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Bifunctional Ionic Liquid Catalyst Containing Sulfoacid Group and Hexafluorotitanate for Room Temperature Sulfoxidation of Sulfides to Sulfoxides Using Hydrogen Peroxide

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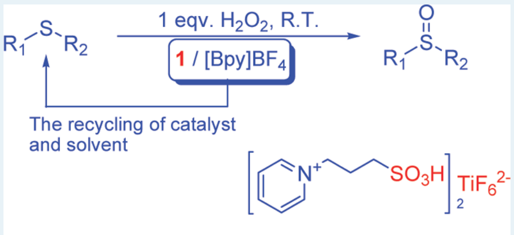
ABSTRACT: A bifunctional ionic liquid (IL), bis-[*N*-(propyl-1-sulfoacid)-pyridinium] hexafluorotitanate (**1**), was synthesized and proved to be an efficient and recyclable catalyst for room temperature sulfoxidation of sulfides using H_2O_2 as the oxidant. The synergetic catalysis derived from the incorporated functional moieties in the IL structure was embodied in **1**. The UV−vis and Raman spectra indicated that the remarkable catalytic performance of **1** was related to the easy generation and regeneration of the active peroxo-Ti species.



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KEYWORDS: *bifunctional ionic liquid, synergetic catalysis, sulfoxidation, hexafluorotitanate, hydrogen peroxide*

INTRODUCTION

The interest in developing efficient catalytic systems for the sulfoxidation of organic sulfides to sulfoxides is primarily initialized by the importance of sulfoxides as intermediates of biologic molecules,[1] chiral auxiliaries,[2] and oxo-transfer reagents.[3,4] The traditional methods using peracids,[5] $MeNO_2$ solution in dilute HNO_3/H_2SO_4,[6] iodic acid (HIO_3),[7] or other hypervalent iodine reagents[8] as oxidants in stoichiometric ratio or large excess have serious disadvantages because of the formation of large amounts of byproduct-containing effluents together with the target molecules.[9] A system without any catalyst and solvent for sulfoxidation of some sulfides by H_2O_2 had also been reported by Fu's group, but a low reaction rate was observed at ambient conditions, especially for the sulfides with electron-withdrawing substituents and poor solubility in aqueous H_2O_2.[10] From the above-mentioned as well as environmental and economic points of view, the catalytic oxidation of sulfides using environmentally benign H_2O_2 as the oxidant is more desirable.[11]

Recently, H_2O_2-based sulfoxidation systems with homogeneous or heterogeneous organocatalysts,[12] acid catalysts,[13] enzymes,[14] and transition metal catalysts (such as vanadium,[15] ruthenium,[16] iron,[17] manganese,[18] selenium,[19] and titanium[20,21]) have been reported. Among abundant transition metal catalysts, titanium-based homogeneous systems for sulfoxidation have been widely investigated because of their high activity and selectivity,[11,21−23] which was inspired by the pioneering work by Kagan[24]and Modena.[25] However, the reported methods rarely offer ideal combinations of simplicity, rapid and selective reaction, high yields of products, wide generality, economic applicability, and environmental friendliness.[13] Many transition metal catalysts are expensive, difficult to prepare, and unable to be recovered and reused. The use of excess H_2O_2 (1.1−8.0 equiv to substrates) leads to overoxidation of sulfides to sulfones. Moreover, the use of volatile and toxic solvents largely defeats the merits of H_2O_2 as a green and clean oxidant.[11,20]

To establish a selective sulfoxidation system with the features of environmental friendliness and high efficiency, the utilization of ionic liquids (ILs) has been regarded as a promising approach in recent years.[12,26−38] A nonvolatile IL, which can be functionalized flexibly and diversely, provides two modifiable platforms (cation and anion) for synthesizing task-specific bifunctionalized ILs.[39−41] One can expect the synergetic effect derived from the two functional moieties located in the cation and anion, respectively. As part of our continued work about the functionalization of ILs for homogeneous catalysis,[40] herein, we report the synthesis of a bifunctionalized IL (bis-[*N*-(propyl-1-sulfoacid)-pyridinium] hexafluorotitanate, **1**) containing a sulfoacid group ($-SO_3H$) and hexafluorotitanate ion (TiF_6^{2-}) for the first time, which was applied as the catalyst for oxidation of sulfides by H_2O_2 in the room temperature IL of *N*-*n*-butylpyridinium tetrafluoroborate ($[Bpy]BF_4$, Scheme 1). The hydrophilicity and polarity of $[Bpy]BF_4$ made it suitable as a solvent for **1**, aqueous H_2O_2 (30%), and sulfide substrates. The purpose of incorporating the sulfoacid group and hexafluorotitanate simultaneously is to lock each functional individual into the structure of an IL to induce the bifunctional synergetic effect, to ensure homogeneous catalysis, and to fulfill the recyclability of **1** in $[Bpy]BF_4$.

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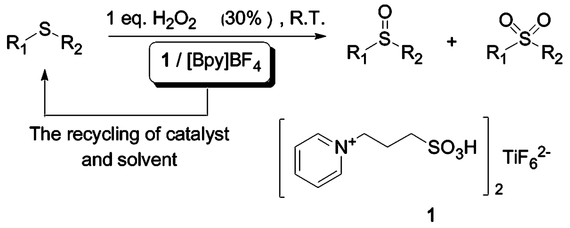
Scheme 1. Sulfoxidation of Sulfides Using H_2O_2 Catalyzed by a Bifunctional Catalyst (1) Derived from the Pyridinium-Based IL in $[Bpy]BF_4$



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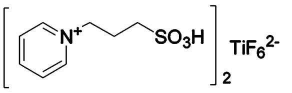
RESULTS AND DISCUSSION

Investigation on the Catalytic Performance of 1 for Sulfoxidation. The sulfoxidation of diphenyl sulfide using H_2O_2 was selected as a model reaction to investigate the catalytic performance of **1**. To elucidate the individual and synergetic role of $-SO_3H$ and TiF_6^{2-} in **1**, the catalysis of **2**, **3**, and H_2TiF_6 were also studied in parallel (Table 1). At room temperature, without the presence of any catalyst, the oxidation of diphenylsulfide by H_2O_2 in $[Bpy]BF_4$ was negligible (Table 1, entry 1). When 7 mol % of **1** was used, 84% of diphenylsulfide was converted with 83% selectivity to diphenylsulfoxide (Table 1, entry 2). Under the same conditions, **2** possessing the $-SO_3H$ acidic group but without TiF_6^{2-} as the counteranion led to 51% conversion of diphenylsulfide (entry 3); **3** with TiF_6^{2-} as the counteranion but lacking $-SO_3H$ in the cation led to only 15% conversion (entry 4). Since **1**, **2**, and **3** are all amphipathic catalysts due to possessing the lipophilic pyridinium-based organic group in the cation and the hydrophilic TiF_6^{2-} or SO_4^{2-} as counteranion, they exhibit similar accessibility to the substrate (diphenylsulfide) and the oxidant (aqueous H_2O_2), which can rule out the influence of the mass transfer limitation on the activities of **1**–**3**. Therefore, the difference in conversions for **1**–**3** (entries 2–4) revealed that the catalytic behaviors of $-SO_3H$ and TiF_6^{2-} reinforced each other when they were combined together in **1** as one unit, and that the observed cooperative effect in **1** was caused by a specific synergetic interaction between $-SO_3H$ and TiF_6^{2-}, but not attributed to pure statistic reasons. When H_2TiF_6 was used as the catalyst, the relatively lower conversion of 74% was obtained, in comparison with that for **1** (entry 5 vs 2). Although the catalytic nature for H_2TiF_6 and **1** are identical because both featur a combination of proton acid and TiF_6^{2-} counteranion, H_2TiF_6 is absolutely hydrophilic, whereas **1** is amphipathic. As a result, the accessibility of H_2TiF_6 to the lipophilic diphenylsulfide is limited to some extent, leading to the depressed reaction rate and then the decreased conversion (74%). Hence, the advantage of the organic salt of **1** over inorganic H_2TiF_6 is its amphipathic character with available accessibility to both aqueous H_2O_2 and lipophilic sulfides.

When the different ILs were used as solvents, amphipathic $[Bpy]BF_4$ was found to be the best choice because of its available accessibility to aqueous H_2O_2 and lipophilic diphenylsulfide (entry 2). As for hydrophobic $[Bmim]PF_6$, which is not suitable to be the solvent for the aqueous H_2O_2 involved reactions, much lower conversion of diphenylsulfide was obtained because of the resultant mass transfer limitation (37%, entry 6). As for amphipathic $[Bmim]BF_4$, which is a N-heterocyclic carbene (NHC) ligand, only the moderate conversion was observed, probably because of the unfavored ligation of $[Bmim]BF_4$ with **1** (entry 7).

It has been known that hydrolysis of BF_4^- and PF_6^- counteranions in ILs always happens under conditions of acidic surroundings, long reaction time, and high temperature, leading to the formation of HF.[42−44] However, under the mild conditions applied in our experiments (2 h, room temp), the concentration of F^- in the reaction solution upon completion was <2 wt % (which was determined by ion chromatography), indicating a slight hydrolysis of BF_4^- or PF_6^- in the course of the reaction. Anyway, the presence of a small amount of HF in the reaction system did not deteriorate the activity of **1**, since when 1 mmol of HF was added additionally to the reaction system, a similar conversion of diphenylsulfide and selectivity to sulfoxide was obtained under the same conditions (entries 8 vs 2).

Table 1. Comparison of Sulfoxidation of Diphenylsulfide Using H_2O_2 Catalyzed by Different Catalysts[a]



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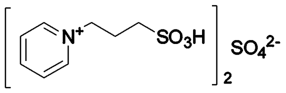

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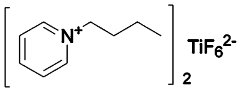

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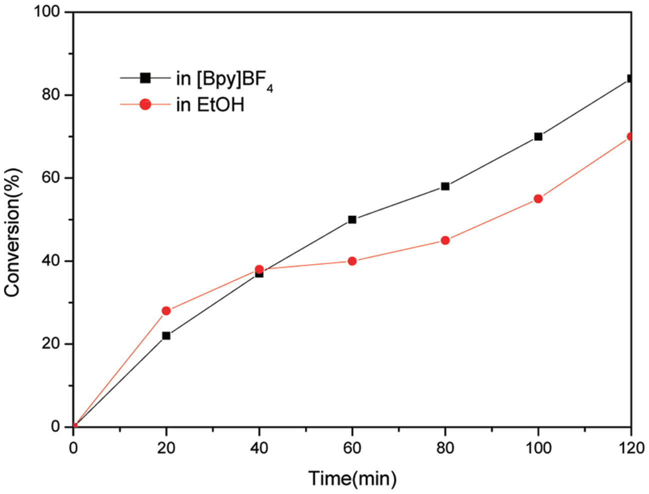
entry	catalyst	solvent	conversion (%)	selectivity (%) sulfoxide	selectivity (%) sulfone
1		$[Bpy]BF_4$	<3		
2	**1**	$[Bpy]BF_4$	84	87	13
3	**2**	$[Bpy]BF_4$	51	93	7
4	**3**	$[Bpy]BF_4$	15	85	15
5	H_2TiF_6	$[Bpy]BF_4$	74	85	15
6	**1**	$[Bmim]PF_6$[b]	37	85	15
7	**1**	$[Bmim]BF_4$[c]	68	85	15
8[d]	**1**	$[Bpy]BF_4$	83	88	12
9	**1**	DMF	52	71	29
10	**1**	EtOH	70	84	16
11	**1**	MeCN	26	74	26

[a] Catalyst 0.35 mmol, diphenylsulfide 5.0 mmol, 30% H_2O_2 5.0 mmol, solvent 3 mL, room temperature (~25 °C), 2 h. [b] $[Bmim]PF_6$, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate. [c] $[Bmim]BF_4$, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate. [d] 1 mmol of 40% aqueous solution of HF was added additionally.

Among the volatile organic solvents such as DMF, EtOH, and MeCN with high polarity, EtOH proved to be the best choice because of the relative weaker interaction with **1** in comparison with DMF and MeCN (entries 9–11). The conversions of diphenylsulfide in [Bpy]BF_4 and EtOH along with the reaction time are given in Chart 1. At the initial stage, the reaction rate in EtOH is faster than in [Bpy]BF_4 because of the total miscibility of aqueous H_2O_2 and lipophilic diphenylsulfide in EtOH and then the good mass transfer efficiency; however, the overall reaction is predominantly controlled by the activity of the peroxo-Ti species derived from **1**. In [Bpy]BF_4, the oxygen transfer from the active peroxo-Ti species to the substrate is obviously faster than that in EtOH (see the information from Figures 1 and 3, and the discussion in Identification and Characterization of Peroxo-Ti Species), leading to the faster reaction rate and, finally, the higher conversion.

Chart 1. The Conversions of Diphenylsulfide along with the Reaction Time Catalyzed by 1 in [Bpy]BF_4 and EtOH, Respectively



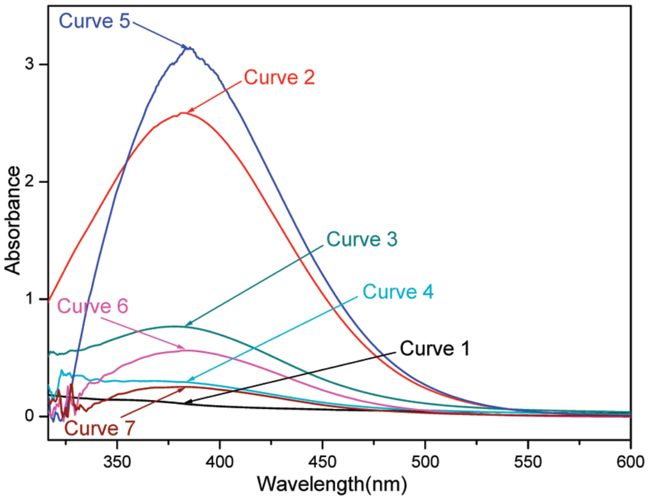


Figure 1. The evolving oxidation processes of thioanisole catalyzed by **1** in [Bpy]BF_4 using H_2O_2. Curve 1, **1**. Curve 2, **1** + H_2O_2, immediately. Curve 3, **1** + H_2O_2 + thioanisole , 2 min (recorded after thioanisole was added for 2 min). Curve 4, **1** + H_2O_2 + thioanisole, 5 min. Curve 5, **1** + H_2O_2 + thioanisole + H_2O_2, immediately. Curve 6, **1** + H_2O_2 + thioanisole + H_2O_2 + thioanisole, 2 min. Curve 7, **1** + H_2O_2 + thioanisole + H_2O_2 + thioanisole, 5 min.

On the other hand, under the mild conditions (30% aqueous H_2O_2 5.0 mmol, room temp, 2 h), the spontaneous decomposition of H_2O_2 did not happen in the presence of **1** (**2**, or **3**) in [Bpy]BF_4 (H_2O_2 decomposition rate <1%, determined by the means of iodometry), indicating the high efficiency of H_2O_2 utilization. It is also believed that the readily oxidized substrate could serve as the traps of radical intermediates, thus inhibiting the radical decomposition of H_2O_2.[45]

The results in Table 2 indicate that the excess of H_2O_2 could lead to the significant drop in the selectivity to sulfoxide as a result of the overoxidation of sulfoxide to sulfone (entries 2 and 3). When iodosylbenzene (PhIO) or *m*-chloroperbenzoic acid (*m*-CPBA) was used as the oxidant instead of H_2O_2, the conversion of diphenylsulfide decreased dramatically, suggesting the exclusive activation of **1** by H_2O_2.

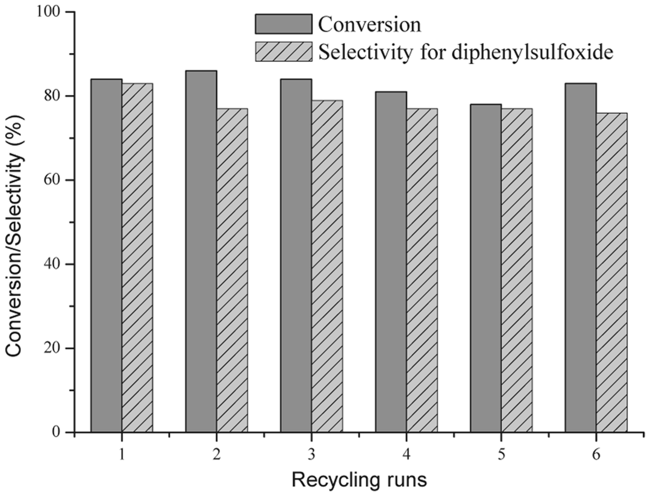
Table 2. Sulfoxidation of Diphenylsulfide Catalyzed by 1 with Different Oxidants in [Bpy]BF_4[a]

			selectivity (%)	
entry	oxidant (mmol)	conversion (%)	sulfoxide	sulfone
1	H_2O_2 (5.0)	84	87	13
2	H_2O_2 (6.0)	85	78	22
3	H_2O_2 (10.0)	91	43	57
4	PhIO (5.0)	35	100	0
5	*m*-CPBA (5.0)	53	63	37

[a] **1** 0.35 mmol, diphenylsulfide 5.0 mmol, [Bpy]BF_4 3 mL, room temperature (~25 °C), 2 h.

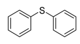
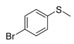
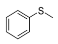
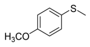
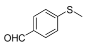
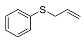
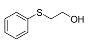
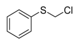
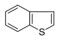
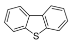
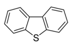
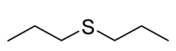
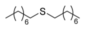
For practical application, the request for easily separable and recyclable catalysts is driven by economic considerations and environmental concerns. To demonstrate this issue, recovery and recycling experiments were conducted over **1** in [Bpy]BF_4 for oxidation of diphenylsulfide (Chart 2). Upon completion of

Chart 2. Recycling of 1 in [Bpy]BF_4 for Sulfoxidation of Diphenylsulfide[a]



[a] Conditions: **1** 0.35 mmol, [Bpy]BF_4 3 mL, diphenylsulfide 5.0 mmol, 30% H_2O_2 5.0 mmol, room temperature (~25 °C), 2 h. Water was removed before next use.

Table 3. Sulfoxidation of the Different Sulfides Catalyzed by 1 Using H_2O_2 in [Bpy]BF_4[a]

entry	substrate	time	conversion (%)	selectivity (%)	
				sulfoxide	sulfone
1		2 h	84	83	17
2		2 h	96	94	6
3		2 h	97	95	5
4		2 h	98	97	3
5		2 h	89	91	9
6		10 min	92	83	17
7		2 h	95	95	5
8[b]		2 h	79	74	9
9[c]		2 h	83	98	2
10[c]		2 h	68	99	1
11		10 h	25	43	57
12[d,e]		2 h	93	94	0
13[d,e]		2 h	59	41	0

[a] 1 0.35 mmol, sulfide 5 mmol, [BPy]BF_4 3 mL, 30% H_2O_2 5.0 mmol, room temperature if not specified. [b] Diphenyl sulfide was found as the byproduct, which was confirmed by GC−MS. [c] Temperature 50 °C. [d] Urea hydrogen peroxide (UHP) was in place of a H_2O_2 aqueous solution as the oxidant. [e] The hydrolysis products of thiol and alcohol were found, which were confirmed by GC−MS.

each run, the reaction mixture was extracted with diethyl ether to separate the substrate and the products out of the IL phase. Before the next run, water and residual H_2O_2 were removed from the IL phase on a rotary evaporator. After six runs, the activity of **1** was well maintained. However, a drop in selectivity after the first run was observed, which is maintained thereafter. In the first run, the amount of H_2O_2 was 5 mmol precisely, leading to 87% selectivity to diphenylsulfoxide. In the recycling uses, although we tried to remove H_2O_2 completely on the rotary evaporator, it was found that a small amount of H_2O_2 was still left in the residuals in each run. The accumulative H_2O_2 led to the decreased selectivity to diphenylsulfoxide in the second run thereafter (77−79%) because of the slight overoxidation of sulfoxide to sulfone.

The loss of **1** in terms of the Ti amount after six-run recycling is below the detection limit (<0.1 μg/g on the basis of the ICP analysis), indicating that **1** was tightly locked in the similar structured [Bpy]BF_4 medium without any leaching in the course of ether extraction.

The generality of **1** for sulfoxidation by H_2O_2 was examined on a series of sulfides with different electronic and steric effects under similar conditions. As shown in Table 3, the monophenyl sulfides with less steric hindrance were converted to the corresponding sulfoxides in excellent yields without obvious discrimination of the electronic effect (Table 3, entries 2−7). The sulfoxidation of 4-(methylthio)benzaldehyde possessing an aldehyde group (Table 3, entry 5) or allyl phenyl sulfide possessing a C=C double bond (Table 3, entry 6) yielded only to the corresponding sulfoxides with good chemselectivity. The oxidation-sensitive aldehyde group or C=C double bond was not sacrificed under the mild oxidation conditions. However, for the sulfoxidation of chloromethyl phenyl sulfide with the strong electron-withdrawing effect, a decreased conversion was observed, and the byproduct of 1,2-diphenyldisulfide was found, as well, as a result of the hydrolysis of chloromethyl phenyl sulfide itself and the subsequent oxidation (Table 3, entry 8).

The sulfoxidations of benzothiophene and dibenzothiophene, despite their expressed super conjugation and large steric hindrance, were successful, with excellent selectivity to the sulfoxides at somewhat elevated temperature (up to 50 °C; Table 3, entries 9 and 10). It was found that the prolonged reaction time could not efficiently increase the conversion of dibenzothiophene, but sacrifice the selectivity to sulfoxide dramatically (Table 3, entry 11). When an aqueous solution of H_2O_2 was used as the oxidant of the aliphatic sulfides, only the hydrolysis of the substrates was observed. Therefore, in these two cases, urea hydrogen peroxide (UHP) was used instead of H_2O_2. Dipropyl sulfide was converted to its oxide in high yield (Table 3, entry 12), but the selectivity of the sulfoxidation of dioctyl sulfide to dioctyl sulfoxide was quite low because of the unavoidable hydrolysis, leading to the formation of 1-octanethiol and 1-octanol as the main byproducts (Table 3, entry 13).

Identification and Characterization of Peroxo-Ti Species. The identification and characterization of the peroxo intermediates in the catalytic oxidations is an important task. The peroxo-Ti complexes are believed to be the active species in the oxygen transfer process and substrate activation.[21,46] To obtain the information on the nature of the active peroxo-Ti species in sulfoxidation catalyzed by **1**, the evolving processes of **1** with addition of H_2O_2 was investigated by means of in situ UV−vis and Raman spectra.

UV−Vis Analysis. The evolving processes of the oxidation of thioanisole catalyzed by **1** in $[Bpy]BF_4$ using H_2O_2 (30%) were monitored on a Shimadzu UV 2550 spectrophotometer at ambient temperature (~25 °C). The only difference in the performed experiments was the concentration of **1** ($\sim 4.0 \times 10^{-5}$ M), which was much lower than for the real oxidation of thioanisole (Table 3, entry 3), required for UV−vis detection. The UV−vis spectra were recorded upon consecutive addition of $[Bpy]BF_4$, **1**, H_2O_2, and thioanisole in an ultraviolet cuvette (3 mL). To observe the clear absorbances of the present peroxo-Ti species and avoid interference from the absorbance of the organic moieties in the cations, the mixtures of $[Pspy]BF_4$, [*N*-(propyl-1-sulfoacid)pyridinium tetrafluoroborate] and thioanisole in $[Bpy]BF_4$ were used as the reference sample with the same concentration as in the testing sample when **1** and thioanisole were added to the test sample. As shown in Figure 1, there is no absorbance observed for **1** in $[Bpy]BF_4$ (Figure 1, curve 1). When H_2O_2 was added to **1**-$[Bpy]BF_4$, a strong absorbance band appeared at ~385 nm (Figure 1, curve 2) immediately, which was ascribed to the ligand-to-metal charge transfer (CT) transition of the formed peroxo-Ti species. This assignment is in agreement with Zecchina's observations.[47]

When thioanisole was treated with the formed peroxo-Ti species, the absorbance of 385 nm decayed rapidly as a result of the consumption in the oxidation of thioanisole to the sulfoxide (Figure 1, curves 3 and 4). The subsequent addition of H_2O_2 led to the complete regeneration of the peroxo-Ti species instantaneously (Figure 1, curve 5), which disappeared again when thioanisole was recharged (Figure 1, curves 6 and 7). UV−vis analysis shows that the formation of the peroxo-Ti species and regeneration of **1** in the course of sulfoxidation by H_2O_2 can be successfully accomplished; however, under similar conditions and in UV−vis monitoring, if PhIO or *m*-CPBA was used as the oxidant instead of H_2O_2, no absorbance band was observed at all. This observation is consistent with the results in Table 2, probably because of the poor coordination of PhIO and *m*-CPBA with **1** and then the infeasible oxidation of **1** to its peroxo-Ti species.

In contrast, similar monitoring processes were applied to sulfoxidation by H_2O_2 in $[Bpy]BF_4$ catalyzed by **3** (Figure 2). Because of the lack of $-SO_3H$ group in the cation, the appearance and disappearance of the band at ~385 nm was not so rapid because of the inefficient formation of the peroxo-Ti species and, consequently, the slower oxygen transfer. On the other hand, in addition to the peroxo-Ti species absorbance at ~385 nm, the shoulder peak at 340 nm was evident, which could be attributed to the O-to-Ti CT transition of the hydrolyzed peroxo-Ti species (Figure 2, curve 2). Furthermore, a continuous red shift of the absorbances was observed as a result of the formation of the hydrolyzed peroxo-Ti species in various polymerized states.[47]

When the oxidation of thioanisole using H_2O_2 catalyzed by **1** was performed in EtOH (Figure 3), the similar profiles were observed in Figure 1. However, the oxygen transfer rate from the peroxo-Ti species to thioanisole was more sluggish than what occurred in $[Bpy]BF_4$. After ~25 min, the formed peroxo-Ti species was still observable (Figure 3, curve 5), whereas in $[Bpy]BF_4$, the absorbance of peroxo-Ti species at 385 nm completely disappeared in 5 min due to the rapid oxygen transfer into thioanisole (Figure 1, curve 4).

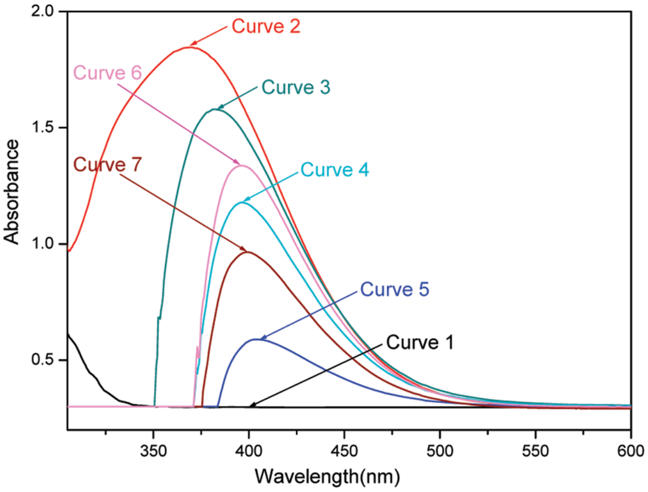


Figure 2. The evolving oxidation processes of thioanisole catalyzed by **3** in $[Bpy]BF_4$ using H_2O_2. Curve 1, **3**. Curve 2, **3** + H_2O_2, immediately. Curve 3, **3** + H_2O_2 + thioanisole, 2 min (recorded after thioanisole was added for 2 min). Curve 4, **3** + H_2O_2 + thioanisole, 5 min. Curve 5, **3** + H_2O_2 + thioanisole, 15 min. Curve 6, **3** + H_2O_2 + thioanisole + H_2O_2, immediately. Curve 7, **3** + H_2O_2 + thioanisole + H_2O_2 + thioanisole, 5 min.

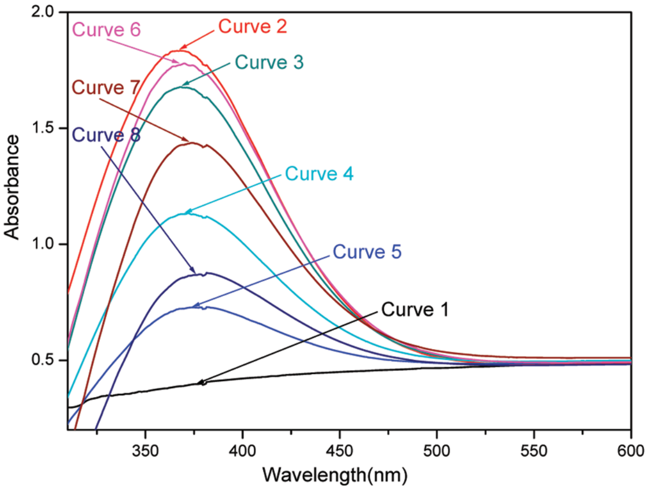


Figure 3. The evolving oxidation processes of thioanisole catalyzed by **1** in EtOH using H_2O_2. Curve 1, **1**. Curve 2, **1** + H_2O_2, immediately. Curve 3, **1** + H_2O_2 + thioanisole, 5 min (recorded after thioanisole was added for 5 min). Curve 4, **1** + H_2O_2 + thioanisole, 15 min. Curve 5, **1** + H_2O_2 + thioanisole, 25 min. Curve 6, **1** + H_2O_2 + thioanisole + H_2O_2, immediately. Curve 7, **1** + H_2O_2 + thioanisole + H_2O_2 + thioanisole, 5 min. Curve 8, **1** + H_2O_2 + thioanisole + H_2O_2 + thioanisole, 15 min.

The analysis results presented by Figures 1−3 reveal the significant roles of the $-SO_3H$ group and $[Bpy]BF_4$ in promoting the formation of the active peroxo-Ti species and also preventing it from hydrolysis and subsequent polymerization.

Raman Analysis. Raman spectra can provide very useful and distinct information on the peroxo species formed in an aqueous solution, since water is a very poor Raman scatterer and does not appreciably cover the vibrational manifestations of the solutes. For the sake of simplicity, we will here describe only the main Raman features in the narrow interval (1400−

400 cm^{-1}) where the ν(O−O) modes are expected.[47] Since Raman spectra will be heavily interfered by the manifestation of the stretching and bending vibrations of the organic groups located in **1**, H_2TiF_6, which possesses a catalysis nature identical to **1**, was used instead to characterize the formed peroxo-Ti species. The aqueous solutions of H_2O_2 (30%), H_2TiF_6 (60%), and the mixture of (30%) and H_2TiF_6 (60%) were used without other treatment for Raman detection.

As shown in Figure 4, the typical ν(O−O) of aqueous H_2O_2 was found at 875 cm^{-1} (Figure 4, Curve 1), which was consistent with the reported data.[47] For H_2TiF_6, two strong vibrations were observed at 647 and 505 cm^{-1} (Figure 4, curve 2), which are due to the presence of two different types of Ti−F bonds in the equatorial plane and axial position.[48] At a range of 1000−750 cm^{-1}, the wide and weak vibration bands were attributed to the $F_xTi(OH)_y$ ($x + y = 4$) species due to the slight hydrolysis of H_2TiF_6.

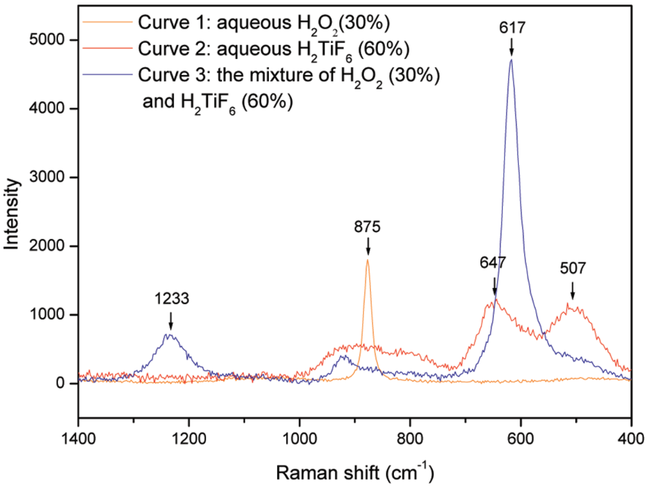
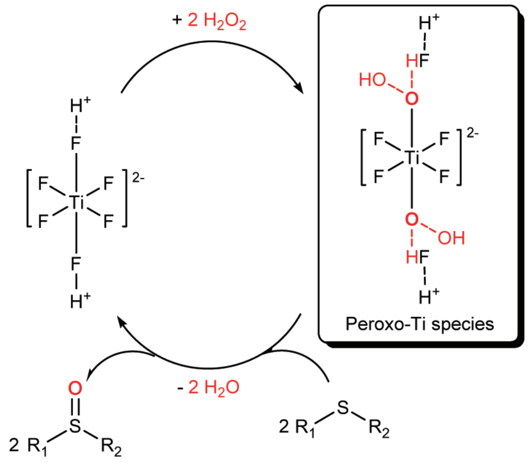


Figure 4. Raman spectra of H_2O_2, H_2TiF_6, and the mixture of H_2TiF_6 and H_2O_2.

Upon mixing H_2O_2 and H_2TiF_6, a yellow solution was obtained, and the new Raman bands appear at 1233 and 617 cm^{-1} (Figure 4, curve 3), due to the possible formation of the peroxo-Ti species according to the pioneer work by Zecchina.[47] Actually, when TiF_6^{2-} ion is oxidized by H_2O_2 to generate the peroxo-Ti species, because of the strong electronegativity of the F atom and the more ionic character of the Ti center in 6-fold coordination for the TiF_6^{2-} anion, it is conjectured that the vibration energy of the related O−O bond will definitely be reinforced, leading to the dramatic blue shift for the O−O vibration. Hence, herein, the band at 1233 cm^{-1} was tentatively attributed to the O−O vibration in the formed peroxo-Ti species, and the band at 617 cm^{-1} was assigned to the vibration of Ti−F bonds in the equatorial plane. The slight red shift compared to the band of 647 cm^{-1} was due to the interaction by the adjacent Ti−OO group.

On the basis of the observed Raman bands in Figure 4 and the corresponding attributions, a possible structure of the formed active peroxo-Ti species derived from the oxidation of H_2TiF_6 by H_2O_2 is proposed in Scheme 2. The strong interaction between F···H in H_2TiF_6 facilitates the oxidative insertion of H_2O_2 into the Ti−F bond in the axial positions, leading to the successful formation of the peroxo-Ti species. Subsequently, the formed peroxo-Ti species transfers the active oxygen atoms into the sulfides, leading to the production of the corresponding sulfoxides and then the concurrent regeneration of H_2TiF_6. This mechanism is also applicable to the sulfoxidation using H_2O_2 catalyzed by **1**. With the presence of water, the proton (H$^+$) of $-SO_3H$ in **1** that can be released easily will interact with TiF_6^{2-}, like what happened in the case of H_2TiF_6 to synergetically motivate the formation the active peroxo-Ti species.

Scheme 2. The Proposed Mechanism for Sulfoxidation Catalyzed by H_2TiF_6 (or 1) Using H_2O_2



CONCLUSIONS

The synergetic catalytic effect coming from $-SO_3H$ and TiF_6^{2-} was embodied in the newly designed sulfoacid−hexafluorotitanate(IV) bifunctionalized IL of **1** for sulfoxidation using H_2O_2 (30%). Under the mild conditions, a wide range of sulfides with different steric/electronic effects and containing the oxidation-sensitive groups (such as aldehyde group or C═C double bond) could be converted into the corresponding sulfoxides with high selectivity in the **1**−[Bpy]BF_4 system. The resultant IL phase could be recycled for six runs without any loss in activity. The UV−vis analysis indicates that the presence of a $-SO_3H$ group in **1** dramatically facilitates the formation of the active peroxo-Ti species and inhibits the hydrolysis of it, which can guarantee the perfect redox cycle between **1** and the active peroxo-Ti species (385 nm). The Raman characterization gives further supportive information on the formation of the peroxo-Ti species with characteristic vibration at 1233 cm^{-1}.

EXPERIMENTAL

Reagents and Analysis. The chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. (Shanghai, China) and used as received. The FT-IR spectra were recorded on a Nicolet Nexus 670 spectrometer (Thermo Nicolet Corporation, USA). The ^{1}H NMR spectra were recorded on a Bruker Avance 500 spectrometer (Bruker Corporation, Germany). The concentration of Ti in the sample was quantified using an inductive coupled plasma atomic emission spectrometer (ICP−AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation, USA). The concentration of F$^-$ in the sample was determined by ion chromatography (Dionex ICS-2500, Dionex Corporation, USA). TG/DTA was performed in air flow with a temperature ramp of 10 °C min^{-1} between 50 and 800 °C, using a Mettler TGA/SDTA 851^e instrument (Mettler-Toledo International Inc., Switzerland) and STARe thermal analysis data processing system. Gas chromatography (GC) was performed on a Shimadzu 2014 (Shimadzu Corporation, Japan) equipped with a DM-1 capillary column (30 m × 0.25 mm × 0.25 μm, Dikma Technologies Inc., Beijing, China). GC–mass spectrometry (GC–MS) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector (Agilent Technologies, Inc., USA).

UV–vis spectra were recorded on a Shimadzu UV 2550 spectrophotometer (Shimadzu Corporation, Japan). Raman spectra were recorded on a Jobin Yvon T64000 Raman spectrometer equipped with a CCD multichannel detector (Jobin Yvon Corporation, France). The sample in form of solution was detected at room temperature.

Synthesis. *Bis-[N-(propyl-1-sulfoacid)-pyridinium] Hexafluorotitanate (**1**).* The mixtures of 1,3-propanesultone (12.2 g, 0.1 mol) in 100 mL of acetone and pyridine (7.9 g, 0.1 mol) in 100 mL of acetone were stirred vigorously at ambient temperature for 72 h. The obtained white solid, after washing with acetone and drying under vacuum, was then treated with 0.05 mol of aqueous hexafluorotitanic acid (H_2TiF_6, 60% aqueous solution, commercial). The reaction mixture was stirred at ambient temperature for 24 h, and finally, the solvent was removed from solution on a rotary evaporator. The residue was dissolved in ethanol, and the obtained solution was then filtered off. Bis[*N*-(propyl-1-sulfoacid)-pyridinium] hexafluorotitanate ($[Pspy]_2TiF_6$, **1**) was obtained as a sticky liquid after concentration of the filtrate. Yield: 70%. TG/DTA (in air flow): 350 °C (thermal decomposition). FT-IR (KBr disk, cm^{-1}): 1633 (s), 1493 (s), 1182 (vs, broad, $-SO_3H$), 1040 (s, $-SO_3H$), 857 (m), 775 (m), 738 (m), 681 (m), 616 with shoulder 583 (vs, broad), 530 (m). ^1H NMR (D_2O, δ, ppm): 8.79 (2H, d, $J = 6.0$), 8.46 (1H, t, $J = 7.8$), 7.98 (2H, t, $J = 6.9$), 4.68 (2H, t, $J = 7.5$), 2.89 (2H, t, $J = 7.3$), 2.37 (2H, m). Elemental analysis for CHN: C 33.82, H 4.21, N 4.86 (Calcd.: C 33.93, H 4.27, N 4.95). ICP–AES analysis for Ti (Calcd.): 8.59 wt % (8.45 wt %).

*Bis-[N-(propyl-1-sulfoacid)-pyridinium] Sulfate (**2**).* Compound **2** was prepared according to procedures similar to those described for **1**, only an aqueous solution of H_2SO_4 was used instead of H_2TiF_6. Yield: 78%. TG/DTA (in air flow): 322 °C (thermal decomposition). FT-IR (KBr disk, cm^{-1}): 1633 (s), 1493 (m, pyridinium), 1195 (vs, $-SO_3H$), 1037 (s, $-SO_3H$), 861 (w), 775 (w), 681, 609. The ^1H NMR spectra of 2 in D_2O was the same as those for **1**. Elemental analysis for CHN: C 38.44, H 4.75, N 5.53 (Calcd.: C 38.39, H 4.83, N 5.60).

*Bis-(N-n-butylpyridinium) Hexafluorotitanate (**3**).* Into 100 mL of ethanol solution of *N*-*n*-butylpyridinium chloride (17.4 g, 0.1 mol), an excess of aqueous solution of H_2TiF_6 (0.06 mol, 60%) was added. After vigorous stirring at 70 °C for 24 h, the solvent was removed from the reaction solution. The obtained residue was dissolved in CH_2Cl_2 (20 × 5 mL), and the organic phase was concentrated under vacuum to yield bis[*N*-*n*-butylpyridinium] hexafluorotitanate ($[Bpy]_2TiF_6$, **3**) as a sticky liquid. Yield: 83%. TG/DTA (in air flow): 259 °C (thermal decomposition). FT-IR (KBr disk, cm^{-1}): 1634 (s), 1488 (s), 1218 (vs), 1172 (s), 1051 (s), 856 (m), 775 (m), 738 (w), 690 (s), 592 (s), 530 (m). ^1H NMR (D_2O, δ, ppm): 8.69 (2H, d, $J = 6.0$), 8.37 (1H, t, $J = 7.8$), 7.90 (2H, t, $J = 6.9$), 4.44 (2H, t, $J = 7.5$), 1.82 (2H, m, $J = 7.5$), 1.17 (2H, m, $J = 7.5$), 0.76 (3H, t). Elemental analysis for CHN: C 49.84, H 6.44, N 6.51 (Calcd.: C 49.78, H 6.50, N 6.45). ICP–AES analysis for Ti: 10.87 wt % (Calcd.: 11.02 wt %).

General Procedures for Sulfoxidation Using H_2O_2 Catalyzed by 1. For a typical experiment, to 3 mL of $[Bpy]BF_4$ was sequentially added diphenylsulfide (or other sulfides, 5 mmol), **1** (0.35 mmol), and an aqueous solution of H_2O_2 (30%, 5 mmol). The obtained mixture was stirred vigorously at room temperature. Upon completion of the reaction, diethyl ether was used to extract the organic compounds (2 mL × 5). The conversion of diphenyl sulfide was based on GC analysis with *n*-dodecane as internal standard. The selectivities of products were based on GC analysis using the normalization method. The products were further identified by GC–MS.

Before the next run, the water from the remaining IL mixture should be removed on a rotary evaporator.

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