# CHAPTER 5

Chapter 5

Peroxoniobium(V)-catalyzed Selective Oxidation of Sulfides with Hydrogen Peroxide in Water: An Eco-compatible Route to Sulfoxides or Sulfones

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Facile and selective transformation of thioethers to the corresponding sulfoxides or sulfones with 30% H_2O_2 has been achieved in aqueous medium, by using newly synthesized peroxoniobium(V) complexes, monomeric heteroleptic as well as polymer-anchored pNb macrocomplexes as reusable catalysts.
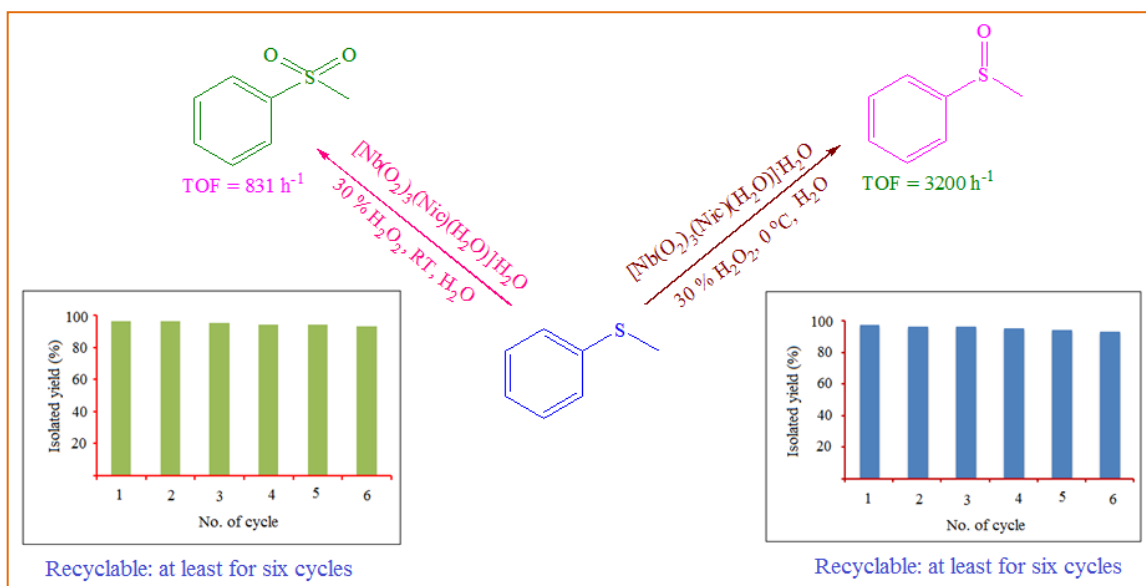
5.1   Introduction

In view of the current ecological concerns, the demand for new alternative catalytic oxidation processes that employ benign solvent, green oxidants and reagents which co-produce only innocuous waste, seems to have intensified [1-16]. Sustainability of a chemical transformation is mainly governed by the solvent, reagents and catalysts used in addition to the work-up procedure employed [17].

Chemoselective oxidation of organic sulfides represents one of the most fundamentally important reactions in the domain of organic chemistry. The practical utility of sulfoxides and sulfones as high-value commodity chemicals and their versatility as precursors for gaining access to a variety of chemically and biologically active molecules, including drugs and chiral auxiliaries, have been adequately highlighted in the literature [18-22].

A number of highly promising new catalytic strategies for selective sulfoxidation using various oxidants have been developed in the past few years based on transition metal catalysts, particularly those from groups 4-7 in their highest oxidation states such as titanium [23,24], vanadium [25-29], chromium [30,31], iron [17,32], molybdenum [1,33-38], tungsten [2-8,37] and rhenium [39]. Many of the available methods, however, rely upon the use of toxic and volatile organic solvents and harmful oxidants or require harsh reaction conditions, which lower the practical importance of otherwise efficient oxidation catalysts. Thus, notwithstanding the enormous progress in the development of catalytic protocols to achieve selective oxidation of sulfides, the important criterion of ecological sustainability is still a challenging issue to address. For example, there are very limited reports on metal-catalyzed sulfoxidation reaction in an aqueous medium [6,32,34,36,40-45].

The use of water as the most environmentally and economically attractive solvent for chemical synthesis of materials, represents a challenging issue from the green chemistry perspectives. Water holds great promise as an alternative to traditional organic solvents as it is inexpensive, safe and non-volatile, with unique redox stability and high heat capacity [46,47]. Although, traditionally, water is referred to as "the universal solvent", in organic synthesis, water has been treated as a contaminant mainly due to the concern regarding solubility [46]. However, since the 'on water' approach pioneered by

Sharpless [47], which demonstrated that solubility is not a requisite to reactivity and that many organic transformations can be performed efficiently in aqueous solvent, there has been phenomenal progress in the field of water-based organic synthesis [47-49]. This also necessitated the development of water-tolerant catalysts to support such transformations.

It is worthy to note that, in the recent past several new catalysts based on polymer-immobilized peroxotungsten (pW) and peroxomolybdenum (pMo) complexes were developed by other workers of our group, which displayed excellent stability, selectivity and efficiency with respect to yield, TON and TOF for the oxidation of thioethers under very mild conditions [2,35,36]. A few of these supported catalysts also effectively catalyzed the oxidative bromination of a variety of activated aromatics at ambient temperature and near-neutral pH [50].

Inspired by the above findings and in continuation of our work on peroxoniobates, in the present study, we focused on exploring the potential of the newly synthesized monomeric as well as water soluble polymer immobilized pNb compounds, **3.1**, **3.2**, **4.3** and **4.4** for their catalytic activity in selective oxidation of organic sulfides under mild condition, preferably in aqueous medium, using H_2O_2 as an oxidant. Out of the multitude of available organic oxidants, 30% aqueous H_2O_2 has been recognized as the best waste-preventing terminal oxidant because of the high oxygen content, cost, safety and easy handling [11-13,51,52]. Moreover, Nb being non-toxic to animals [53], peroxoniobium (pNb) based systems have been considered ideal for green chemistry application [54]. The catalytic potential of discreet synthetic hetero-ligand pNb complexes as catalysts in sulfide oxidation remains yet to be fully explored [55-57].

We were particularly interested to verify the scope of generating new pNb based catalysts using WSP as supports. We anticipated that the combination of WSP support with a pNb species would add advantages of polymeric reagent such as stability and phase homogeneity to the catalyst and reagents to the inherent oxidant ability of the pNb species to afford immobilized recoverable catalysts usable in aqueous medium. Although a homogeneous catalyst usually exhibits superior activity and selectivity compared to its heterogeneous counterpart, its recovery often involves tedious separation processes from organic products and lowered activity of recovered catalyst [4,46]. It has however been

demonstrated that employing water soluble catalysts, with water as the reaction medium, it is possible to combine catalytic efficiency with easy recovery of the catalyst through simple phase separation, owing to poor solubility of the organic products in water [4,46].

In this Chapter, we report the catalytic activity of the immobilized complexes **3.1** and **3.2** and heteroleptic pNb compounds **4.3** and **4.4**, for the controlled oxidation of sulfides with H_2O_2 in an aqueous medium, in terms of selectivity, yield, reusability, and sustainability, to obtain sulfoxides or sulfone. The two classes of compounds investigated enabled us to draw comparison on their efficacy as catalysts in the chosen reactions.

5.2   Experimental section

5.2.1   General procedure for oxidation of sulfides to sulfoxides [catalysts: PANb (3.1), PSSNb (3.2), NbA (4.3) or NbN (4.4)]

In a representative procedure, an organic substrate (5 mmol) was added to a solution of a catalyst (0.002 mmol) in water (5 mL) and then 30% H_2O_2 as oxidant (1.13 mL, 10 mmol) was added, maintaining a catalyst:substrate molar ratio of 1:2500 and a substrate:H_2O_2 molar ratio of 1:2 in a 50 mL round-bottomed flask. The reaction was conducted at 0 °C in an ice bath under continuous stirring. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the products were extracted with diethyl ether and dried over anhydrous Na_2SO_4 and distilled under reduced pressure to remove excess diethyl ether. The corresponding sulfoxide obtained was purified by column chromatography on silica gel using ethyl acetate and n-hexane (1:9). The products obtained were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy, and in the case of solid sulfoxides products, in addition to the above spectral analysis, we have also carried out melting point determination (see **Appendix 5A**).

5.2.2 General procedure for oxidation of sulfides to sulfones [catalysts: PANb (3.1), PSSNb (3.2), NbA (4.3) or NbN (4.4)]

To a stirred solution of the catalyst (0.005 mmol) and 30% H_2O_2 (10 mmol), the organic substrate (5 mmol) was added in water (5 mL) maintaining a catalyst: substrate molar ratio of 1:1000 and a substrate:H_2O_2 ratio of 1:2 at room temperature (RT) under continuous stirring. The reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the products were extracted with diethyl ether and dried over anhydrous Na_2SO_4 and distilled under reduced pressure to remove excess diethyl ether. The corresponding sulfone obtained was purified by column chromatography on silica gel using ethyl acetate and n-hexane (1:9). The IR, ^{1}H NMR, and ^{13}C NMR spectroscopy tools were used to characterize the products. In addition to the above spectral analysis, we have also carried out melting point determination for the products (see **Appendix 5A**).

5.2.3 Regeneration of the catalyst

Any of the following procedures could be adopted to regenerate the catalysts for reuse. The regeneration of the catalyst was carried out for the reaction using methyl phenyl sulfide (MPS). After completion of the oxidation reaction and subsequent extraction of the organic reaction product, the aqueous part of the reaction mixture was transferred to a 250 mL beaker. Keeping the solution in an ice bath, 30% H_2O_2 was added to it maintaining a Nb:peroxide ratio of 1:2, followed by addition of pre-cooled acetone under constant stirring until a white pasty mass separated out. From this precipitate, the catalyst was finally obtained as a microcrystalline solid by solvent induced precipitation with acetone as described in the Chapter 3 and Chapter 4. The regenerated pNb catalyst was then placed into a fresh reaction mixture consisting of MPS and hydrogen peroxide in water, and the reaction was allowed to proceed under optimized conditions as mentioned under **Section 5.2.1** (for sulfoxide) or **Section 5.2.2** (for sulfone). The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the process was repeated for a total of six reaction cycles.

In an alternative procedure, recycling of the catalyst could be performed *in situ* after completion of the reaction cycle and extraction of the organic reaction product. Regeneration of the used reagent could be achieved by adding 30% H_2O_2 and a fresh batch of substrates to the aqueous portion of the spent reaction mixture, maintaining the same procedure as mentioned under **Section 5.2.1** (for sulfoxide) or **Section 5.2.2** (for sulfone), and conducting the reaction under optimized conditions. Each of the procedures was repeated for six reaction cycles.

5.3   Results and discussion

5.3.1   Oxidation of sulfides to sulfoxides – Optimization of reaction condition

Catalytic performances of the title pNb complexes in oxidation of various organic sulfides using 30% aqueous H_2O_2 as a terminal oxidant in neat water have been investigated. In a preliminary experiment, the reaction of MPS with H_2O_2 (1 equiv.) in the presence of the water-soluble catalyst **NbA**, maintaining a catalyst:substrate molar ratio of 1:1000, was conducted in water at ambient temperature under magnetic stirring. The reaction proceeded rapidly within a reasonably short period in the presence of each of the catalysts. The reaction under these conditions was, however, observed to be mildly exothermic, leading to the formation of a mixture of 1a and 1b with a molar ratio of 85:15, as presented in **Table 5.1** (entry 1). Subsequently, the reaction conditions for selective sulfoxidation including substrate:oxidant stoichiometry, catalyst concentration, solvent type and reaction temperature were optimized using MPS as the model substrate and the **NbA** complex as the catalyst. We have attempted to control the degree of oxidation by lowering the reaction temperature to 0 °C by conducting the reaction in an ice bath.

As has been anticipated, the reaction indeed proceeded smoothly to yield sulfoxide with 100% selectivity and nearly 70% conversion under these conditions. Complete oxidation of MPS to pure sulfoxide could be attained with excellent TOF (without affecting the selectivity) by increasing the oxidant:substrate molar ratio to 2:1 without altering the other reaction conditions.

5.3.1.1 The influence of catalyst amount on the catalytic efficiency

We have examined the effect of the catalyst amount on the rate and selectivity of the reaction under otherwise identical reaction conditions. As illustrated in **Table 5.1**, although the rate was faster at higher catalyst concentration and a reasonably good TOF could be attained even at a catalyst:substrate ratio of 1:3000, the optimal catalyst:substrate molar ratio was found to be 1:2500 for achieving the highest TOF along with complete selectivity. The pNb species has an important contribution in facilitating the reactions, which was confirmed by conducting a control experiment without the catalyst. The reaction was extremely slow and nonselective in the absence of the catalyst, affording a mixture of sulfoxide and sulfone in < 9% yield under the optimized reaction conditions (**Table 5.1**, entry 12). We have also compared the catalytic efficiency of the newly developed catalysts with the neat tetraperoxoniobate (**NaNb**) complex $Na_3[Nb(O_2)_4]\cdot13H_2O$ under analogous reaction conditions. As shown in **Table 5.1** (entry 10), the reaction proceeded smoothly in the presence of **NaNb** as well, although product selectivity could not be obtained under the maintained reaction conditions. From these observations, it is apparent that the co-ligand environment influences the catalytic activity of the pNb compounds.

5.3.1.2 Effect of solvent

In addition to water, we have screened the sulfoxidation reaction in relatively safer organic solvents such as CH_3OH and CH_3CN. The solvent effect has been evaluated in the oxidation of MPS. Interestingly, the catalytic protocol for sulfoxidation was found to be compatible with these organic solvents as well; however, the efficiency of the catalysts was observed to vary with the nature of the solvent. Although the catalysts are insoluble in neat organic solvents, including methanol or acetonitrile, in the presence of aqueous H_2O_2 used as an oxidant, each of the catalysts dissolves completely in these water-miscible solvents, leading to the homogeneity of the catalytic process. It is pertinent to note that we have strategically avoided the use of hazardous chlorinated solvents in the present work. The data presented in **Table 5.1** (entries 8 and 9) demonstrate that although the **NbA** is highly potent in methanol as well as in acetonitrile, MeOH proved to be a relatively better solvent, affording both product selectivity and high yield at ambient temperature (**Table 5.1**, entry 8). Significantly, the

Table 5.1 Optimization of reaction conditions for selective oxidation of methyl phenyl sulfide (MPS) by 30% H_2O_2 catalyzed by pNb complexes[a]
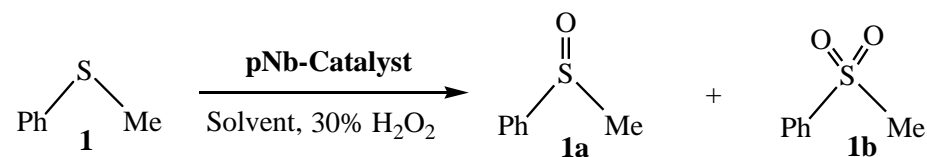
Entry	Molar ratio Cat:MPS	30% H_2O_2 (equiv.)	Solvent	Time (min)	Isolated Yield(%)	1a : 1b	TON	TOF (h^{-1})
1	1:1000[b]	1	H_2O	75	76	85:15	760	608
2	1:1000[c]	1	H_2O	75	70	100:0	700	560
3	1:500[c]	2	H_2O	38	97	85:15	485	766
4	1:1000[c]	2	H_2O	40	95	100:0	950	1425
5	1:2000[c]	2	H_2O	43	96	100:0	1920	2679
6	**1:2500[c]**	**2**	**H_2O**	**50**	**97**	**100:0**	**2425**	**2910**
7	1:3000[c]	2	H_2O	75	95	100:0	2844	2275
8	1:2500[b]	2	CH_3OH	115	75	100:0	1875	978
9	1:2500[b]	2	CH_3CN	120	70	100:0	1750	875
10[d]	1:2500[c]	2	H_2O	95	97	55:45	2425	1531
11[e]	1:2500[c]	2	H_2O	20	96	100:0	2400	7200
12[f]	-	2	H_2O	50	9	90:10	-	-

[a]Reactions were carried out with 5 mmol of substrate in 5 mL of solvent. Catalyst amount = 2.22 mg for 0.005 mmol of **NbA**. [b]Reaction at room temperature. [c]Reaction at 0 ^{o}C in ice bath. [d]$Na_3[Nb(O_2)_4]\cdot13H_2O$ as catalyst, [e]Using H_2SO_4 (1 mmol), [f]Blank experiment (without catalyst).
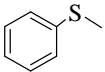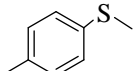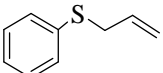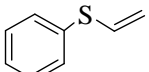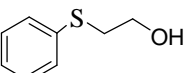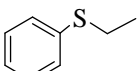
selective sulfoxidation in the chosen organic solvents could be achieved at room temperature. It is thus remarkable that by using the same set of catalysts, it is possible to achieve selective oxidation of sulfide in water and organic solvents under mild reaction conditions. Water, however, proved to be the best solvent with respect to catalyst efficiency as demonstrated by higher TOF and product selectivity, notwithstanding the insolubility of most of the chosen organic substrates in water. This is not surprising, considering the observations made by Sharpless *et al.* [47] that several reactions involving water-insoluble organic reactants could proceed optimally in pure water. Our results are also in agreement with earlier findings that chemoselective sulfoxidation is favoured in polar protic solvent with strong hydrogen bonding ability [58-60].

The sulfoxidation reaction has been carried out at the natural pH attained by the reaction mixture (*ca.* 5). However, a substantial increase in TOF was noted on addition of acid to the reaction medium (**Table 5.1**, entry 11). The finding is in accord with the reports related to other peroxo metal systems (Ti, Mo and W) [61-65], where it has been demonstrated that the use of acidic additives led to an improvement in catalytic activity of the peroxometallates. The role of protons in the activation of titanium peroxo complexes has been extensively investigated by Kholdeeva and co-workers [63]. In the present work, however, since our goal has been to maintain a mild reaction condition, addition of acid or other additives was avoided as far as possible. Therefore no attempt has been made to adjust the pH of the reaction.
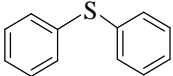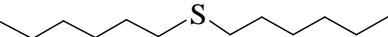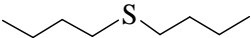
5.3.1.3 Selective sulfoxidation catalyzed by NbA, NbN, PANb and PSSNb

The aforementioned findings were further exploited to obtain pure sulfoxide from a series of aryl alkyl, aryl vinyl, aryl alcohol and dialkyl sulfides listed in **Table 5.2** and **Table 5.3**. Evidently, all the catalysts were effective in leading to the facile and selective transformation of each of the substrates to the corresponding sulfoxide with impressive yield, although the **NbN** catalyst displayed relatively superior activity than **NbA** (**Table 5.2**). The transformations worked well for both aliphatic and aromatic substrates irrespective of having electron-donating or electron withdrawing moieties. The nature of the substrate and the attached substituent, however, appeared to influence the rates of oxidation [8,52]. The observed trend in variations in the rate of oxidation of the chosen

Table 5.2 Selective oxidation of sulfides to sulfoxides catalyzed by **NbA** and **NbN**[a]

NbA or NbN, (C:S = 1:2500)

30 % H_2O_2 (2 equivalents), 0 °C, H_2O

Entry	Substrate	NbA				NbN			
		Time (min)	Isolated Yield of sulfoxide (%)	TON[b]	TOF[c] (h⁻¹)	Time (min)	Isolated Yield of sulfoxide (%)	TON[b]	TOF[c] (h⁻¹)
1.		50	97	2425	2910	45	96	2400	3200
		50	93[d]	2325	2790	45	94[d]	2350	3133
		50	96[e]	2400	2880	45	95[e]	2375	3166
2.		45	97	2425	3233	40	95	2375	3562
3.		85	93	2325	1641	75	94	2350	1880
4.		240	95	2375	593	225	93	2325	620
5.		115	97	2425	1265	105	95	2375	1357
6.		55	96	2400	2618	50	95	2375	2850
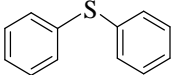
Entry	Substrate	NbA				NbN			
		Time (min)	Isolated Yield of sulfoxide (%)	TON[b]	TOF[c] (h⁻¹)	Time (min)	Isolated Yield of sulfoxide (%)	TON[b]	TOF[c] (h⁻¹)
7.		210	93	2325	664	195	94	2350	723
8.		30	97	2425	4850	25	96	2400	5760
9.		40	96	2400	3600	35	93	2325	3985
10.		40	97	2425	3637	35	95	2375	4071

[a]Optimized condition: 5 mmol substrate, 10 mmol 30% H_2O_2 and 0.002 mmol catalyst in H_2O at 0 °C. [b]TON (turnover number) = mmol of product per mmol of catalyst. [c]TOF (turnover frequency) = mmol of product per mmol of catalyst per hour. [d]Yield of 6th reaction cycle, [e]Scale up data (6.24 g of MPS).

Table 5.3 Selective oxidation of sulfides to sulfoxides catalyzed by **PANb** and **PSSNb**[a]

Entry	Substrate	PANb				PSSNb			
		Time (min)	Isolated Yield of sulfoxide (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated Yield of sulfoxide (%)	TON[b]	TOF[c] (h^{-1})
1.		60	94	2350	2350	55	96	2400	2609
		60	92[d]	2300	2300	55	93[d]	2325	2527
		60	93[d]	2325	2325	55	94[e]	2350	2554
2.		55	93	2325	2527	50	95	2375	3167
3.		100	93	2325	1392	90	92	2300	1533
4.		315	94	2350	447	300	93	2325	465
5.		100	96	2400	1437	90	97	2425	1617

Entry	Substrate	PANb				PSSNb			
		Time (min)	Isolated Yield of sulfoxide (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated Yield of sulfoxide (%)	TON[b]	TOF[c] (h^{-1})
6.		360	91	2275	379	330	92	2300	418
7.		15	96	2400	9600	15	97	2425	9700

[a]Optimized condition: 5 mmol substrate, 10 mmol 30% H_2O_2 and 0.002 mmol catalyst in H_2O at 0 °C. [b]TON (turnover number) = mmol of product per mmol of catalyst. [c]TOF (turnover frequency) = mmol of product per mmol of catalyst per hour. [d]Yield of 6th reaction cycle, [e]Scale up data (6.24 g of MPS)..

substrates is consistent with the previous findings that with increasing nucleophilicity of the sulfide, the rate of oxidation with H_2O_2 increases [8,52]. It is therefore not unexpected that dialkyl sulfides were oxidized by H_2O_2 at a faster rate leading to the highest TOF, relative to conjugated systems such as allylic and vinylic sulfides or aromatic sulfides. It is notable that even in the case of a less nucleophilic diaromatic sulfide the corresponding sulfoxide was effectively obtained.

A comparison of the catalytic efficiency of the two classes of catalysts used *viz.,* free monomeric and WSP supported pNb compounds, in terms of their TOF and TON revealed that macro complexes showed slightly less activity *vis-a-vis* their monomeric counterpart in the case of most of the substrates. However, with respect to the substrate dimethyl sulfide, the TOF obtained using the immobilized catalysts were nearly double compared to that observed with the monomeric catalysts. Between the two supported catalysts investigated, **PSSNb** exhibited higher performance in comparison to **PANb** (**Table 5.3**).

A salient feature of the methodology, which enhances the synthetic utility of the oxidation, is the excellent chemoselectivity displayed by the catalysts for the sulfur group of substituted sulfides such as allylic, vinylic and alcoholic sulfides, with co-existing sensitive functional groups (**Tables 5.2** and **5.3**, entries 3-5). Importantly, allylic and vinylic sulfoxides were obtained without an epoxidation product. Moreover, the -OH group of alcoholic sulfides and the benzylic C-H bond remained unaffected when the benzylic and alcoholic sulfides could be oxidized to the corresponding sulfoxide under the maintained reaction conditions. The potential of the developed protocol for scaled-up synthetic application has been demonstrated by conducting the oxidation with 6.24 g of thioanisole (ten fold scale) under optimized conditions (**Tables 5.2** and **5.3**, entry 1e). The H_2O_2 efficiency in the oxidation in the presence of the catalysts was found to be higher than 90%. The H_2O_2 efficiency, which is a measure of the effective use of H_2O_2, has been defined as $100 \times$ moles of H_2O_2 consumed in the formation of oxyfunctionalized products per mole of H_2O_2 converted [51].

5.3.2   Oxidation of sulfides to sulfones

Clean conversion of MPS to sulfone could be achieved with high yield in an aqueous medium, in the presence of each of the catalysts, simply by extending the reaction time after initial formation of sulfoxides and conducting the reaction at room temperature. The optimization of reaction conditions, accomplished by using MPS as a substrate and **NbA** as a catalyst, revealed that the best rate and TOF could be obtained by maintaining the catalyst:substrate ratio of 1:1000 using 2 equiv. of H_2O_2 (**Table 5.4**, entry 1).

Table 5.4 Optimization of reaction conditions for **NbA** catalyzed selective oxidation of methyl phenyl sulfide (MPS) to sulfone[a]

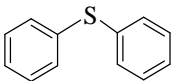| Entry	Molar ratio (Catalyst:MPS)	H_2O_2 (equiv.)	Solvent	Time (min)	Isolated yield (%)	1a:1b	TON	TOF(h^{-1})
1.	**1:1000**	**2**	**H_2O**	**80**	**96**	**0:100**	**960**	**720**
2.	1:2000	2	H_2O	175	95	0:100	1900	651
3.	1:2500	2	H_2O	240	96	25:75	2400	600
4.	1:1000	2	CH_3OH	240	96	70:30	960	240
5.	1:1000	2	CH_3CN	240	93	75:25	930	232
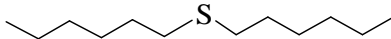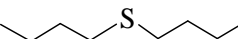
[a]Reactions are carried out with 5 mmol of substrate in 5 mL of solvent at room temperature.

Apart from MPS, the protocol could be conveniently applied to obtain pure sulfone from a variety of aromatic and aliphatic sulfides as shown in **Tables 5.5** and **5.6**. The transformations were chemoselective (**Table 5.5** and **5.6**, entries 3-5) and amenable for scale-up (**Tables 5.5** and **5.6**, entry 1e) as has been observed in the case of sulfoxidation reaction. These findings underscore the synthetic value of the

Table 5.5 Selective oxidation of sulfides to sulfones catalyzed by **NbA** and **NbN**[a]

Entry	Substrate	NbA				NbN			
		Time (min)	Isolated Yield of sulfone (%)	TON[b]	TOF[c] (h⁻¹)	Time (min)	Isolated Yield of sulfone (%)	TON[b]	TOF[c] (h⁻¹)
1.		80	96	960	720	70	97	970	831
		80	93[d]	930	697	70	93	930	797
		80	95[e]	950	712	70	94[e]	940	805
2.		75	95	950	760	65	97	970	895
3.		145	93	930	384	135	94	940	431
4.		255	94	940	221	250	93	930	235
5.		190	97	970	306	180	95	950	316
6.		90	95	950	633	80	94	940	705

Continued...

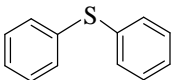| Entry	Substrate	NbA				NbN			
		Time (min)	Isolated Yield of sulfone (%)	TON[b]	TOF[c] (h⁻¹)	Time (min)	Isolated Yield of sulfone (%)	TON[b]	TOF[c] (h⁻¹)
7.		315	93	930	177	310	93	930	180
8.		65	94	940	867	55	96	960	1047
9.		70	93	930	797	60	93	930	930
10.		70	95	950	814	60	94	940	940

[a]Optimized condition: 5 mmol substrate, 10 mmol 30% H_2O_2 and 0.005 mmol catalyst in H_2O at RT. [b]TON (turnover number) = mmol of product per mmol of catalyst. [c]TOF (turnover frequency) = mmol of product per mmol of catalyst per hour. [d]Yield of 6th reaction cycle, [e]Scale up data (6.24 g of MPS).

Table 5.6 Selective oxidation of sulfides to sulfones catalyzed by **PANb** and **PSSNb**[a]

Entry	Substrate	PANb				PSSNb			
		Time (min)	Isolated Yield of sulfone (%)	TON[b]	TOF[c] (h⁻¹)	Time (min)	Isolated Yield of sulfone (%)	TON[b]	TOF[c] (h⁻¹)
1.		65	97	970	898	60	97	970	970
		65	93[d]	930	861	60	94[d]	940	940
		65	95[e]	950	880	60	96[e]	960	960
2.		60	94	940	940	55	93	930	1011
3.		255	93	930	219	240	94	940	235
4.		300	94	940	188	270	93	930	207
5.		180	96	960	320	150	97	970	388

Entry	Substrate	PANb				PSSNb			
		Time (min)	Isolated Yield of sulfone (%)	TON[b]	TOF[c] (h^{-1})	Time (min)	Isolated Yield of sulfone (%)	TON[b]	TOF[c] (h^{-1})
6.		380	93	930	150	360	93	930	155
7.		10	96	960	5647	10	97	970	5706

[a]Optimized condition: 5 mmol substrate, 10 mmol 30% H_2O_2 and 0.005 mmol catalyst in H_2O at RT. [b]TON (turnover number) = mmol of product per mmol of catalyst. [c]TOF (turnover frequency) = mmol of product per mmol of catalyst per hour. [d]Yield of 6th reaction cycle, [e]Scale up data (6.24 g of MPS).

methodology. It is interesting to note that, in the present case of oxidation of the substrates to sulfone, the immobilized catalysts **3.1** and **3.2** displayed consistently superior activity providing nearly 5-fold higher TOF for oxidation of dimethyl sulfide (**Table 5.6** entry 7).

5.3.3   Recyclability of the catalysts

The reusability of the catalysts for subsequent cycles of oxidation was assessed by employing MPS as the substrate. The catalysts afforded regeneration *in situ* after separation of the organic product from the reaction mixture on completion of the reaction and could be reused without further conditioning. Regeneration was accomplished by simply charging the aqueous part of the spent reaction mixture with 30% H_2O_2 and a fresh batch of substrates on completion of each reaction cycle. In an alternative approach, the regenerated catalysts could also be isolated into the solid state by solvent-induced precipitation with acetone after treating the aqueous extract of the spent reaction mixture with 30% H_2O_2. Nevertheless, the *in situ* regeneration of the catalyst offers obvious advantages as the procedure does not require tedious separation and subsequent purification steps, which are usually associated with soluble catalysts [46]. The activity and selectivity of the catalysts remained unaltered for at least up to 6 reaction cycles as illustrated in **Tables 5.2** and **5.3** (entry 1d), **Tables 5.5** and **5.6** (entry 1d) and **Figs. 5.1** and **5.2**.

In order to further confirm that the catalysts remain intact after their use in catalytic cycles, the recovered catalysts were characterized by elemental analysis and spectral studies. The IR and Raman spectra of each of the regenerated catalysts resembled closely the corresponding spectrum of the starting catalyst, displaying the typical absorptions for the triperoxoniobium moiety and the respective metal bound co-ligand, indicating that the coordination environment of the complexes was not altered during the catalytic process. The IR spectrum of the regenerated catalyst **NbA** is presented in **Fig. 5.3 (b)**. No significant change was observed in the niobium and peroxide contents of the recovered catalysts in comparison to the respective original complex. It is thus evident that the metal complexes retain their structural integrity even after several catalytic cycles.

Interestingly, the procedure with **NbA** used as a catalyst provided an overall TOF of *ca.* 17,130 h^{-1} (*ca.* 18,999 h^{-1} for **NbN**) after 6 cycles of oxidation of MPS to sulfoxides and *ca.* 4,259 h^{-1} (*ca.* 4,884 h^{-1} with **NbN**) for conversion to sulfone. For pNb macrocomplexes, overall TOF of *ca.* 17136 h^{-1} was observed for **PSSNb** (*ca.* 14,100 h^{-1} for **PANb**) after 6 cycles of oxidation of MPS to sulfoxides and *ca.*5,690 h^{-1} with **PSSNb** (*ca.*5,268 h^{-1} with **PANb**) for conversion to sulfone. These results, obtained under truly mild reaction condition in aqueous medium, further demonstrate the superior activity of the catalysts over other reported methods for sulfide oxidation involving Nb(V) catalysts [55-57,66,67], as well as many other protocols based on Mo(VI) [1,37,38,58,68-76] or W(VI)/H$_2$O$_2$ [3-7,38,] systems.
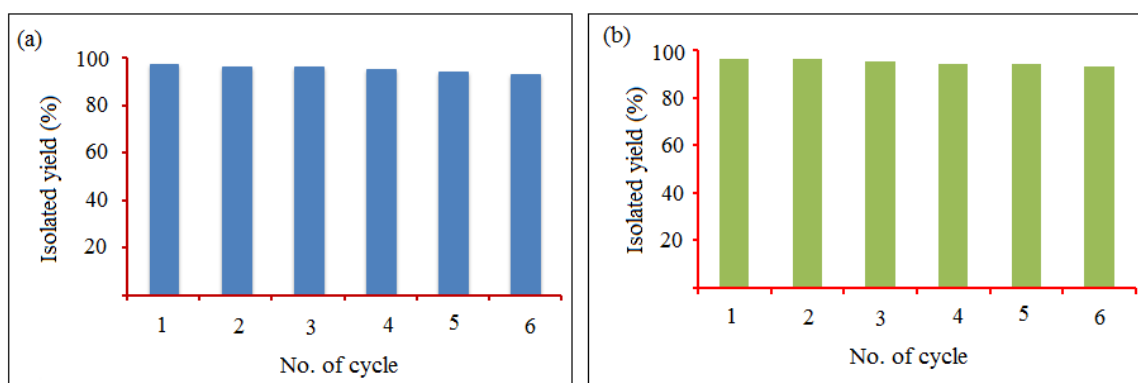

Fig. 5.1 Catalyst regeneration up to 6th reaction cycle. Recyclability of **NbA** (used as representative catalyst) for the selective oxidation of MPS to (a) sulfoxide or (b) sulfone.

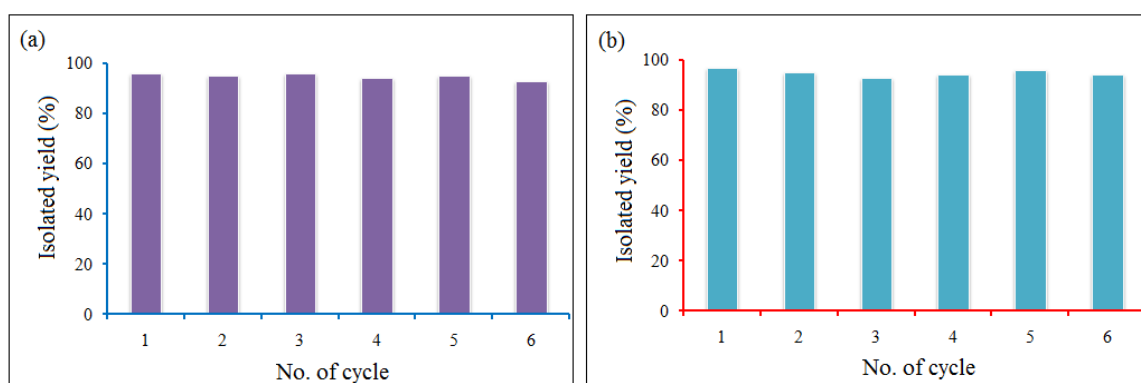**Fig. 5.2** Catalyst regeneration up to 6th reaction cycle. Recyclability of **PSSNb** (used as representative catalyst for macro pNb complex) for the selective oxidation of MPS to (a) sulfoxide or (b) sulfone.
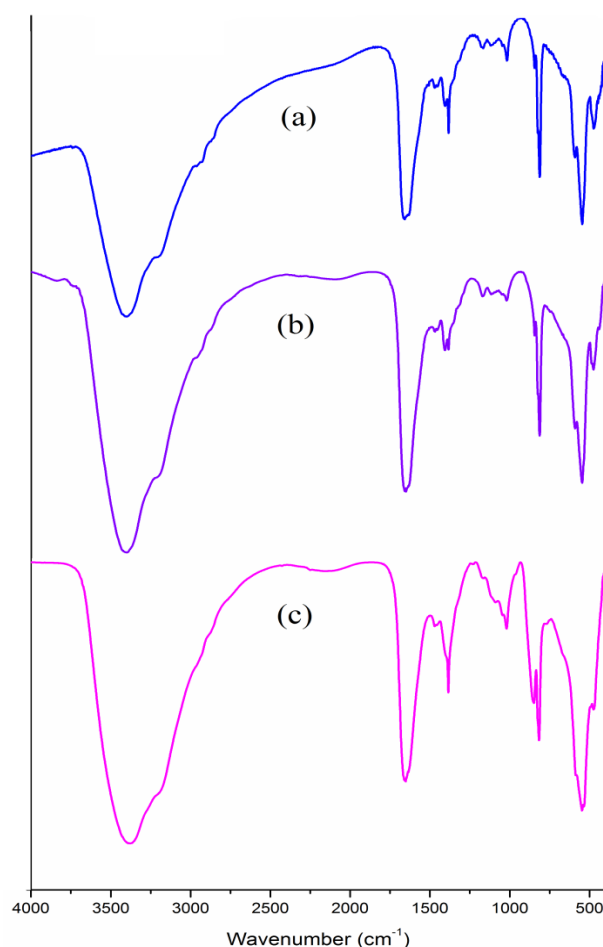
Fig. 5.3 IR spectra of (a) **NbA**, (b) Regenerated **NbA** after the 2nd cycle of reaction and (c) Diperoxoniobate complex recovered after oxidation of MPS by **NbA**, in absence of H_2O_2.

5.3.4 The proposed mechanism

Based on our results and taking into account earlier findings on the catalytic activity of some other peroxometal systems [2,35], a credible mechanism for the pNb-catalyzed selective oxidation of sulfides to sulfoxides or sulfone by H_2O_2 has been proposed (**Fig. 5.4**), which satisfactorily describes the principal features of our findings from the present study.

As shown in **Fig. 5.4**, with the **NbA** catalyst as a representative, it is possible that the reaction proceeds through the formation of the diperoxoniobate intermediate **II**, subsequent to the facile transfer of electrophilic oxygen from the triperoxoniobium complex **I** to the substrate **V** to yield sulfoxides (reaction a). The intermediate **II** combines with the peroxide of H_2O_2 to regenerate the starting triperoxoniobate complex

(reaction b) leading to a catalytic cycle. The resulting sulfoxides formed may undergo further oxidation in a separate cycle by reacting with a triperoxo Nb species to yield sulfone (reaction c). The sulfone formation thus seems to be a two-step process. The greater ease of oxidation of sulfide to sulfoxide compared to the second oxidation of sulfoxide to sulfone is likely to be a consequence of higher nucleophilicity of sulfide relative to sulfoxide. The proposed mechanism is in line with the reaction pathway proposed previously for peroxoniobate-catalyzed oxidation of sulfide [77,78] and *in situ* generated pNb catalyzed asymmetric epoxidation of allylic alcohols [79]. .

It is worth noting that although the mechanism of action of peroxo complexes of other d^0 metals such as V(V) [80-82], Mo(VI) [35,37,68,76,82-90] and W(VI) [2,37,76,90-93] has been extensively investigated in organic oxidation, the chemistry of Nb(V) peroxide still remains relatively unexplored. The previous studies from several laboratories including ours [2,35,91,94] have shown that during substrate oxidation performed by active diperoxo complexes of Mo(VI) or W(VI), a more stable monoperoxo species is formed which is practically inactive in oxidation [37,81,87-90]. Taking into account this finding, it is reasonable to expect the formation of a less reactive diperoxoniobate (**DPNb**) intermediate from an active triperoxoniobate (**TPNb**) species during sulfide oxidation, as shown in the proposed mechanism (reaction intermediate **II**). In order to establish the involvement of such an intermediate in the reaction pathway, a separate experiment was conducted using **NbA** as a stoichiometric oxidant of MPS, maintaining an **NbA**:substrate molar ratio of 1:1 in the absence of H_2O_2 at 0 °C. The substrate was completely and selectively transformed into sulfoxide within a reaction time of *ca.* 40 minutes. The product isolated from the aqueous part of the spent reaction mixture was subsequently subjected to spectral and elemental analyses. The data obtained indicated a Nb:peroxo ratio of 1:2, clearly suggesting the formation of a **DPNb** species. This was further confirmed from the IR spectrum which showed two distinct bands, in addition to the coordinated amino acid ligands, characteristic of a **DPNb** moiety [**Fig. 5.3 (b)**] in contrast to the three peroxo absorptions of the original triperoxoniobium catalyst. Similar reaction of MPS conducted with the isolated **DPNb** complex was noted to be extremely slow, as has been anticipated, remaining incomplete even after 14 h of reaction time. The aforementioned findings lent further credence to the proposed mechanism.
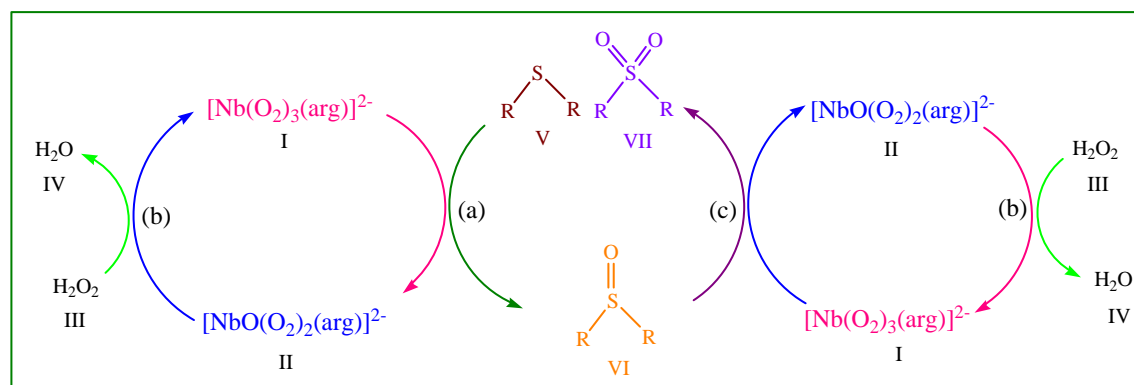
Fig. 5.4 Schematic representation of reactions occurring with pNb catalysts, **NbA** (**4.3**) as representative. [a] The reaction proceeds through the formation of the diperoxoniobate intermediate **II** by the transfer of electrophilic oxygen from the triperoxoniobium complex **I** to the substrate **V** to yield sulfoxides. [b] The intermediate **II** combines with the peroxide of H_2O_2 to regenerate the starting triperoxoniobate complex **I**. [c] The sulfoxide **VI** may further undergo oxidation in a separate cycle by reacting with a triperoxo Nb species to yield sulfone **VII**.

5.4 Conclusions

In summary, it has been demonstrated that synthesized triperoxoniobium(V) complexes, *viz.,* **NbA** and **NbN** as well as the immobilized compounds, **PANb** and **PSSNb** could act as efficient catalysts in the selective oxidation of variously substituted sulfides to selectively obtain sulfoxide or sulfone with 30% H_2O_2 in neat water. The reactions proceeded under mild conditions to afford the resulting products with impressive yield and TON or TOF. It has been observed that the catalysts display excellent chemoselectivity toward the sulfur group of substrates with other oxidizable functional groups, including the hydroxyl group and C=C bonds. The adherence of the developed protocol to the principles of green chemistry is ensured by the fact that the reactions, apart from using neat water as a standard green solvent and aqueous 30% H_2O_2 as an oxidant, employ a non-toxic pNb catalyst which can be reused in subsequent cycles without losing its activity. In addition, the catalytic oxidation was absolutely free from organic co-solvent, co-catalyst or any other auxiliaries, involved easy work-up procedure and was amenable for ready scalability. All of these features make the presented catalytic strategies attractive and interesting from both economic and environmental viewpoints.

Appendix: 5A Characterization of Sulfoxides and Sulfones:

(a) Methylphenyl sulfoxide: Isolated as light yellow solid; mp 28-29°C; ν (KBr)/cm^{-1} 1047;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 2.73(s, 3H); 7.30-7.36(m, 1H); 7.40-7.49(m, 2H); 7.61-7.69(m, 2H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 43.92; 123.52; 128.68; 130.98; 145.49
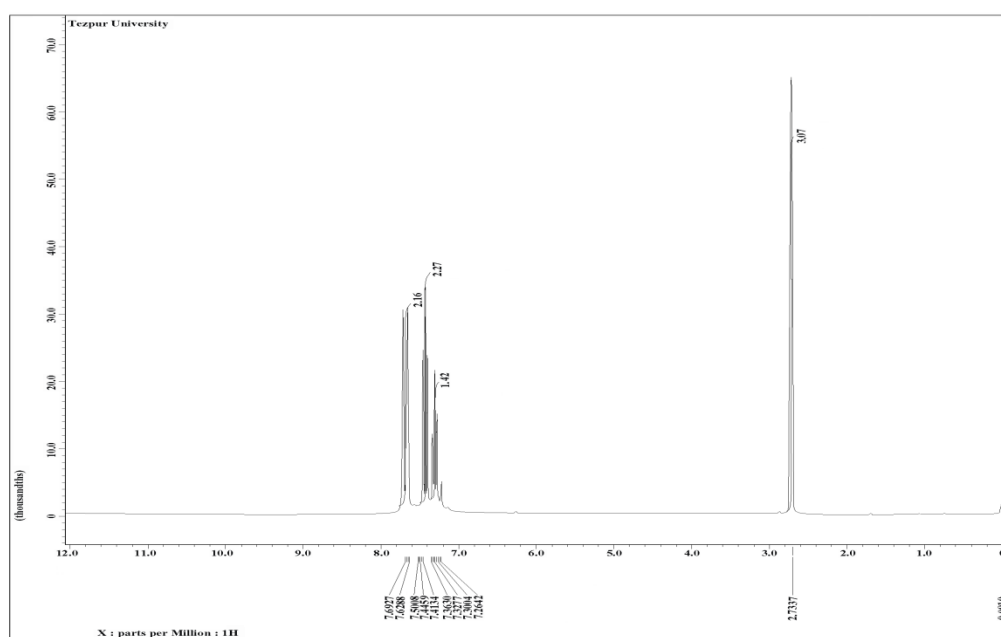
Fig. 5A.1 ^{1}H NMR spectra of methyl phenyl sulfoxide.
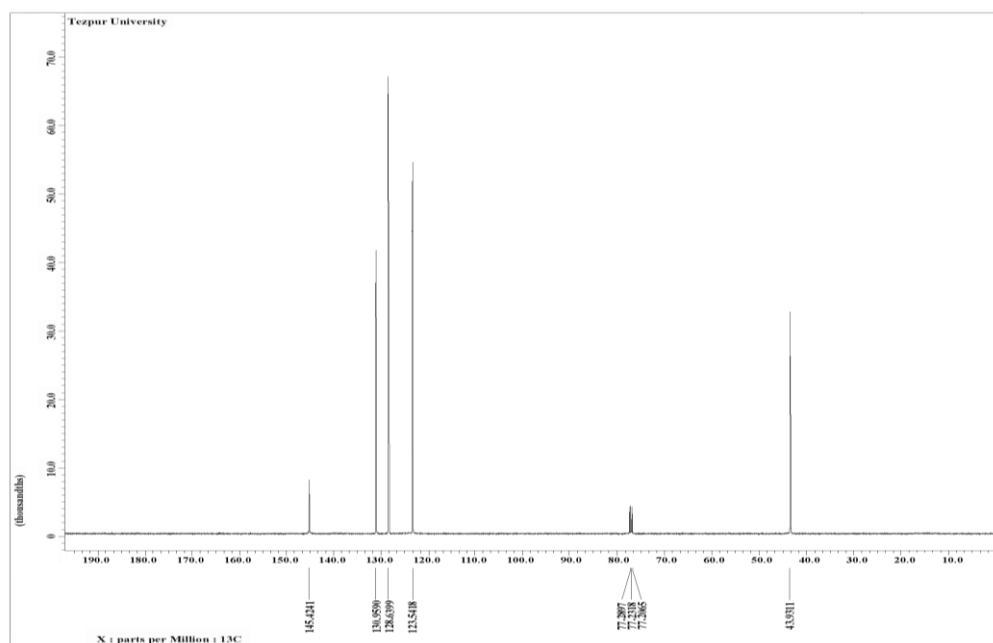
Fig. 5A.2 ^{13}C NMR spectra of methyl phenyl sulfoxide.

(b) Methylphenyl sulfone: Isolated as white solid; mp 85-86°C; ν (KBr)/cm^{-1} 1320, 1164;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 3.01(s, 3H); 7.52-7.58(m, 1H); 7.61-7.69(m, 2H); 7.91-7.95(m, 2H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 44.82; 126.21; 128.52; 133.24; 137.42
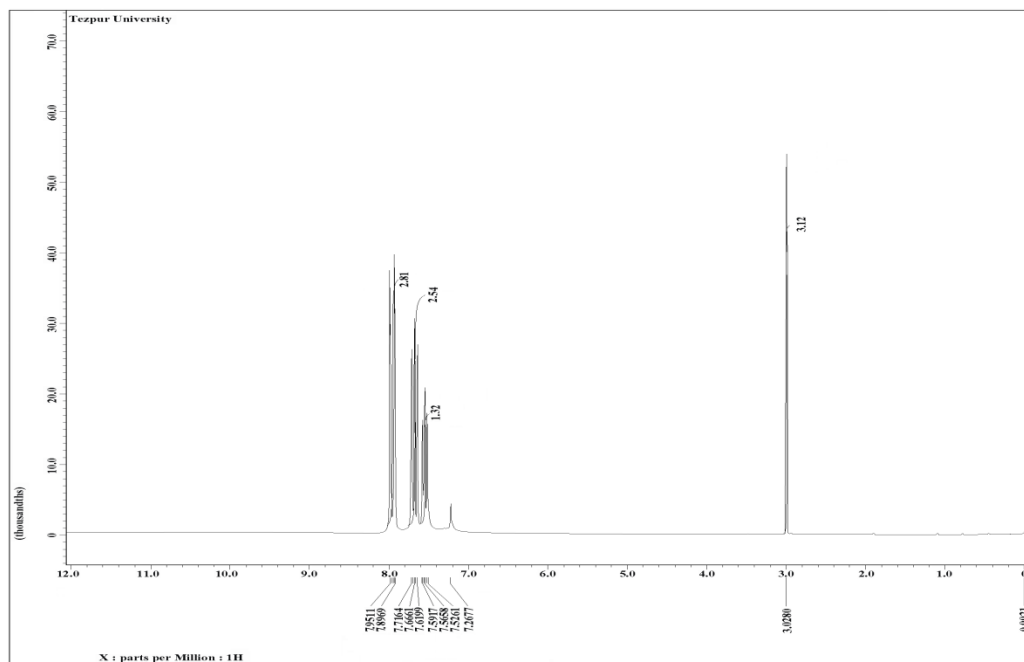

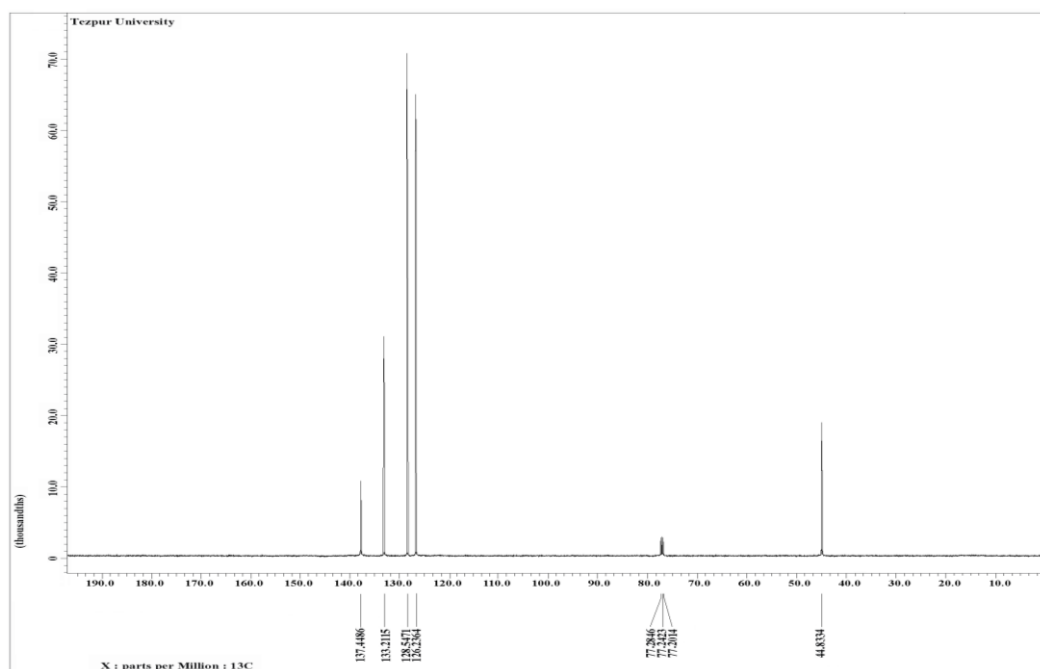**Fig. 5A.3** ^{1}H NMR spectra of methyl phenyl sulfone.

Fig. 5A.4 ^{13}C NMR spectra of methyl phenyl sulfone.

(c) Methyl-p-tolyl sulfoxide: Isolated as pale yellow liquid; mp 43-45 ^{o}C; ν (KBr)/cm^{-1} 1036;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 7.53 (d, 2H); 7.32 (d, 2H); 2.70 (s, 3H); 2.42 (s, 3H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 142.58; 141.57; 129.99; 123.61; 44.00; 21.41

(d) Methyl-p-tolyl sulfone: Isolated as white solid; mp 85-87°C; ν (KBr)/cm^{-1} 1293, 1146

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.84 (d, 2H); 7.38 (d, 2H); 3.04 (s, 3H); 2.46 (s, 3H)

^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 144.69; 137.63; 129.96; 127.38; 44.63; 21.64

(e) Allylphenyl sulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1044;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 3.41(dt, 2H, J=7.11, 1.12 Hz); 5.00(dq, 1H, J=1.42, 17.10 Hz); 5.15(dq, 1H, J=1.12, 10.22 Hz); 5.45(ddt, 1H, J=7.11, 10.22, 17.10 Hz); 7.26-7.30(m, 1H); 7.37-7.39(m, 2H); 7.60-7.63(m, 2H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 60.38; 117.99; 124.70; 125.08; 129.09; 131.24; 142.19

(f) Allylphenyl sulfone: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1319, 1147;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 3.94(dt, 2H, J= 7.19, 1.22 Hz); 5.00(dq, 1H, J= 1.48, 17.21 Hz); 5.17(dq,1H, J= 1.22, 10.31 Hz); 5.62(ddt, 1H, J= 7.19, 10.31, 17.21 Hz); 7.38-7.41(m, 1H); 7.63-7.69(m, 2H); 7.90-7.93(m, 2H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 60.66; 117.56; 124.66; 128.87; 129.07; 133.79; 138.25

(g) Phenylvinyl sulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1053;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 5.93(d, 1H, J=10.13 Hz); 6.28(d, 1H, J=15.89 Hz); 6.56-6.69(m, 1H); 7.27-7.36(m, 1H); 7.45-7.52(m, 2H); 7.63-7.69(m, 2H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 120.59; 124.59; 129.35; 131.17; 142.96; 143.40

(h) Phenylvinyl sulfone: Isolated as white solid; mp 63-64°C; ν (KBr)/cm^{-1} 1365, 1162;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 6.12(d, 1H, J=9.60Hz); 6.44(d, 1H, J=16.42Hz); 6.64-6.77(m, 1H); 7.44-7.52(m, 1H); 7.58-7.67(m, 2H); 7.87-7.91(m, 2H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 127.85; 129.33; 133.77; 138.51; 139.70

(i) 2-(Phenylsulfinyl)ethanol: Isolated as light brown solid; mp 42-43°C; ν (KBr)/cm^{-1} 1039;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 2.41(s, 1H); 3.13(t, 2H, J=5.31 Hz); 3.86(t, 2H, J=5.26 Hz); 7.28-7.37(m, 1H); 7.48-7.56(m, 2H); 7.64-7.69(m, 2H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 56.19; 60.94; 125.41; 129.99; 131.24; 144.51

(j) 2-(Phenylsulfonyl)ethanol: Isolated as white solid; mp 96-97°C; ν (KBr)/cm^{-1} 1338, 1155;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 2.49(s, 1H); 3.31(t, 2H, J=5.46 Hz); 3.96(t, 2H, J=5.26 Hz); 7.45-7.52(m, 1H); 7.58-7.67(m, 2H); 7.89-7.96(m, 2H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 57.39; 61.57; 128.93; 129.54; 134.06; 140.74

(k) Ethylphenyl sulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1054;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 1.23(t, 3H, J=6.61 Hz); 2.69-2.78(q, 1H, J=6.61 Hz); 2.91(q, 1H, J=6.61 Hz) 7.13-7.48(m, 3H); 7.49-7.84(m, 2H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 10.39; 47.19; 125.42; 129.85; 131.47; 145.69

(l) Ethylphenyl sulfone: Isolated as white solid; mp > 261 $^{\circ}$C; ν (KBr)/cm^{-1} 1322, 1153;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 1.30(t, 3H, J=7.11 Hz); 3.09(q, 2H, J=7.11 Hz); 7.59(m, 3H); 7.99(m, 2H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 7.34; 50.28; 127.86; 128.92; 133.47; 138.31

(m) Diphenyl sulfoxide: Isolated as white solid; mp 70 $^{\circ}$C; ν (KBr)/cm^{-1} 1043;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 7.63-7.68(m, 4H); 7.43-7.51(m, 6H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 144.71; 129.87; 128.23; 123.71

(n) Diphenyl sulfone: Isolated as pale yellow solid; mp 125-127°C; ν (KBr)/cm^{-1} 1322, 1155;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 7.91-7.99(m, 4H); 7.44-7.53(m, 6H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 141.78; 133.21; 129.31; 127.68

(o) Dimethyl sulfoxide: Isolated as liquid; ν (KBr)/cm^{-1} 1050;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 2.61(s, 6H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 40.54

(p) Dimethyl sulfone: Isolated as white solid; mp 236-237°C; ν (KBr)/cm^{-1} 1316, 1139;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 3.28(s, 6H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 44.61

(q) Dihexyl sulfoxide: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1042;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 0.95 (t, 6H, J= 7.65 Hz); 1.21-1.37 (m, 12H); 1.68 (m, 4H); 2.71 (t, 4H, J=6.71Hz)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 13.54; 21.91; 32.85; 27.64; 28.53; 52.64

(r) Dihexyl sulfone: Isolated as pale yellow liquid; ν (KBr)/cm^{-1} 1323, 1161;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 0.95 (t, 6H, J= 7.66 Hz); 1.21-1.38 (m, 12H); 1.91 (m, 4H); 3.36 (t, 4H, J=6.71 Hz)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 13.48; 21.78; 32.64; 27.91; 26.45; 53.72

(s) Dibutyl sulfoxide: Isolated as white solid; mp 32-33°C; ν (KBr)/cm^{-1} 1061;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 0.96(t, 6H, J=7.41 Hz); 1.37-1.48(m, 4H); 1.69-1.78(m, 4H); 2.62-2.68(m, 4H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 13.72; 22.15; 24.50; 51.96

(t) Dibutyl sulfone: Isolated as white solid; mp 42-43°C; ν (KBr)/cm^{-1} 1344, 1134;

^{1}H NMR (400 MHz; CDCl$_3$, δ): 0.96 (t, 6H, J=7.41 Hz); 1.39-1.49 (m, 4H); 1.79-1.89(m, 4H); 2.87-2.93(m, 4H)

^{13}C NMR (100.5 MHz; CDCl$_3$, δ): 13.52; 21.76; 23.92; 52.54

Splitting patterns are designated as s (singlet), d (dublet), t (triplet), dt (double triplet), ddt (double-double triplet), q (quartet), dq (double quartet), m (multiplet).

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