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# $VO_2F(dmpz)_2$ : a new catalyst for selective oxidation of organic sulfides to sulfoxides with $H_2O_2$

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Sulfoxides and sulfones are of immense interest because of their extensive applications as reagents in organic chemistry as well as synthetic intermediates for the construction of various chemically and biologically active molecules.<sup>1</sup> For this reason the oxidation of sulfides to sulfoxides or sulfones has been the subject of extensive studies. There are many reagents available for the oxidation of sulfides such as halogen compounds,<sup>2</sup> nitrates,<sup>3</sup> transition metal oxides,<sup>4</sup> oxygen, and hydrogen peroxide.<sup>5</sup> Incidentally, most of these reagents are not satisfactory for medium to large-scale synthesis for one or the other reasons like low content of effective oxygen, over oxidation, the formation of environmentally unfavorable by-products, and cost effectiveness. Generally, it is important to stop the oxidation at the sulfoxide stage by controlling the electrophilic character of the oxidant, but this requirement is often hard to meet and failure results in over oxidation to sulfones. The reported methods rarely offer the ideal combination of simplicity of method, selective reactions, and high yields of products and often suffer from a lack of generality and economic viability, and hence the search for newer methods for the selective oxidation of sulfides to sulfoxides has continued. Over the years, hydrogen peroxide has attracted much attention because it is an ideal waste-avoiding oxidant, cheap, and the most attractive from the environmental viewpoint. Although it is a powerful oxidant, the reactions of hydrogen peroxide are generally rather slow, and the challenge is

## ABSTRACT

A newly developed and structurally characterized vanadium complex  $[VO_2F(dmpz)_2]$  (dmpz = 3, 5 dimethyl pyrazole) is reported as recyclable catalyst for the selective oxidation of organic sulfides with  $H_2O_2$  in CH<sub>3</sub>CN at sub-ambient temperature.  $[VO_2F(dmpz)_2]-H_2O_2$  system chemoselectively oxidizes alkyl as well as aryl sulfides in the presence of oxidation prone functional groups such as C=C, -CN, and -OH. Refractory sulfides (dibenzothiophenes) are also oxidized to sulfoxides.

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to overcome this kinetic barrier in more cost-effective and 'green chemical' ways. Therefore, the development of catalysts for tuning the oxidation potentiality of H<sub>2</sub>O<sub>2</sub> will be quite valuable. Incidentally, vanadium(V) compounds are known for activating  $H_2O_2$ through the formation of mono, di, tri, and tetra peroxovanadates and they are useful in oxidizing organics.<sup>6</sup> Dioxovanadium(V) complexes are studied as biomimetic synthetic models,<sup>7</sup> since they can be converted into oxoperoxovanadate which resembles the active site of vanadium haloperoxidase enzymes. Taking a lead from our earlier experience in vanadium chemistry, we elected to develop an effective penta-coordinated hetero-ligand vanadium(V) complex as an efficacious catalyst for the titled selective oxidation. A penta coordinated complex is expected to facilitate in situ coordination of H<sub>2</sub>O<sub>2</sub> thereby activating the oxidant. This Letter involves the preparation of VO2F(dmpz)2, complete characterization and its catalytic efficacy for selective oxidation of organic sulfides at sub ambient temperature (Scheme 1).

Strategically, the preparation and characterization of the catalyst was the first task. To this end, we have prepared the catalyst by reacting  $V_2O_5$  with  $NH_4HF_2$  followed by the addition of dmpz









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**Figure 1.** The ORTEP view of VO<sub>2</sub>F(dmpz)<sub>2</sub>, the catalyst with selected bond distances (Å) and bond angles (°): V–F, 1.607 (6); V–O1, 1.70 (3); V–O2, 1.75 (3); V–N1, 2.07 (3); V–N3, 2.15 (3); F–V–O1, 126 (2); F–V–O2, 112 (2); F–V–N1, 92 (1); F–V–N3, 93 (1); O1–V–O2, 122.1(7); O1–V–N1, 92 (1); O1–V–N3, 86 (1); O2–V–N1, 87 (1); O2–V–N3, 90 (1); N1–V–N3, 174.7 (5).

to afford VO<sub>2</sub>F(dmpz)<sub>2</sub>.<sup>8</sup> The role of NH<sub>4</sub>HF<sub>2</sub> was not only to perform fluoridation but also to provide mild acidity (pH  $\sim$ 4) of the reaction medium. This has facilitated the coordination of 3, 5 dimethyl pyrazole (dmpz) through its non-protonated N-donor atom. A higher acidity is not conducive to the synthesis. The catalyst is found to be a highly crystalline lemon yellow solid, stable in air, soluble in nearly all-polar solvents, and decomposes at 156 °C. Its solution electrical conductance value of 26-mho cm<sup>2</sup> mol<sup>-1</sup> in acetonitrile attests its neutral character.<sup>9</sup> Magnetic susceptibility measurement shows that the compound is diamagnetic with gram susceptibility being  $-0.369 \times 10^{-6}$  cgs.<sup>10</sup> The IR spectrum of VO<sub>2</sub>F(dmpz)<sub>2</sub> shows characteristic absorption bands due to coordinated dmpz,<sup>11</sup> fluoride,<sup>12</sup> and oxo ligands.<sup>13</sup> A strong band at 446 cm<sup>-1</sup> is due to v(V-N) stretching. This is very important in support of the dmpz coordination. The strong bands appearing at 953 and 922 are assigned to v(V=0) stretching. Splitting of this band is a clear indication of the occurrence of a *cis*-dioxovanadyl center.<sup>13</sup> The Raman spectrum shows complimentary signals at 547 cm<sup>-1</sup> due to  $v_{V-F}$ , and at 947 and 930 cm<sup>-1</sup> assigned to  $v_{V=0}$ originating from the cis-VO<sub>2</sub> core. The UV-Vis spectrum showed one intense broad band at 245 nm which is ascribed to ligand to metal charge transfer.<sup>14</sup>

The X-ray structural analysis of the compound <sup>15</sup> confirms that it is a penta coordinated mononuclear vanadium(V) species  $[VO_2F(dmpz)_2]$  with space group Cc. The ORTEP diagram of the catalyst shows trigonal bipyramidal geometry (Fig. 1) with dmpz ligands occupying the apical positions and the oxo and fluoride groups in the equatorial site. The V=O bonds and O=V=O angle are slightly greater (mean V=O bond = 1.723 Å and O=V=O angle =122.1°) than generally encountered V=O bond 1.649 Å and O=V=O angle 108.2-110.7°. The aforementioned results establish the identity of the catalyst as claimed.

Our interest in oxidation<sup>6d,6g,16</sup> inspired us to use this complex as a catalyst for sulfide oxidation. The catalyst was screened for oxidation of sulfides with aqueous 30% H<sub>2</sub>O<sub>2</sub>. To optimize the reaction condition, we carried out the oxidation of methyl phenyl sulfide in acetonitrile at room temperature (Table 1). It was found that methyl phenyl sulfide was oxidized to a 3:1 mixture of methyl phenyl sulfoxide and sulfone in the presence of 5 mol% of the catalyst and 2 equiv of H<sub>2</sub>O<sub>2</sub>. We also performed the oxidation in different solvents (Table 1) maintaining the same conditions. Unfortunately, over-oxidation could not be averted. The overoxidation could not be overcome even by lowering the amount of  $H_2O_2$  to 1.1 equiv. The attention was then turned on to the temperature of the reaction. Sulfoxide as the sole product was found when the reaction was carried out at ice-bath temperature. To ascertain the efficacy of the catalyst several reactions were carried out with or without catalyst. The reactions took place in each case with the best performance being in CH<sub>3</sub>CN with 1 mol % of catalyst. Accordingly, all the reactions discussed herein were conducted with this combination.<sup>17</sup> To demonstrate the scope, a series of structurally diverse sulfides were subjected to oxidation under the optimized reaction conditions and the results are presented in Table 2. The reactions went on well affording the products in high yields. It is notable that sulfides were chemoselectively oxidized in the presence of some oxidation prone functional groups such as C=C, -CN, and -OH (Table 2, entries 6-10). However, the oxidation of sulfides containing electron-withdrawing groups (Table 2, entries 15 and 16) was sluggish producing the corresponding sulfoxides in very low yields. The presence of electron-withdrawing (-NO<sub>2</sub> in the present case) groups reduces the electron density on the sulfur atom thereby decreasing its nucleophilicity. This probably explains the low yields. Oxidation of refractory sulfur such as dibenzothiophene (DBT) and substituted DBT is quite challenging with the standard oxidation procedures.<sup>18</sup> Considering the pressing need for reducing the sulfur content of transportation fuel to abate environmental pollution, it was thought worthwhile to explore the efficacy of the newly developed catalyst for this purpose. Significantly, upon treatment with  $VO_2F(dmpz)_2-H_2O_2$ system DBT and substituted DBT were oxidized to the corresponding sulfoxides (Table 2, entries 11-13). It may be mentioned that with the increase in alkyl chain length of the sulfides, the rate of reaction becomes slower Table 2, entries 4, 5, and 7). This may be due to the orientation of hydrophobic alkyl chain around the sulfur atom. Dimethyl sulfide (DMS) can be selectively oxidized to dimethyl sulfoxide (DMSO) with this protocol (entry 14). Oxidation of DMS to DMSO has direct relevance in the commercial preparation of ranitidine hydrochloride, where DMSO is one of the essential ingredients and methyl sulfide is an unavoidable polluting effluent, which can be recycled through methylation followed by selective oxidation.<sup>19</sup> In catalysis, recyclability is one of the important attributes. To this end, we have conducted a series of reactions with methyl phenyl sulfide by using the aqueous phase containing VO<sub>2</sub>F(dmpz)<sub>2</sub>, obtained after extraction of the reaction mixture with ethyl acetate. This was charged with fresh substrate and 1.1 equiv of H<sub>2</sub>O<sub>2</sub>. The catalyst could be reused for at least five reaction cycles with consistent activity. Importantly, the reaction

Table 1

Optimization of reaction condition for selective oxidation of methyl phenyl sulfide oxidation

•			5 1 5				
Entry	Catalyst mol %	Time (h)	Temp (°C)	H <sub>2</sub> O <sub>2</sub> equiv.	Solvent	Sulfoxide (%)	Sulfone (%)
1	5	2.5	27	2	CH <sub>3</sub> CN	75	20
2	5	2.5	27	2	C <sub>2</sub> H <sub>5</sub> OH	70	23
3	5	5	27	2	H <sub>2</sub> O	55	20
4	5	3	27	1.1	CH₃CN	65	20
5	5	3.5	0-5	1.1	CH₃CN	95	<1
6	3	4.0	0-5	1.1	CH <sub>3</sub> CN	95	<1
7	1	5	0-5	1.1	CH <sub>3</sub> CN	95	<1
8	1	12	0-5	0	CH <sub>3</sub> CN	0	-
9	0	12	0-5	1.1	CH <sub>3</sub> CN	35	-
10	5	5.5	0-5	1.1	C <sub>2</sub> H <sub>5</sub> OH	92	3

#### Table 2

VO<sub>2</sub>F(dmpz)<sub>2</sub> catalyzed oxidation of organic sulfides with H<sub>2</sub>O<sub>2</sub> in CH<sub>3</sub>CN

$\mathbf{R}^{1} \overset{\mathbf{S}}{\mathbf{R}^{2}} \overset{\mathbf{VO}_{2}\mathbf{F}(\mathbf{dmpz})_{2}, \mathbf{H}_{2}\mathbf{O}_{2}}{\mathbf{CH}_{3}\mathbf{CN}, 0.5 \ ^{\circ}\mathbf{C}} \overset{\mathbf{O}}{\mathbf{R}^{1}} \overset{\mathbf{O}}{\overset{\mathbf{S}}{\mathbf{R}^{2}}}$							
Entry	Substrate	Time (h)	Sulfoxide <sup>a</sup>				
1	S.CH3	5	95,90 <sup>b</sup> ,86 <sup>c</sup> ,97 <sup>d</sup>				
2	S S	5	93				
3	S C <sub>6</sub> H <sub>13</sub>	5.5	87				
4	S^C <sub>17</sub> H <sub>35</sub>	6.5	95				
5	H <sub>7</sub> C <sub>3</sub> S C <sub>11</sub> H <sub>23</sub>	6	87				
6	S~~	3	97				
7	<sup>∞</sup> S <sup>C</sup> <sub>11</sub> H <sub>23</sub>	6.5	86				
8	MeO	4.5	85				
9	С∽с∽он	4.5	82				
10	<sup>S</sup> √ <sup>CN</sup>	2	85				
11		5	88 <sup>e</sup>				
12	s	8	75 <sup>e</sup>				
13	s	12	80 <sup>e</sup>				
14	H <sub>3</sub> C <sup>S</sup> CH <sub>3</sub>	0.5	99				
15	O <sub>2</sub> N S CH <sub>3</sub>	5	35				
16	O2N S	6	30				

<sup>a</sup> Isolated yield.

<sup>b</sup> Reaction in ethanol.

<sup>c</sup> Yield after fifth cycle.

<sup>d</sup> Yield at 5 g scale.

e Reaction at room temperature.

can be performed on a relatively larger scale (5 g) to give good yields (Table 2, entry 1) showing its prospects for scaled-up applications.

We believe that the reaction proceeds via metal-oxygen shift mechanism in the present reaction as depicted in Scheme 2 and suggested by Chu and Trout.<sup>20</sup> The ease of the formation of sulfoxide is likely to happen through the nucleophilic attack by the sulfide to the electrophilic O–O bond of peroxometal species thus facilitating the regeneration of the catalyst.

It is relevant to mention that a commercially available vanadium complex, VO(acac)<sub>2</sub> (acac = acetyl acetonate), might as well be considered as a catalyst for such oxidations using  $H_2O_2$  as the oxidant. However, the efficacy and selectivity are comparatively low.<sup>21</sup> This is indeed expected because the metal has +IV oxidation state (d<sup>1</sup> system) in VO(acac)<sub>2</sub> whereas +V (d<sup>0</sup> system) in our complex. Hence VO<sub>2</sub>F(dmpz)<sub>2</sub> is more effective in activating  $H_2O_2$ 



Scheme 2. Plausible mechanism of oxidation of sulfide.

thereby rendering the  $VO_2F(dmpz)_2-H_2O_2$  system efficacious, as observed in the present study.

In conclusion, a new penta-coordinated  $VO_2F(dmpz)_2$  catalyst has been developed and fully characterized. It efficiently catalyzes the oxidation of alkyl as well as aryl sulfides by  $H_2O_2$  also in the presence of oxidation prone functional groups such as C=C, –CN, and –OH. The selective oxidation of DMS to DMSO is industrially important in the context of ranitidine hydrochloride. Refractory sulfides are also capable of being oxidized quite effectively which are especially relevant in desulfurization of transportation fuel. The recyclability of the catalyst offers a potentially competitive practical process.

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- 8. Synthesis of Dioxofluoro(bis-dimethylpyrazole) vanadium(V), VO<sub>2</sub>F(dmpz)<sub>2</sub>: An aqueous suspension (15–20 mL) of 0.5 g (2.75 mmol) V<sub>2</sub>O<sub>5</sub> was treated with 0.55 g (9.64 mmol) NH<sub>4</sub>HF<sub>2</sub> followed by heating on a steam bath to get a clear solution. An ethanolic solution (15–20 mL) of 1.33 g (13.73 mmol) of 3,5-dimethyl pyrazole (dmpz) was then added to it and the solution was allowed to concentrate (ca.10–12 mL) by heating on a steam bath. The concentrated solution was kept in a freezer until shiny lemon yellow crystals of VO<sub>2</sub>F(dmpz)<sub>2</sub> were obtained. The compound was separated by decantation and dried in vacuo over conc. H<sub>2</sub>SO<sub>4</sub>. The yield was 1.3 g (81%). Spectral data: IR(KBr): 3257, 1577, 1285, 953, 922 cm<sup>-1</sup>; <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.13 (s, 3H), 2.47 (s, 3H), 5.85 (s, 1H), 11.62 (br s, 1H, N-H); <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  11.74 (2C), 105.04, 145.76 (2C); <sup>19</sup>FNMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  -146.32 (br, 1F). Laser raman: 947, 930, 547 cm<sup>-1</sup>. Anal. Calculated for C<sub>10</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>VF (294.21): C, 40.83; H, 5.48; N, 19.04; O, 10.88; V, 17.32; F, 6.46. Found: C, 40.62; H, 5.18; N, 19.31; V, 17.47; F, 6.21.
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17. Typical procedure for the oxidation of methyl phenyl sulfide: methyl phenyl sulfide (0.248 g, 2 mmol) in acetonitrile (2 ml) solvent was reacted with V0<sub>2</sub>F(dmp2)<sub>2</sub> (0.0059 g, 0.02 mmol) and H<sub>2</sub>O<sub>2</sub> (30% aqueous solution, 25  $\mu$ L, 2.2 mmol) under stirring at ice bath temperature for 5 h and monitored by TLC. On completion of the reaction, acetonitrile was removed under reduced pressure and 1 ml of water was added. The product was extracted with ethyl acetate, dried over anhydrous MgSO<sub>4</sub>, and evaporated to dryness, while the aqueous layer was retained for recovery of the catalyst. In order to remove any traces of VO<sub>2</sub>F(dmp2)<sub>2</sub>, the product was transferred to silica gel (60–120 mesh) column and eluted with ethyl acetate: hexane (1:7). The aqueous layer is concentrated and reused. The spectral data of some representative compounds are given below.

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