The selective oxidation of benzyl alcohols in a membrane reactor

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The selective oxidation of benzyl alcohols by hypochlorite and a phase transfer catalyst has been successfully carried out in a membrane reactor.

Selective oxidation is one of the most important synthetic transformations in organic chemistry based on hydrocarbon resources. It is essential that these transformations are based on the principles of green chemistry and avoid heavy metal reagents, toxic solvents and the generation of large volumes of hazardous waste. The major source of waste in many organic reactions is commonly aqueous or salt effluent produced at the work-up stage when the organic and inorganic components are separated, often *via* an aqueous quench.[1]

Phase transfer catalysis (PTC) has been widely used to transfer inorganic anions into organic media by using catalytic amounts of lipophilic quaternary ammonium or phosphonium salts.[2] Sodium hypochlorite is a non-toxic oxidant, which has been reported to be transferred into the organic phase in the presence of quaternary ammonium salt[3–6] and is capable of oxidising alcohols including benzyl alcohol although it can be difficult to control selectivity.[7–9]

Most PTC reactions are carried out on an industrial scale in stirred tank reactors, which require the separation of products afterwards. Key criteria required in a PTC reactor are high interfacial area with little emulsification to enable easy phase separation. The use of a membrane reactor for a PTC reaction could fulfil these criteria as well as offering the advantages of easy product recovery. Furthermore, the organic-free reduced aqueous phase can be electrochemically regenerated while the organic phase remains uncontaminated with aqueous species thus facilitating continuous reactions. The use of a membrane reactor in a phase transfer catalysed reaction has been theoretically modelled before[10] and tested in a simple anion displacement reaction. It has been shown that the reactor performance depends on the flow rate ratio and conversions are slower than predicted due to mass transfer resistance. The membrane acts as a stable interface and no emulsification problems are involved.

Here we report the selective oxidation of benzyl alcohols using a porous PTFE membrane to separate the aqueous and organic phases. A flat sheet diaphragm reactor shown in Fig. 1, was used to carry out the reaction. In a typical reaction, a 13% aqueous solution of hypochlorite (25 ml), was adjusted to pH 9 and then added in the aqueous side of the reactor. Benzyl alcohol (3 mmol), and tetrabutylammonium hydrogen sulfate (0.3 mmol), were dissolved in DCM on the organic side. A hydrophobic microporous PTFE (0.2 μm) membrane was used and a slight pressure was applied to the aqueous side to avoid any transport of the organic phase into the aqueous phase. The hydrophobic PTFE membrane kept the aqueous phase from entering into the organic phase. The reaction could be run static or continuous with counter flowing aqueous and organic phases.

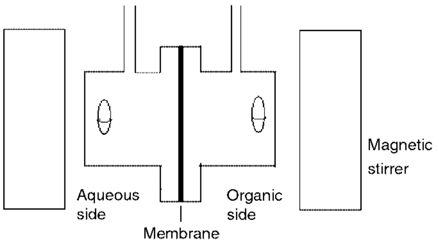
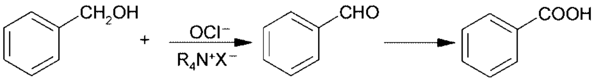


Fig. 1 Schematic diagram of flat sheet diaphragm cell.

The influence of several parameters has been investigated so as to optimise the performance of the system and in particular to avoid further oxidation of the benzaldehyde to benzoic acid [eqn. (1)].



(1)

The effect of benzyl alcohol concentration on the reaction profiles was first investigated (Fig. 2). As the concentration of benzyl alcohol increases the rate of conversion increases slightly. For each reaction a small induction period is observed, due to slow mass transfer of hypochlorite although this is not observed if the system is allowed to equilibrate before the alcohol substrate is added. The rate of the reaction does not depend as much on the concentration of benzyl alcohol as expected, however the concentration of PTC increases the rate due to easier mass transfer. Selectivity to the aldehyde is also reduced at low concentrations of the PTC. Changing the counter anion in the PTC (HSO_4^-, Cl^-, Br^-) has little effect on reaction rate or selectivity but little reaction occurs in the absence of a PTC. While the hypochlorite concentration has only a small effect on the rate of conversion of benzyl alcohol, it strongly influences the selectivity of the reaction. The amount of hypochlorite transferred into the organic phase is dependant on both the concentration of quaternary ammonium in the organic phase and that of the hypochlorite in the aqueous phase. The optimum concentration of hypochlorite at which we obtain a good rate of conversion and very high selectivity to the aldehyde is 13%.

Toluene can be used as a solvent for the reaction, although it decreases the rate of conversion due to slower mass transfer and benzyl chloride was produced from its oxidation under the standard reaction conditions.

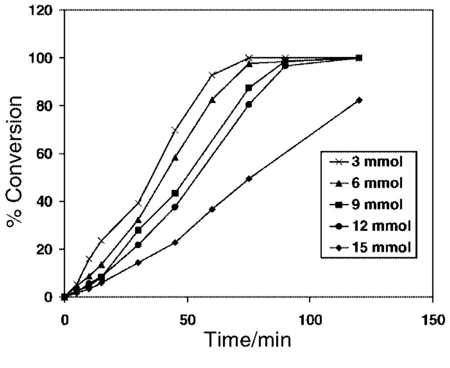


Fig. 2 Influence of the concentration of benzyl alcohol on the conversion of the reaction.

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Table 1 Oxidation of substituted benzyl alcohols to aldehydes under optimum conditions[a]

Substrate (benzyl alcohol)	Time/min	Product	Yield (%)[b]	Selectivity (%)
2-Methylbenzyl alcohol	60	2-Methylbenzaldehyde	97	98
4-Methylbenzyl alcohol	60	4-Methylbenzaldehyde	93	97
4-*tert*-Butylbenzyl alcohol	45	4-*tert*-Butylbenzaldehyde	90	95
4-Methoxybenzyl alcohol	120	4-Methoxybenzaldehyde	78	87
4-Chlorobenzyl alcohol	75	4-Chlorobenzaldehyde	75	84

[a] Reaction conditions: substrate (3 mmol), aqueous solution of NaOCl 13% (25 ml) at pH 9, $TBAHSO_4$ (0.9 mmol) and DCM (25 ml) at rt. [b] By quantitative NMR.

The optimised system was successfully used for the selective oxidation of a series of substituted benzyl alcohols (Table 1). It appears that moving the substituent away from the reaction centre did not affect the yield of the reaction. Insertion of an electron-withdrawing substituent on the benzene ring increases the reaction time and reduces the yield of the produced substituted benzaldehyde products.

In summary, we have shown that it is possible to develop a membrane reactor system for the static or continuous production of benzaldehyde as well as substituted benzaldehydes.

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