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A novel catalytic system poly(1-vinyl-3-dodecylimidazolium tribromide)/TBN for the oxidation of sulfides to sulfoxides with air as oxidant

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ABSTRACT

A novel and recoverable polymeric ionic liquid, poly(1-vinyl-3-dodecylimidazolium tribromide) (Poly[VDIM]Br_3), was successfully prepared and fully characterized. And a highly efficient metal-free catalytic system Poly[VDIM]Br_3/*tert*-butyl nitrite was developed for the oxidation of sulfides. With air as oxidant, we have successfully achieved 19 kinds of sulfides selectively and efficiently oxidized to corresponding sulfoxides using this catalytic system at room temperature.

Introduction

Selective oxidation of sulfides to sulfoxides is a significant and challenging organic reaction [1], because the sulfoxide is a kind of important organic synthesis intermediate [2], which is extensively utilized in medicine, pesticide [3], heavy metal extraction [4], oil desulphurization, organic synthesis [5] and other industries [6,7]. Therefore, a great deal of methods have been issued for the oxidation of sulfides to sulfoxides [8–10]. In recent years, as the oxidant, molecular oxygen has been more and more popular [11], on account of its many outstanding advantages such as environmentally friendly, low cost and by-product as water. Nonetheless, the catalyst was needed to activate molecular oxygen for the oxidation of sulfides. There have been many reports that a dual component catalytic system consisted of bromine-containing and NO_X-containing reagents could successfully achieve the oxidation of sulfides to sulfoxides [12–14], but most of them suffered from the troublesome drawback–the use of transition metal or acid, which may not environmentally friendly. Consequently, we sought to design a new kind of dual component catalytic system free from the drawback.

As we know, ionic liquids (ILs) are green and recyclable reagents and have attracted tremendous research interest [15,16]. Utilized as monomers, ILs have been frequently employed in the synthesis of polymeric ionic liquids (PILs) over the past few years. And the PILs are described as a novel class of materials combining the unique properties of ILs and the specificities of polymers. As compared to ILs, PILs not only inherit the eminent properties of the ILs, such as superior ionic conductivity, strong solubilizing ability and excellent chemical and electrical stability, but also present intrinsic polymer features and enhanced mechanical stability and durability [17]. Possessing these unique characteristics, PILs are promising candidates for different technological fields, such as materials [18], catalysts [19], biotechnology [20], and surface science [21]. Furthermore, the Br_3^--containing regents which are more stable and benign than Br_2 have been extensively utilized, including phosphorus tribromide [22] and benzyltrimethylammonium tribromide [23]. There were a few reports that the Br_3-containing regents were utilized to oxidize the sulfides [24,25], but they were used as oxidant, which were not as green as molecular oxygen as the oxidant. In addition, the catalytic mechanism of Br/NO_X systems have been extensively accepted [26], and *tert*-butyl nitrite (TBN) as a good substitute for NO_X has been reported [27]. And our group have reported related articles of the oxidation of sulfides [28,29]. Accordingly, we designed a kind of Br_3^--containing PIL–poly(1-vinyl-3-dodecylimidazolium tribromide) (Scheme 1), it was not only an eligible substitute for Br_2 but also recoverable.

Herein, we report a novel and efficient catalytic system-Poly [VDIM]Br_3/TBN for selective oxidation of sulfides to corresponding

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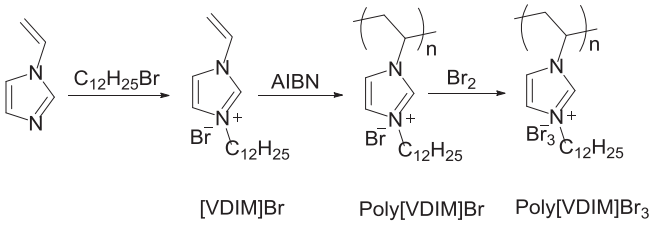


Scheme 1. Synthesis of the Poly[VDIM]Br_3.

sulfoxides under mild and metal-free conditions with air as oxidant (Table 2).

Results and discussion

Optimization of the reaction solvents

In order to find an appropriate solvent for the oxidation of sulfides to sulfoxides, different solvents for the oxidation of methyl phenyl sulfide as a typical example were screened. The results are summarized in Table 1. As is evident in Table 1, the oxidation reaction proceeds more rapidly in acetonitrile.

Table 1
Aerobic oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide by Poly[VDIM]Br_3/TBN as the catalyst in different solvents.[a]

Entry	Solvent	Time (h)	Yield (%)[b]
1	Acetonitrile	2	>99
2	Dichloromethane	2	3
3	Acetone	2	<1
4	Ethyl acetate	2	16
5	Tetrahydrofuran	2	4
6	*n*-Heptane	2	17
7	Acetonitrile/H_2O = 1:1[c]	2	36

[a] Reaction conditions: methyl phenyl sulfide 10 mmol, Poly[VDIM]Br_3 (0.5 mmol, 0.25 g), TBN 0.5 mmol, H_2O 1 mL, solvent 20 mL, 25 °C.
[b] Determined by GC Agilent 6890 N and GC–MS.
[c] Volume ratio.

The oxidation of sulfides to sulfoxides

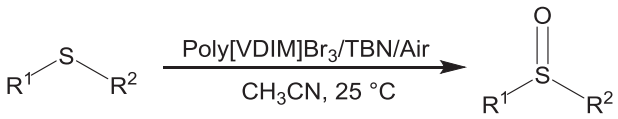
With the optimized conditions in hand, we report on the chemoselective oxidation of a variety of aliphatic and aromatic sulfides to their corresponding sulfoxides by Poly[VDIM]Br_3/TBN catalytic system in presence of water in acetonitrile at room temperature with air as oxidant. The results are shown in Table 2.

With this oxidation system, a variety of sulfides were successfully converted to sulfoxides with high conversion rate and it exhibited excellent catalytic efficiency. As was evident in Table 2, there existed obvious difference between the reaction time of different sulfides. Aromatic compounds sulfides with electron-withdrawing groups took more time than those with electron-donating groups. With regard to methyl phenyl sulfide which was aromatic compound, while its benzene ring was connected with the electron-withdrawing groups (–CO–, –X, $–NO_2$), like entries 5–14, the larger the groups, the time of the reaction may be longer. In addition, the reaction could also be excellently finished when with the electron-donating groups (entries 2–4, 15, 16). Besides, sulfides (entries 12, 14) that were not completely dissolved in acetonitrile probably attributed to considerable molecular volume could also be selectively oxidized to corresponding sulfoxides. With respect to aliphatic compounds sulfides (entries 17–19), the oxidation reaction could also achieve with high selectivity and efficiency.

Mechanism

A plausible mechanism for this novel and metal-free catalytic oxidation process can be described by the dual cycle shown in Scheme 2. Firstly, the lone pair electrons on sulfur atom in sulfide are attacked by Br^+ which is derived from Br_2 in the Poly[VDIM]Br_3

Table 2
Oxidation of sulfides to corresponding sulfoxides.[a]



Entry	R^1	R^2	t/h	Conv. (%)[b]	Sel. (%)[b]	Yield (%)[c]
1	Ph–	CH_3	2.5	>99	>99	97
2	4-$CH_3C_6H_4$–	CH_3	2.5	>99	>99	96
3	4-$CH_3OC_6H_4$–	CH_3	2.5	>99	>99	96
4	2-$CH_3OC_6H_4$–	CH_3	2.5	>99	>99	96
5	4-FC_6H_4–	CH_3	3.0	>99	>99	95
6	4-ClC_6H_4–	CH_3	2.5	>99	>99	96
7	2-ClC_6H_4–	CH_3	6.0	>99	>99	96
8	2-BrC_6H_4–	CH_3	5.0	>99	>99	97
9	4-$NO_2C_6H_4$–	CH_3	13	>99	>99	96
10	4-$HCOC_6H_4$–	CH_3	5.5	>99	>99	95
11	4-$CH_3COC_6H_4$–	CH_3	6.5	>99	>99	96
12	4-$PhCOC_6H_4$–	CH_3	8	>99	>99	96
13	4-$CH_3COOC_6H_4$–	CH_3	8	>99	>99	97
14	4-$PhCOOC_6H_4$–	CH_3	8	>99	>99	97
15	Ph–	CH_3CH_2–	2.5	>99	>94	92
16	Ph–	$HOCH_2CH_2$–	5	>99	>91	88
17	–$(CH_2)_4$–		5	>78	>99	71
18	$CH_3CH_2CH_2CH_2$–	$CH_3CH_2CH_2CH_2$–	5	>99	>99	94
19	$CH_3(CH_2)_{11}$–	CH_3	5	>93	>99	89

[a] Reaction conditions: sulfides (10 mmol), Poly[VDIM]Br_3 (0.5 mmol, 0.25 g), TBN (0.5 mmol), H_2O (0.5 mL), CH_3CN (20 mL), air, 25 °C.
[b] Determined by GC Agilent 6890N and GC–MS.
[c] Isolated yield.