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Clean and selective oxidation of alcohols with n-Bu_4NHSO_5 catalyzed by ionic liquid immobilized TEMPO in ionic liquid [bmim][PF_6]

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ABSTRACT

An efficient oxidation of alcohols with tetra-n-butylammonium peroxymonosulfate catalyzed by ionic liquid immobilized TEMPO in ionic liquid [bmim][PF_6] was reported. TEMPO-IL serves as a homogeneous catalyst to enhance the reaction remarkably. The oxidation proceeded to afford aldehydes or ketones in excellent yields and high selectivity without remarkable over-oxidation to carboxylic acids. It is noteworthy to mention that the catalyst and solvent could easily be recycled and reused without loss of activity. A possible mechanism for the oxidation is proposed.

1. Introduction

The selective oxidation of alcohols to the corresponding aldehydes or ketones is a fundamental transformation both in laboratory synthesis and industrial production [1–3]. Numerous oxidizing reagents (for example, CrO_3, $KMnO_4$, MnO_2, etc.) in stoichiometric amounts have been traditionally employed to accomplish this transformation with considerable drawbacks such as the use of expensive reagents, volatile organic solvents, and discharge of environmentally pernicious wastes [4]. Transition metal-catalyzed oxidations of alcohols using aqueous H_2O_2 or gaseous O_2 as oxidant have also been developed [5–8]. From economic and environmental perspectives, the development of new catalytic oxidation system with cheap and green oxidant is particularly attractive.

Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) has drawn considerable attention as a mild and efficient reagent for various organic transformations in recent years [9–15]. However, oxone is practically insoluble in all solvents except water. The need for aqueous or pH-controlled reactions is perhaps the most significant drawback in the use of oxone for applications in synthetic chemistry [16]. To overcome the need for aqueous conditions, several salts of oxone have been reported, such as tetra-n-butylammonium peroxymonosulfate (n-Bu_4NHSO_5, TBA-OX), tetra-n-pentylammonium peroxymonosulfate, tetra-n-hexylammonium peroxymonosulfate and benzyltriphenylphosphonium peroxymonosulfate. Recently, TBA-OX was demonstrated by Lei et al. to be an effective reagent for the oxidation of alcohols in CH_2Cl_2 or H_2O [17]. Although oxidation of secondary alcohols led to ketones in good yields, oxidation of primary alcohols was proceeded with low conversion and selectivity.

On the other hand, it is well known that nitroxyl radicals, such as 2,2,6,6-tetramethyl-1-piperidinyloxyl free radical (TEMPO) promote oxidation of various alcohols to the corresponding carbonyl compounds effectively under mild reaction conditions [18–20]. However, separation of TEMPO from the products and recycling could be problematic. Numerous immobilized TEMPO variants on both organic and inorganic supports have been synthesized [21–24]. Nevertheless, TEMPO immobilized on inorganic supports in some cases shows lower catalytic activity, and prolonged reaction times are needed for high conversion [25].

Room temperature ionic liquids have received recognition as novel and promising solvents for synthesis chemistry. They have also been referred to as “designer solvents” as their chemical and physical properties could be adjusted by careful choice of the cation or anion. Recent advances in ionic liquids provided efficient routes for the preparation of task-specific ionic liquids (TSILs). Muzart has reviewed the development of ionic liquids as solvents for catalyzed oxidations of organic compounds, and some methods about using ionic liquid immobilized TEMPO were summarized [26].

In continuation of our interest in exploring systems on the oxidation of organic compounds [27], especially alcohols [28–32], here, we would like to report a facile procedure for the oxidation of alcohols to the corresponding aldehydes or ketones with TBA-OX catalyzed by TEMPO or TEMPO-IL (ionic liquid immobilized TEMPO) in 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] (Scheme 1). The catalyst TEMPO-IL, ionic liquid [bmim][PF_6] and the

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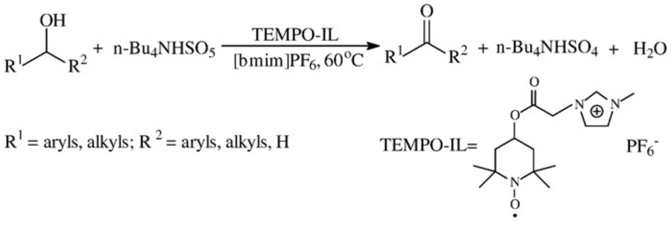


Scheme 1. Oxidation of alcohols catalyzed by TBA-OX/TEMPO-IL in $[bmim]PF_6$.

reduction product $n\text{-}Bu_4NHSO_4$ from the oxidant TBA-OX are easily recovered and reused in the procedure.

2. Experimental

All chemicals (AR grade) were obtained from commercial resources and used without further purification. TBA-OX was prepared from commercially available oxone and $n\text{-}Bu_4NHSO_4$ by a procedure described in the literature [16]. TEMPO-IL was synthesized according to literature [23,24]. Gas chromatography (GC) analysis was performed on an Agilent GC-6820 chromatograph equipped with a 30 m × 0.32 mm × 0.5 μm HP-Innowax capillary column and a flame ionization detector. GC–MS spectra were recorded on Thermo Trace DSQ GC–MS spectrometer using TRB-5MS (30 m × 0.25 mm × 0.25 μm) column. Products were all known compounds and were identified by comparing their physical and spectra data with those reported in the literature.

2.1. Typical experimental procedure for oxidation of alcohols

TBA-OX (0.95 g, 1.00 mmol) was dissolved in $[bmim][PF_6]$ (4 mL) at 60 °C for several minutes, alcohol (0.5 mmol) and TEMPO-IL (0.05 g, 0.1 mmol) were added with stirring. The mixture was stirred at 60 °C for a given time (see Table 2). After completion, the mixture was extracted with ether (3 × 10 mL) and analyzed by GC–MS. The organic layer was dried and concentrated to provide the corresponding product in an almost pure state. If necessary, the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford the analytically pure aldehydes or ketones.

3. Results and discussion

3.1. The solubility properties of TBA-OX

The solubility properties of TBA-OX in some traditional solvents were first investigated. It is completely soluble in water, MeOH, acetone, CH_2Cl_2, $CHCl_3$, MeCN, $MeNO_2$, DMF, and DMSO. Other solvents such as EtOAc, benzene, CCl_4, hexane, THF, toluene and ether are not able to dissolve TBA-OX. To the best of our knowledge, there is no report on the solubility properties of TBA-OX in ionic liquids. So, a variety of ionic liquids, including acidic ionic liquids (Table 1, entries 1–2), neutral ionic liquids (Table 1, entries 3–4) and basic ionic liquids (Table 1, entries 5–7) were tested to dissolve TBA-OX, the results are shown in Table 1. Interestingly, TBA-OX is nearly insoluble in $[bmim][PF_6]$ at low temperature, but miscible at high temperature (see Fig. 1). Furthermore, $[bmim][PF_6]$ is immiscible with water. This could perhaps be beneficial since it can provide an easy route to remove the oxidant and its by-product ($n\text{-}Bu_4NHSO_4$) after completion by simple washing of the reaction mixture with water.

Table 1
Solubility of TBA-OX in ionic liquids.[a,b]

Entry	Ionic liquid	T/°C			
		25	40	60	80
1	$[Hmim][HSO_4]$	s	s	s	s
2	$[Hmim][CF_3COO]$	s	s	s	s
3	$[bmim][PF_6]$	i	i	s	s
4	$[bmim][BF_4]$	i	s	s	s
5	$[bmim][OH]$	i	s	s	s
6	$[H_3N^+\text{–}CH_2\text{–}CH_2\text{–}OH][CH_3CH(OH)COO^-]$	s	s	s	s
7	$[H_3N^+\text{–}CH_2\text{–}CH_2\text{–}OH][CH_3COO^-]$	s	s	s	s

[a] s: soluble; i: insoluble.
[b] 0.25 g TBA-OX in 3 mL ionic liquid.

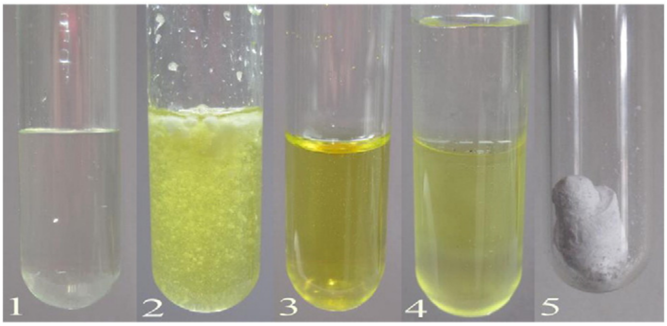


Fig. 1. Photographic plates. (1) $[bmim][PF_6]$: 3 mL; (2) 0.25 g TBA-OX in 3 mL $[bmim][PF_6]$ at RT; (3) 0.25 g TBA-OX in 3 mL $[bmim][PF_6]$ at 60 °C; (4) Photo 3 was washed with 2 mL H_2O after being cooled to RT, the upper layer was H_2O; (5) After completion, the aqueous phase was lyophilized to obtain the $n\text{-}Bu_4NHSO_4$.

3.2. Effects of the catalysts on the reaction rate

The initial experiments were carried out using 4-nitrobenzyl alcohol as the model substrate. When 4-nitrobenzyl alcohol was oxidized with TBA-OX/TEMPO in $[bmim][PF_6]$ at 60 °C for 1 h, the formation of 4-nitrobenzaldehyde as the exclusive product with 94% yield was established. As a control experiment, the same reaction was carried out in the absence of TEMPO and no oxidation product was observed even after stirring for 8 h. The use of TEMPO-IL instead of TEMPO in the oxidation led to similar results, without apparent loss of catalytic activity (see Fig. 2).

3.3. Oxidation of alcohols catalyzed by TEMPO or TEMPO-IL

In order to evaluate the versatility of this novel catalytic system, we applied the procedure to the oxidation of a wide range of alcohols. As shown in Table 2, most alcohols underwent oxidation to afford the

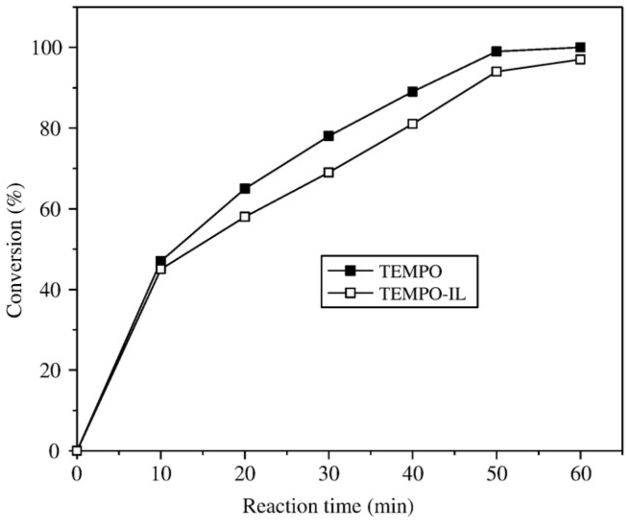
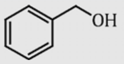
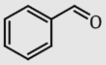
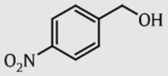
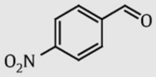
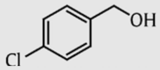
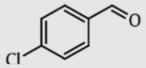
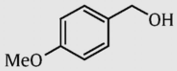
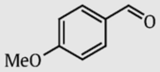
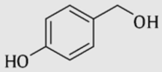
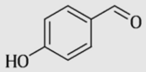
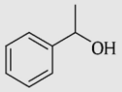
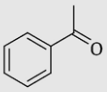
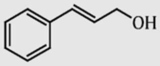
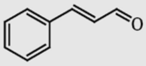
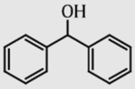
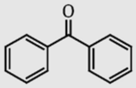
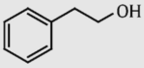
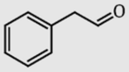
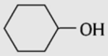
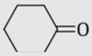
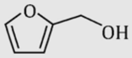
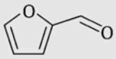
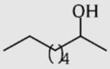
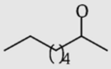


Fig. 2. Comparison with the catalytic activity of TEMPO and TEMPO-IL. Reaction conditions: 4-nitrobenzyl alcohol (0.07 g, 0.5 mmol), TBA-OX (0.95 g, 1 mmol), TEMPO or TEMPO-IL (0.1 mmol), and $[bmim][PF_6]$ (4 mL) at 60 °C.

Table 2
TBA-OX/TEMPO (TEMPO-IL) catalyzed oxidation of alcohols.

Entry	Alcohols	Products	Catalytic system[a]	Time (h)	Yield[b] (%)
1			A B	0.5 0.5	92 90
2			A B	1 1	95 94
3			A B	1 1	96 94
4			A B	1 1	97 98
5			A B	1.5 1.5	90 85
6			A B	1 1	92 90
7			A B	1 1	96 95
8			A B	3 4	98 94
9			A B	3 4	85 80
10[c]			A B	5 7	78 73
11[c]			A B	6 8	48 40
12[c]	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	A B	6 8	72 68
13[c]			A B	6 8	78 71

[a] Catalytic system A: TBA-OX/TEMPO, B: TBA-OX/TEMPO-IL.
[b] Yields of isolated products unless otherwise noted.
[c] Yields were determined by GC.

corresponding aldehydes or ketones in excellent yields. Benzylic alcohols underwent smooth oxidation (Table 2, entries 1–6). Allylic alcohols such as cinnamyl alcohol (Table 2, entry 7) were also oxidized efficiently to the corresponding aldehyde without any observable reaction at the double bond functionality. Electron-rich and electron-deficient benzylic alcohols did not show obvious differences. Aliphatic and heterocyclic alcohols were less reactive than benzylic and allylic alcohols toward this system. Aliphatic alcohols were oxidized to the corresponding aldehydes or ketones in reasonable yields in prolonged reaction times (Table 2, entries 9, 12, and 13). For the oxidation of furan-2-yl methanol, a heterocyclic alcohol, the yield obtained was quite low even in prolonged reaction time (Table 2, entry 11). Use of TEMPO-IL instead of TEMPO as catalyst in this reaction was advantageous because of its similar reactivity to TEMPO but with the additional advantages of simple workup procedure and easy recovery.

3.4. Recycling of the catalysts and ionic liquid

Extraction of the product with ether led to the separation of the catalyst and ionic liquid from the product. The ionic liquid layer was then washed with water to remove n-Bu_4NHSO_4 (the reduction product of TBA-OX). The aqueous phase was removed by decantation and lyophilized to obtain n-Bu_4NHSO_4 (see Fig. 1). n-Bu_4NHSO_4 is a phase transfer catalyst and can be reused in the preparation of TBA-OX. The ionic liquid layer was distilled under vacuum to remove residual ether and water. Fresh substrates were then recharged to the residual liquid layer and the mixture was heated to react once again. The procedure was repeated 5 times in the oxidation of 4-nitrobenzyl alcohol. It was found that if TEMPO-IL was used as a catalyst, there is no apparent loss of catalytic activity in the oxidation (see Fig. 3), and only 2.3% loss of weight was observed after five times recycling. However, when the reaction catalyzed by TEMPO, yields drastically decreased from the first cycle of 95% to the second cycle of 63% and the third cycle of 27%. These results demonstrated that TEMPO is easily removed from the ionic liquid layer by ether extraction during the work up process and TEMPO-IL is not. Therefore, from the point of view on the greener chemical processes, the use of the catalytic system of TBA-OX/TEMPO-IL/[bmim][PF_6] do not lead to three major sources of waste: organic solvents, catalysts and any hazardous by-products.

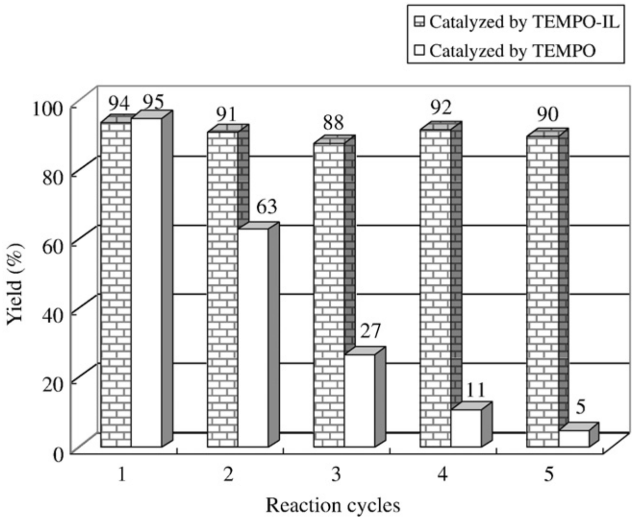


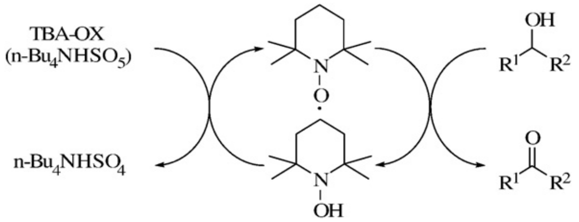
Fig. 3. Recycling of the catalytic system for the oxidation of 4-nitrobenzyl alcohol.

3.5. Mechanistic aspects

For the present TBA-OX/TEMPO catalytic oxidation system, both primary and secondary alcohols give carbonyl compounds. TEMPO must play a key role for this selectivity. TEMPO would be the active oxidant in this reaction. The role of TBA-OX is to regenerate TEMPO or TEMPO-IL. A plausible mechanism of this reaction is depicted in Scheme 2.

4. Conclusion

In summary, an efficient, facile and rapid oxidation of alcohols with TBA-OX/TEMPO-IL system in the ionic liquid [bmim][PF_6] has been developed, which allowed the oxidation of alcohols to aldehydes or ketones in excellent yields and high selectivity without remarkable



Scheme 2. A plausible reaction pathway.

over-oxidation to carboxylic acids. It is noteworthy to mention that the catalyst and solvent could easily be recycled and reused without loss of activity and the oxidant's by-product (n-Bu_4NHSO_4) could also be recycled. The scope and synthetic and industrial applications of the oxidation procedure are currently under investigation.

Acknowledgement

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