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Clean synthesis of adipic acid by direct oxidation of cyclohexene with H_2O_2 catalysed by $Na_2WO_4.2H_2O$ and acidic ionic liquids

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Without any other organic solvents or halide present, direct catalytic oxidation of cyclohexene to adipic acid with hydrogen peroxide catalysed by $Na_2WO_4.2H_2O$ and acidic ionic liquids has been performed with excellent yields and selectivities, and the catalyst system could be easily reused.

Keywords: acidic ionic liquid, oxidation, cyclohexene, adipic acid

Adipic acid is an important intermediate utilised in the production of nylon-6, 6. The usual industrial synthesis of this compound involves nitric acid oxidation.[1] This method inevitably produces nitrous oxide (N_2O), which is commonly thought to cause global warming, and ozone depletion as well as acid rain and smog.[2] Despite the efficient recovery or recycling of N_2O, ~ 400,000 metric tons are still emitted each year, which corresponds to 5 to 8% of the worldwide anthropogenic emission of N_2O. Therefore, the development of environmentally conscious practical procedures for the oxidation of six-carbon feedstocks is highly desirable.[3]

Because of the great potential of ionic liquids (ILs) at room temperature as environmentally benign media for catalytic processes,[4] much attention has currently been focused on the organic reactions catalysed with or in such liquids, and many organic reactions, especially reactions promoted with acid-base catalysts, were performed in ionic liquids with good results.[5] At the same time, acidic ionic liquids used in previous literature were usually based on $AlCl_3$, and are not stable, and reuse was also difficult. Hence, non-chloroaluminiate ILs, which are air and moisture stable, have recently been developed and applied to acid-catalysed reactions.[6-12] Compared with chloroaluminate ILs, the preparation procedures of these Brønsted acidic ILs are relatively simple and can be accomplished by neutralisation of acid and base.[9,11]

In our previous work, our group had reported the method of replacing $[CH_3\,(n\text{-}C_8H_{17})_3\,N]\,HSO_4$ with the simple sulfate and hydrochloride of a higher primary or tertiary amine[13] and shown that the acidity of the ligand plays a very important role for the $Na_2WO_4.2H_2O$ catalysed oxidation of cyclohexene with 30% aqueous hydrogen peroxide.[14] In continuation of this work we now report for the first time an efficient and environmentally benign method for synthesis of adipic acid (Fig. 1) catalysed by $Na_2WO_4.2H_2O$ and an acidic ionic liquid with 30% aqueous hydrogen peroxide without any other organic solvents or halide present. The catalyst system was easily reused.

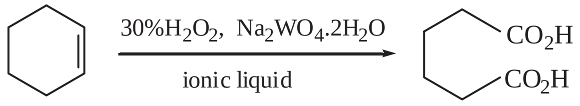

Fig. 1 The oxidation of cyclohexene.

Experimental

Materials and reagents

All solvents and chemicals in the experiments were commercially available and used without further purification unless otherwise stated. *N*-methylimidazole and 1,4-butane sultone were purchased from Aldrich.

Preparations of room temperature ionic liquids

The ionic liquids (Fig. 2) 1-*n*-butyl-3-methylimidazolium tetrafluoroborate([bmim][BF_4]), 1-methyl-3-butylimidazole chloride([bmim]Cl), 1-(4-sulfonic acid)butyl–3-methylimidazolium hydrogen sulfate ([$(CH_2)_4SO_3HMIm$][HSO_4]), 1-(4-sulfonic acid)butylpyridinium

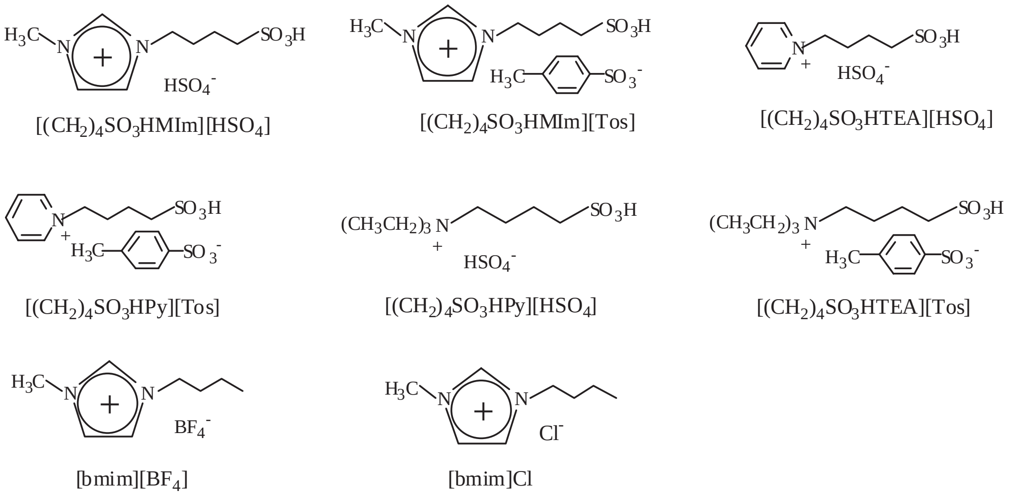

Fig. 2 The structure of ionic liquid in the study.

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Table 1 Influence of different ionic liquids on cyclohexene oxidation[a]

Entry	IL	IL/mmol	Conversion/%	Selectively/%
1	/	/	30	40.9
2	[bmim][BF_4]	2.5	53	79.3
3	[bmim]Cl	2.5	51	75.1
4	[$(CH_2)_4SO_3$HMIm][HSO_4]	2.5	100	91.2
5	[$(CH_2)_4SO_3$HPy][HSO_4]	2.5	100	89.2
6	[$(CH_2)_4SO_3$HTEA][HSO_4]	2.5	100	83.1
7	[$(CH_2)_4SO_3$HMIm][Tos]	2.5	100	94.2
8	[$(CH_2)_4SO_3$HPy][Tos]	2.5	100	91.5
9	[$(CH_2)_4SO_3$HTEA][Tos]	2.5	100	86.3
10	[$(CH_2)_4SO_3$HMIm][Tos]	1.25	100	90.2
11	[$(CH_2)_4SO_3$HMIm][Tos]	5.0	100	95.1
12	[$(CH_2)_4SO_3$HMIm][Tos]	7.5	100	96.7(92.3)[b]
13	[$(CH_2)_4SO_3$HMIm][Tos]	10	100	97.0

[a]Conversion and selectivity are based on GC/MS , reaction condition: $Na_2WO_4.2H_2O$ 2.5 mmol, 30% aqueous H_2O_2 440 mmol, cyclohexene 100 mmol, refluxed and stirred for 10 h.
[b] Data in parentheses are isolated yields.

hydrogen sulfate ([$(CH_2)_4SO_3$HPy][HSO_4]), N-(4-sulfonic acid) butyltriethylammonium hydrogen sulfate ([$(CH_2)_4SO_3$HTEA] [HSO_4]), 1-(4-sulfonic acid)butyl-3-methylimidazolium *p*-toluenesulfonate([$(CH_2)_4SO_3$HMIm][Tos]), 1-(4-sulfonic acid)butylpyridinium p-toluenesulfonate ([$(CH_2)_4SO_3$HPy][Tos]), and N-(4-sulfonic acid) butyl triethylammonium p-toluenesulfonate ([$(CH_2)_4SO_3$HTEA][Tos]) were synthesised according to the procedures reported in the literature.[6,11]

Catalytic oxidation

A 150 ml flask equipped with a magnetic stirring bar and a reflux condenser was charged with 0.825 g (2.5 mmol) of $Na_2WO_4.2H_2O$, 2.5 mmol of ionic liquid, and 44.5 ml (440 mmol) of 30% aqueous H_2O_2. The mixture was vigorously stirred at room temperature for 15 min and then 10.5 ml (100 mmol) of cyclohexene was added. The biphasic mixture was refluxed for 10 h with stirring at 1000 rpm. The homogeneous solution was allowed to stand at 5 °C for 24 h, and the resulting white precipitate was separated by filtration and washed with 20 ml of cold water. The product was dried at room temperature and had a melting point of 151 to 152 °C. Qualitative and quantitative analyses of organic products were conducted with a Hewlett-Packard 6890/5793 GC-MS and a SP-3400 GC-FID detector equipped with a capillary column. The concentration of reactant and product was directly given by the system of the GC chemstation according to the area of each chromatograph peak.

Results and discussion

The experimental results indicated that the acidic ionic liquids had strong impact on the catalytic oxidation (Table 1). Acidic ionic liquids were found to be essential for the reaction, as the reaction gave little product in the absence of them (Table 1, entries 1–3). However, the conversion and selectivity for adipic acid could be greatly enhanced when acidic ionic liquids were present (Table 1, entries 4–9). The best catalytic performance could be achieved when [$(CH_2)_4SO_3$HMIm][Tos] was used, *i.e.* in addition to complete conversion of cyclohexene, 94.2% selectivity for adipic acid was obtained (Table 1, entry 7). The main byproducts were cyclohexanediol and pentanedioic acid detected by GC/MS. When the acidic ionic liquids have the same anion, the best results were obtained in acidic ionic liquids whose cation contains the imidazole ring, indicating that cation had some effect on the selectivity (Table 1, entries 4 and 7). When the acidic ionic liquids have the same cation, the yields and selectivities in ionic liquids with Tos^- were higher than that with [HSO_4^-], although the acidities of ionic liquids with [HSO_4^-] were stronger than those with [Tos^-]. These might be related to the different oleophilic properties of these acidic ionic liquids. Since the peroxytungstate was water-soluble but immiscible with cyclohexene, it must penetrate from the aqueous H_2O_2 phase into the oil phase before initiating oxidation of cyclohexene. When the peroxytungstate was in acidic ionic liquids, the resultant catalyst system not only possessed the capability of carrying active oxygen species but also became oleophilic, and the more oleophilic a catalyst system the better catalyst performance was.

The amount of the IL affected the selectivity of product significantly. As shown by entries 10–13 in Table 1, the selectivity of the product increased with the increasing amount of the IL when there was not enough IL in the reactor, but did not change considerably as the amount of IL was more than 7.5 mmol. The main reason may be that an acidic environment is essential for an oxidation reaction involving H_2O_2 as oxidant,[15] and the acidity of the reaction media would directly depend upon the acidity of the acidic ionic liquid. When the amount of IL was 7.5 mmol, 96.7% selectivity (isolated yields, 92.3%) for adipic acid was achieved (Table 1, entry 12). It is worth mentioning that such a yield and selectivity was the same as or better than that obtained from the previous literature.[13,14,16,17] This means that the phase transfer catalyst or organic acid ligand could be replaced by an acidic ionic liquid without any loss of yield and selectivity for adipic acid production and moreover the catalyst system itself is more environmentally friendly.

Once the reaction is complete, attention is paid to product isolation and catalyst recycling. As it was one of the most effective acidic ionic liquids, [$(CH_2)_4SO_3$HMIm][Tos] was selected to investigate the possibility of reusability. For each reaction cycle, 0.825 g (2.5 mmol) of $Na_2WO_4.2H_2O$, 7.5 mmol of ionic liquid, and 44.5 ml (440 mmol) of 30% aqueous H_2O_2 were added to a round-bottom flask successively. The mixture was vigorously stirred at room temperature for 15 min and then 10.5 ml (100 mmol) of cyclohexene was added. The biphasic mixture was refluxed for 10 h with stirring at 1000 rpm. After reaction, the homogeneous solution was allowed to stand at 5 °C for 24 h, and the resulting white precipitate was separated by filtration and washed with 20 ml of cold water. The mother liquor was concentrated to 10 ml and allowed to stand at 5 °C for 24 h, and the resulting white precipitate was separated by filtration and washed with 10 ml of cold water. The mother liquor was concentrated again to 5 ml. The reactor containing this concentrate, which contained the catalyst and ionic liquid was charged with 44.5 ml of aqueous 30% H_2O_2. This procedure was repeated for four cycles. The conversion rate and selectivity are listed in Table 2. It can be seen that the catalytic activity was slightly decreased after catalyst and ionic liquid were used 4 times. This indicated that the catalyst system was recyclable. The slight decrease of activity might be ascribed to the mechanical loss during the separation of product rather than the oxidation of the cation. Although the [bmim] cation was oxidised by oxygen,[18] no oxidation products of the cation were detected by GC-MS in our experiment. The reason may be that the oxidation ability of H_2O_2 is lower than that of O_2 or that the catalytic system is different.

Although detailed reaction mechanism is not clear at this stage, a visible colour change could be seen when H_2O_2 was mixed with the acidic ionic liquids and Na_2WO_4, indicating some kind of reaction happened among them. On the basis of the above results, we are inclined to believe that the peroxytungstate formed an acidic ionic liquid-peroxytungstate complex, which not only possessed the capability of carrying active oxygen species but also became

Table 2 Recycling of the catalyst system [a]

Run	Conversion/%	Selectively/%
1	100	96.7
2	100	95.3
3	100	93.6
4	100	92.3

[a]Conversion and selectivity are based on GC/MS, [$(CH_2)_4SO_3$HMIm][Tos] 7.5 mmol, other reaction conditions same as in Table 1.

oleophilic. If so, the ionic liquid cannot act as a phase transfer catalyst. Further investigations of the mechanism are on going.

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