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Comparison of the phase transfer oxidation of benzyl alcohol in a pump cell and stirred-tank reactor

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The oxidation of benzyl alcohol by electrogenerated hypobromite in a two-phase emulsion has been studied using a quaternary ammonium salt as a phase transfer agent. The performances of a stirred-tank batch reactor and a bipolar electrochemical pump cell have been compared and the differences found are discussed in terms of the different mixing/transport/reaction regimes of the two cells. Benzaldehyde can be produced at a rate of $0.2\,mol\,h^{-1}\,dm^{-2}$ of electrode area for $4.20\,kWh\,kg^{-1}$.

1. Introduction

Phase transfer catalysis is being applied increasingly to organosynthesis [1–4], but so far has only been used infrequently in electrochemical systems [5]. A paper by Lee and Freedman [6], who oxidised benzyl alcohols to the corresponding aldehydes using an emulsion of aqueous sodium hypochlorite and ethyl acetate containing tetrabutylammonium bisulphate as the phase transfer agent, led Pletcher and Tomov [7] to study the same system, but with electrochemical generation of hypobromite from aqueous sodium bromide. Good material yields were obtained for a number of substituted benzyl alcohols but the success of the overall reaction was somewhat dependent upon the design of the stirrer used in the stirred-tank batch reactor, i.e. it depended upon the contacting pattern. The work reported here concerns the use of an electrochemical pump cell for this reaction and a comparison of its performance with that of the stirred tank.

2. Phase transfer oxidations

The overall scheme for the reaction can be sketched as follows:

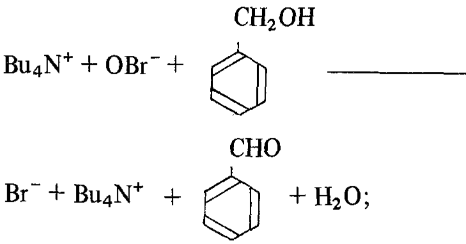
Cathode $$2H_2O + 2e \rightleftharpoons 2OH^- + H_2\uparrow \qquad (1)$$

Anode $$2Br^- \rightleftharpoons Br_2 + 2e \qquad (2)$$

Bulk $$Br_2 + H_2O \rightleftharpoons HOBr + HBr \qquad (3)$$

Ion pairing $$\begin{array}{rcl} Bu_4NHSO_4 \rightleftharpoons & Bu_4N^+ & + HSO_4^- \\ HOBr \rightleftharpoons & OBr^- & + H^+ \end{array} \qquad (4)$$

The hypobromite anion is carried into the organic phase, where oxidation takes place:



(5)

The Bu_4NBr so formed is transferred back to the aqueous phase so that the cycle may be repeated.

Clearly the rapid hydrolysis of electrogenerated Br_2 is necessary, and this is achieved by maintaining the pH greater than 8.5; the aqueous phase is made about 0.5 M in sodium bicarbonate and the cathodic reaction increases the pH naturally to about 10.5. The necessary conditions are good mixing, the production of a stable emulsion, a high enough interphase transport rate and a high enough temperature for the chemical reaction to keep pace with the electrochemical generation of HOBr. A high steady-state concentration of HOBr in the aqueous phase is undesirable since it leads unproductively to the formation of bromate, either chemically or electrochemically:

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$$2HOBr + OBr^- \rightarrow O_3Br^- + 2H^+ + 2Br^- \quad (6)$$

$$6OBr^- + 3H_2O \rightleftharpoons 2O_3Br^- + 4Br^- + 6H^+ + \tfrac{3}{2}O_2 + 6e. \quad (7)$$

The bromate tends to precipitate out as orange crystals of tetrabutylammonium bromate, so a visual check is easy.

3. Experimental

The stirred-tank reactor consisted of a water-jacketed glass beaker with 100 cm^2 discs of nickel (cathode) and platinum (anode) gauze spaced about 1.0 cm apart near the bottom. A stirrer on the axis produced fairly intense mixing. The bipolar pump cell [8, 9] had platinised titanium anodes and graphite (Morganite EY 110) cathodes, spaced about 0.8 mm apart: since this cell pumps itself, it was connected to a reservoir, heat exchanger, gas disengager and flowmeter to make a recycle loop without the need for an additional pump. The flow rate was 1.7 dm^3 min^{-1} and there were 50 cm^2 of either polarity of electrode.

Suitable chemical conditions were established in a number of screening experiments [10] using the stirred tank; the best combination was 350 cm^3 of aqueous solution made 1 M in NaBr and 0.5 M in $NaHCO_3$, 65 cm^3 of the organic phase containing 0.1 mol of the alcohol in amyl acetate with 2 wt% of Bu_4NHSO_4, 45° C and pH approximately 11. A similar mixture was used for the pump cell [10] but the volumes were 285 cm^3 of the aqueous phase and 50 cm^3 of the organic phase. The concentration of alcohol was varied from 1.95 mol dm^{-3} to 5.85 mol dm^{-3}.

Analyses were performed on a Perkin Elmer F17 GC using 2 m long columns containing 4% XE-60 on Chromosorb W; the temperature was programmed from 120° C to 160° C at 10° C min^{-1}.

4. Results

In the case of the stirred tank the graph of conversion against charge passed was almost linear up to conversions in excess of 90% (Fig. 1) suggesting that the conditions specified above were fulfilled, even though the current efficiency was only about 54%. The same was not true of the pump cell. Fig. 2 shows that although the concentration/charge history was almost independent of the voltage applied (across two gaps in series), and hence the current density, the performance fell off with increasing conversion. Increasing the concentration of alcohol in the organic phase up to 3.9 mol dm^{-1} increased the rate of conversion (Fig. 3) and gave an almost linear charge/conversion plot up to about 20% conversion of the alcohol; however, even higher concentrations showed worse performances. The specificity performance of the system is thus strongly a function of the stirring conditions. The overall performance for a variety of conditions is shown as a carpet plot in Fig. 4.

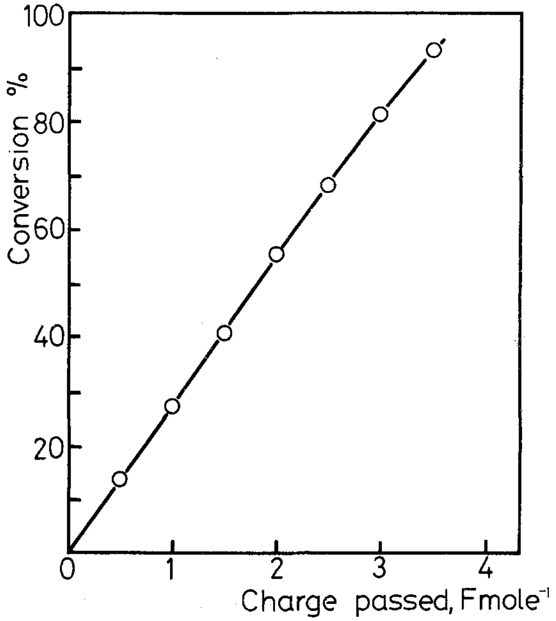

Fig. 1. Conversion versus charge for stirred-tank reactor. 8 V, 350 cm^3 of 1 M NaBr/0.5 M $NaHCO_3$, 0.1 mol of benzyl alcohol to 65 cm^3 with amyl acetate, 2 wt% Bu_4NHSO_4, 45° C, pH 11.

5. Discussion

The stirred tank approximates to an ideal batch reactor with dropwise addition of reagent. Provided a turbine stirrer was used to prevent strong axial flow through the net electrodes, which favoured the electrochemical oxidation of hypobromite to bromate and other parasitic reactions, the stirring could be considered to be perfect and the steady-state concentration of hypobromite in the aqueous phase uniform and low. The concentration of the OBr^- in the organic phase was within a factor of 0.7 mmol dm^{-3} and the ratio of quaternary salt to

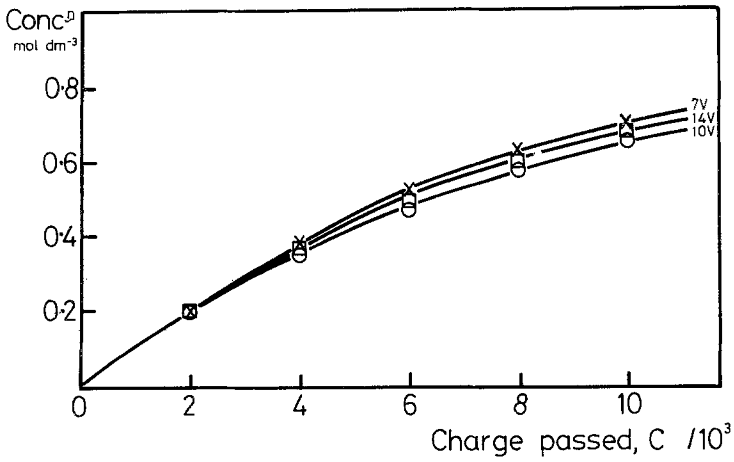

Fig. 2. Concentration of benzaldehyde versus charge for pump cell. 210 cm^3 of aqueous phase, 50 cm^3 organic phase containing 0.1 mol benzyl alcohol.

OBr$^-$ about 400 : 1, while the ratio of alcohol to OBr$^-$ was about 1900 : 1 at the beginning of the experiment; even at 90% conversion of the alcohol there was still a large excess of alcohol, making Reaction 5 pseudo-first-order, and a large excess of Bu$_4$N$^+$ to support the phase transfer. This explains why Pletcher and Tomov's results [7] were independent of the concentration of Bu$_4$N$^+$ added. (Benzyl alcohol has a finite solubility in water, leading to reaction in the aqueous phase [6], although at a reduced rate and at a lower current efficiency than found here [9].)

The situation in the stirred tank can be contrasted sharply with that in the pump cell, which produces microemulsions with a very high interfacial area. It has been shown that the fluid in a pump cell is highly mixed by the tangential shear [11], but that it proceeds radially outwards as a dispersive plug flow [12]. The small interelectrode volume of the cell (which is one of its features) means that the local concentration of hypobromite in the aqueous phase is high, while the high interfacial area ensures that the concentration in the organic phase is also high, provided there is enough Bu$_4$N$^+$ to support the phase transfer. At an applied voltage of 10 V the ratio of Bu$_4$N$^+$ to OBr$^-$ was about 50 : 1 in the cell and the ratio of alcohol to OBr$^-$ was therefore about 225 : 1 in each droplet at the beginning of the experiment. Note that the departure from linearity (Fig. 1) for the stirred tank begins at about 90% conversion, or an alcohol/OBr$^-$ ratio of about 190 : 1. On increasing the concentration of alcohol in the organic phase to 3.9 mol dm^{-3}, the alcohol/OBr$^-$ ratio was raised to 450 : 1 and the performance considerably improved. To a first approxi-

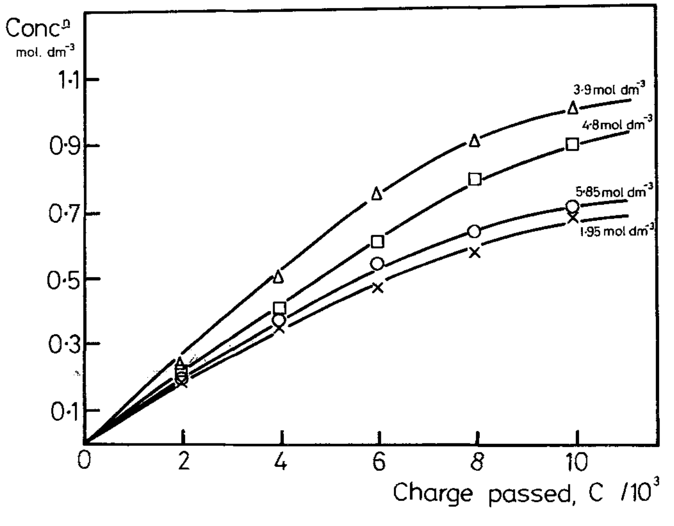

Fig. 3. Effect of concentration of benzyl alcohol on concentration/charge history.

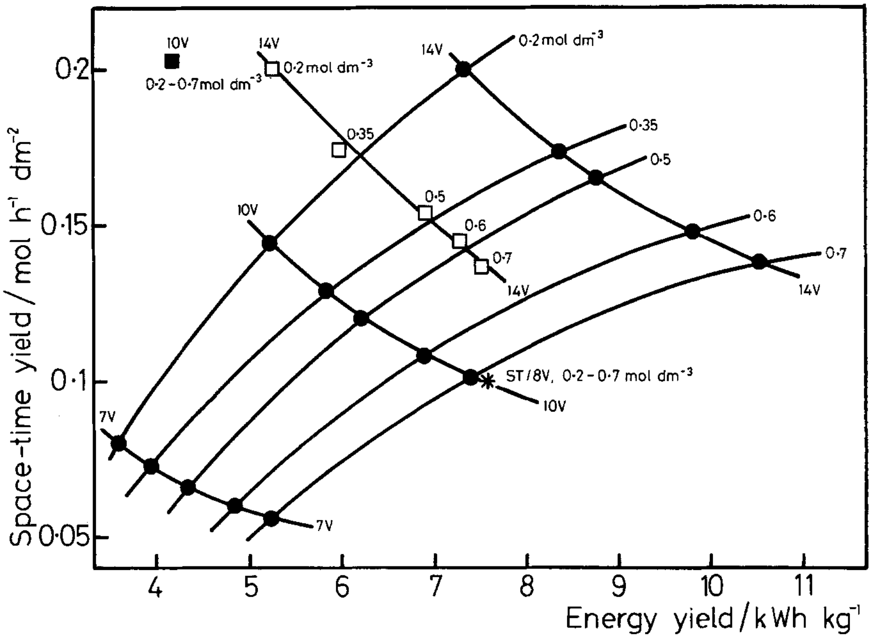

Fig. 4. Carpet plot of space–time yield versus energy yield. ● pump cell, 1.95 mol dm^{-3} of benzyl alcohol in organic phase, □ pump cell, 3.9 mol dm^{-3} of benzyl alcohol in organic phase, * stirred tank, 1.33 mol dm^{-3} benzyl alcohol in organic phase (0.1 mol in 0.075 dm^3).

mation therefore, the concentrations of reactants are 'frozen' at the values they have within the volume of the pump cell and change in the reservoir only by reaction. By contrast, the stirred tank produces a relatively coarse emulsion; and it is well known that segregation is unimportant for a macrofluid in a batch reaction [13]. At present it is not clear why further improvement is not seen above 3.9 mol dm^{-3} in the pump cell, unless the solubility of the ion pair is reduced by the increasing mole fraction of alcohol.

In Fig. 4 the operating locus for the stirred tank is reduced to a single point, indicating that the generation of hypobromite, its phase transfer and its reaction in the organic phase are in balance, so that space–time yield and power consumption are independent of the conversion of benzyl alcohol across wide limits. In contrast, the pump cell shows variations of the figures of merit under most conditions. However, at 10 V applied (across two gaps) and with 3.9 mol dm^{-3} of benzyl alcohol in the organic phase, another stationary point was obtained, showing that generation, mixing, transport and reaction were again in balance; no doubt other such points exist under different conditions at higher current densities. This is important since the space–time yields of emulsion reactions are low; the processes are therefore relatively uneconomic although attractive from other points of view. Clearly such systems are worthy of further study in cells with inherently better space–time yields than stirred-tank reactors.

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