128	3220, 1375	–	1510	1055	–
$(Ph)_2S{=}O$	1139	3225, 1415	–	1506	1058	–
	994	2815, 1410	994	–	1040	–
	1005 (68)	2930, 1325	995 (310)	–	1045 (51)	–
Catalyst (VOY^1)	–	3010, 1425	1124(56)	1602(87)	–	977 (67)

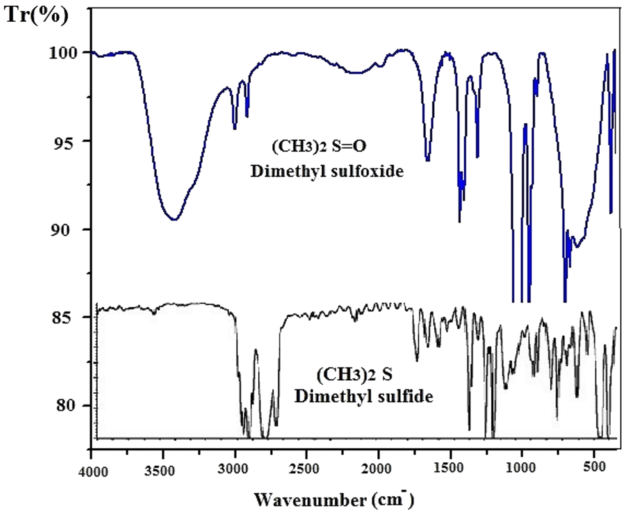


Fig. 4 IR spectrum of dimethyl sulfide and dimethyl sulfoxide

The kinetic studies display that the oxidation of sulfide is a second order reaction and is not acid catalyzed, so the reaction times remained constant as a result of increasing the acidities of the medium by the addition of glacial acetic acid. However, experiments demonstrate that dry hydrogen peroxide in glacial acetic acid does not generate per acetic acid on standing. Further, kinetic study with per acetic acid under identical reaction conditions reveal that the oxidation of sulfides is very fast; too fast to follow by titrimetry. Although the precise mechanism of this transformation is still uncertain, the oxidation probably involves the electrophilic attach of the peroxide oxygen on the sulfide sulfur atom [30]. Moreover, this oxidation system is clean, safe and operationally simple and the yields of the byproducts are high, so the oxidation method meets the needs of contemporary green chemistry and is suitable for practical synthesis.

The redox behaviors of totally compounds were studied in DMF solution by tetra butyl ammonium hexa fluoro phosphate [TBAH] in the function of the supporting electrod. The redox potentials are extracted by reference the Ag/AgCl.

Nearly, totally the complexes with N, O giver Schiff bases obtained from salen and salophen showed irreversible reduction in the region of 0.5–1.2 v [31]. When these quantities are assessed with the fresh complexes, it has been realized that with the attachment of pyridine ring in the Schiff base structure, its electron withdrawing character was improved. Subsequently, declines the electron denseness in the region of the metal core, perhaps by reason of a diminutive lived reduced situation of the metal ion or because of oxidative degradation of the Schiff bases.

The spectral variations studied (as presented in Fig. 5) upon addition of H_2O_2 to the solution of catalyst (vanadium (IV) Schiff base complex), in acetic acid, is credited to the construction of a reactive vanadium (V)-oxo intermediate. The spectral structures observed former for vanadium (V)-oxo complexes are similar to those detected in the contemporary situation (Fig. 5), [32, 33].

At the potential (0.812 v) the oxidation of the vanadium (IV) to vanadium (V) takes place as a reversible one-electron transfer. An explanatory cyclic voltammogram of complex VOY^1 is presented in Fig. 6. Catalyst plays a major role in the reduction–oxidation pathway.

$$\text{Ox}: \text{V(IV)OY}^1 \xrightarrow{E=0.812} \text{V(V)OY}^1 + e \tag{1}$$

$$\text{Red}: \text{V(V)OY}^1 + e \xrightarrow{E=0.725} \text{V(IV)OY}^1 \tag{2}$$

Table 5 Oxidation of dimethyl sulfide

Item	Complex.1 (mmol)	H_2O_2 (mmol)	Solvent (2 ml)	Time (min)	T(°C)	Conversion (%)	Sulfoxide selectivity (%)[a]
1	1	8	CH_3COOH	32	25	95	82
2[b]	1	–	CH_3COOH	500	25	4	98
3	1	8	CH_3OH	24	25	59	59
4	1	8	CH_3CH_2OH	35	25	95	56
5	1	8	CH_3CN	195	25	85	64
6	1	8	CH_3COOH	23	47	95	61
7	1	8	CH_3COOH	12	56	95	45
8	1	8	CH_3COOH	32	74	95	35
9	1	3	CH_3COOH	32	25	28	75
10	1	6	CH_3COOH	32	25	45	68
11	1	12	CH_3COOH	32	25	95	62
12	Without catalyst	8	CH_3COOH	32	25	39	98
13[b]	VO (acac)$_2$	8	CH_3COOH	32	25	52	98

[a] Separated yields

[b] The reaction was carried out under an atmosphere of O_2 as a substitute of in the existence of 20% H_2O_2

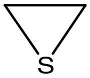
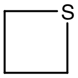
From the data CV, the following mechanism are expected.

$$V(IV)OY^1 + H_2O_2 \xrightarrow{H^+} V(V)OY^1 + HO_2^{\cdot}$$

$$V(V)OY^1 + HO_2^{\cdot} \xrightarrow{H^+} V(IV)OY^1 + H_2O_2$$

Great amount oxidation of dimethyl sulfide (10 mmol) was also examined and the consequences displayed that oxidation occur in proper yield.

Table 6 Oxidation of sulfides to sulfoxides with H_2O_2 catalyzed by complex.1 (VOY^1)

Item	Substrate	Time (min)	Conversion (%)	Sulfoxide (%)[b,c]
1	Me–S–Me	15	98	82
2	$CH_3–CH_2–S–CH_3$	18	98	91
3	$(CH_3–CH_2)_2S$	24	98	87
4	$CH_3–CH_2–CH_2$-S-CH_3	7	98	95
5	CH_2=CH–S–CH_3	22	93	94
6	$(CH_2=CH)_2S$	12	93	80
7	Ph–S–CH_3	25	92	91
8	Ph–S–Ph	22	92	89
9		12	88	84
10		15	90	83

[a] 2 mmol of substrate at room temperature with 1 mmol of VO^{2+} catalyst 1, and 8 mmol of 20% aqueous H_2O_2, in glacial acetic acid (2 ml)

[b] Separated yields

[c] The products were established by comparison of physical and spectroscopic properties with authentic compounds

The results display that the anodic peak potential (Epa) agreeing to the intramolecular reductive bond of the imine units differs as would be anticipated from the electronic influences of the replacements at locations 5 and 5′. Hence, (E_{pa}) progresses further positive corresponding to the order: ($R=F>H$).

Conclusion

Oxidation of sulfides was functioned at room temperature in the attendance of a catalytic amount of the vanadium (IV) complex or (VOY^1) utilizing 20% H_2O_2 in the role of the oxidant, Scheme 1 and glacial acetic acid in the role

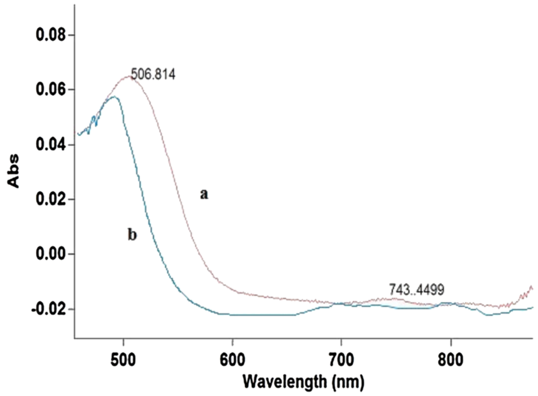


Fig. 5 Spectral changes associated with the formation of a possible V-oxo intermediate species: **a** absorption spectrum of VOY^1 in acetic acid; **b** spectrum of the resulting solution obtained after addition of 20% H_2O_2 at room temperature

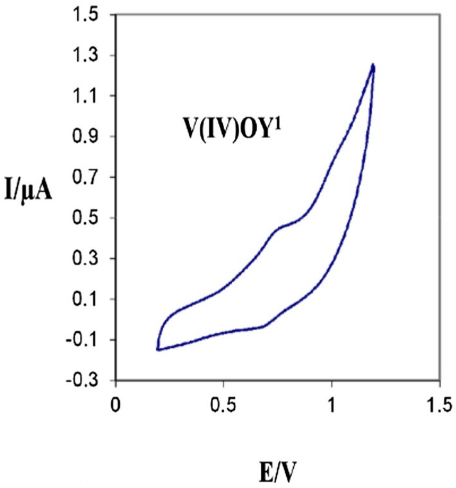


Fig. 6 Cyclic voltammogram of V(IV)OY^1

of the solvent. Our research to appropriate single crystal of (VOY^1) for X-ray diffraction calculation have been prosperous. For the conversion of sulfides to sulfoxides of various catalysts are applied. It must be noted that in previous work of the vanadyl complexes synthesized (VOY^1) was applied as a catalyst in the epoxidation of styrene but the new work on the conversion of sulfides to sulfoxides use of vanadyl complex (VOY^1). In perpetuation of our effort on the discriminating oxidation of hydrocarbons, we describe a mainly appropriate and selective oxidation of sulfides to the matching sulfoxides consuming H_2O_2 catalyzed with VO^{2+} Schiff base complex.1 (VOY^1). The oxidation happen to afford dimethyl sulfoxide in 82% yield at the attendance of VOY^1 and 8 equiv of 20% H_2O_2 in 32 min, Table 3, item 1. The great extra of hydrogen peroxide needed was a result of its disintegration in the attendance of the VO^{2+} catalyst.

The oxidation of other sulfides such as ethyl methyl, diethyl, methyl propyl, methyl vinyl, divinyl, phenyl methyl, diphenyl and cyclic sulfides were then examined using the optimized reaction conditions, Table 4. In all cases, the reactions resulted in 98% conversion of the sulfides. In the case of vinyl sulfides, Table 4, items 5 and 6, no oxidation was observed at the C–H bonds. Similarly, the carbon–carbon double bonds in vinyl sulfides remained intact during the oxidation, Table 4, items 5 and 6. This procedure can also be applied to the oxidation of cyclic sulfides, Table 6, items 9 and 10.

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