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Electrochemical conversion of 2,3-butanediol to 2-butanone in undivided flow cells: a paired synthesis

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A procedure has been developed for converting 2,3-butanediol in *ca.* 10% aqueous solution to 2-butanone by passing it through a porous anode at which it is selectively oxidized to acetoin by electrogenerated NaBrO and then pumping to a porous cathode at which it is reduced to 2-butanone. The not fully optimized yields and current efficiencies are 75% and 60%, respectively. The procedure employs: Pb/Hg or Zn/Hg cathodes, graphite anodes, pH *ca.* 7, ambient temperature, current density of 2 mA cm^{-2}, five minute residence time outside the cell, packed bed electrodes, and parallel electrolyte and current flow.

1. Introduction

As part of a broad programme pursued here and elsewhere whose main thrust is to explore the possibilities of converting electrochemically biomass-derived materials to (a) fuels or fuel components and/or (b) commercial organic chemicals, we have used 2,3-butanediol (*1*) as a feedstock. Our results on reduction of derivatives of this 1,2-diol to 2-butene (Category a) are reported elsewhere [1]; this paper concerns the conversion of the diol to 2-butanone (*3*) (Category b). This objective has been achieved in a paired synthesis using undivided flow cells. Without full optimization yields of 75% and current efficiencies of 60% have been obtained.

$$\underset{1}{\mathrm{CH_3CH(OH)CH(OH)CH_3}} \xrightarrow[\text{Indirect}]{\text{Anodic}} \underset{2}{\mathrm{CH_3COCH(OH)CH_3}} \xrightarrow[\text{Direct}]{\text{Cathodic}} \underset{3}{\mathrm{CH_3COCH_2CH_3}} \qquad (1)$$

Background material on paired synthesis, including definition and incentives for further research, has been discussed [2–4]. Work in this area is expanding [5]. The abundant technical problems that must be solved in order to design a successful paired synthesis in *divided* cells are multiplied when operation in *undivided* cells is desired. Unfortunately at the present state-of-the-art, each new candidate synthesis must be analysed individually in order to particularize the problems and to formulate initial means for solving them. Both the problems and the putative solutions are, as usual, subject to re-definition as the experimental work progresses. When a sufficient variety of successful projects of this nature has been disclosed it may then be possible to establish some general guidelines.

A rational approach to the designs of systems suitable for the conversion of *1* to *2* required that we take cognisance of the following facts:

1. Starting with *1*, one of the OH groups must be reductively replaced by H and the second oxidized to carbonyl. Since electrochemical methodology requires *two* redox reactions, the overall results must preferably be superior to those obtained by the single-step acid-catalysed pinacol rearrangement of *1*. This possibility was briefly examined. Heating *1* with the strong acid cation resin (Dowex 50W-X-8) yielded 2-methyl-1-propanal and its acetal with *1* (2-isopropyl-4,5-dimethyl dioxalane) as major products and a minor component of *2*. After our work was completed much better results were reported by Emerson *et al.* [6].

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2. Un-derivatized simple alcohols with free –C–OH groups are not cathodically reduced to –CH while alcohols containing an adjacent electron-withdrawing group, especially carbonyl (cf. *2*) are so reduced [7].

3. Indirect oxidation preferably *via* hypohalite made *in situ* [8] or supplied from an external source [9, 10] is superior to direct oxidation of *sec*-alcohols to ketones. This type of indirect oxidation applied to *1* however engenders certain problems:

(a) *1* may be overoxidized

$$1 \xrightarrow{xO^-} 2 \xrightarrow{xO^-} \underset{4}{CH_3COCOCH_3}$$

so that in an undivided cell reduction of *4* to *2* or *1* could be an energy-wasting process.

(b) Compounds *2*, *3*, and *4* have acetyl groups and can, therefore, at appropriate values of $pH > 7$, undergo the Haloform Reaction [11]. The latter would, amusingly, achieve a very useful purpose in converting the very water-soluble *1* to two sparingly soluble products, oxalic acid (or calcium salt) and chloroform but it is a 16-electron process!

(c) The anodically generated 'mediator' XO^- can either by disproportionation or by further anodic oxidation be converted to XO_3^- which is *not* an oxidant for *1* and which consumes $6e^-$ at the cathode in order to become recyclable (as X^-).

(d) Perhalates, particularly IO_4^-, oxidatively cleave 1,2(≡ 2, 3)-glycols at the C–C bond to two molecules of carbonyl compound [12].

Conventional H-cells were used in preliminary experiments designed to determine whether the crucial reactions required for a successful paired synthesis could indeed be achieved i.e. efficient controlled oxidation of *1* to *2* and efficient reduction of *2* to *3*. The results obtained were then used as a guide in designing and operating the continuous flow cells.

2. Experimental details

2.1. *Materials*

Electrolyte solutions were made with doubly-distilled water. The 2,3-butanediol (Aldrich) was a mixture of 77% meso- and 23% DL-isomers. The acetoin (*2*) (85% aqueous solution) and 2-butanone (both Mallinckrodt), and 2,3-butanedione and sodium bromide (both Baker) were used as received.

2.2. *Electrodes*

1.6 mm thick lead sheets (Mallinckrodt) and zinc shot (Baker) were used as cathode materials, and graphite (ARCO Graphite) was used as anode. Metal electrodes were polished with fine Emery paper and washed with acetone to remove dirt and grease. To amalgamate the metal electrodes the method of Creighton [13] was adopted: after the electrodes were washed with dilute nitric acid and rinsed thoroughly with distilled water, they were immersed in aqueous mercurous nitrate solution to deposit mercury on the surface. They were then washed with distilled water and wiped with soft paper. Metallic mercury was finally put on the electrode and any excess was wiped off. The electrode potentials are referred to the SCE.

2.3. *Analyses*

The qualitative analysis of the electrolysed solution was carried out by gas chromatography (Varian Model 1200) using a flame ionization detector. A Carbowax 20M column (2 m long) was used; the single injection volume was 3×10^{-6} dm^{-3}. The operating conditions were: N_2 flow-rate 20 $cm^3 min^{-1}$; injection temperature, 423 K; detector, 473 K; column temperature programming, 330–443 K at 3 min after the injection.

2.4. *Cells*

2.4.1. Divided cells. A conventional H-cell with medium porosity sintered glass membrane was used both for voltammetry and small-scale preparative electrolyses. Each chamber had *ca.* 60 cm^3 capacity.

2.4.2. Undivided flow cells. The two types of cell (A and B) that were used are shown schematically in Figs. 1 and 2.

Cell A was made of four polyethylene blocks machined to have a cylindrical bore (2.5 cm diameter). The dimensions of the cell were $7.6 \times 7.6 \times 10$ cm^3. The electrical connections were a lead rod and a platinum wire for the cathode and anode, respectively; a Luggin capillary, made of a fine

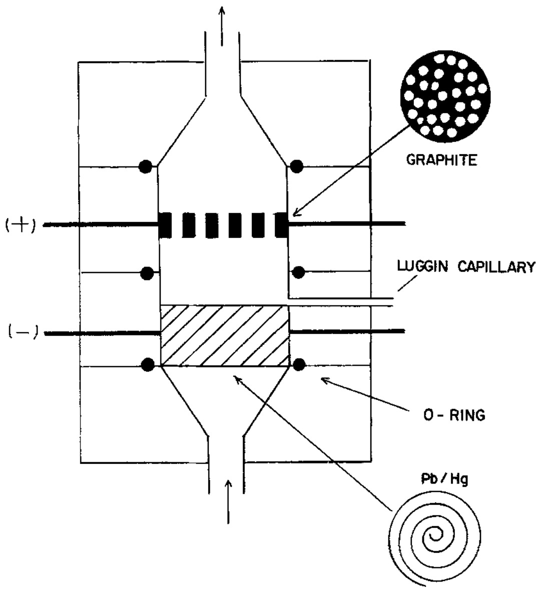

Fig. 1. A schematic diagram of the undivided flow cell A.

vinyl tubing, was connected to the saturated calomel electrode. The cathode had a total surface area of 30 cm^2 and the graphite anode is shown as its actual size in Fig. 1.

Cell B was made of a glass tube (5 cm diameter and 10 cm long). Glass beads were placed below the cathode to ensure a uniform current distribution through the packed-bed electrodes. Glass beads were also placed above the anode to decrease the total void space in the cell. Perforated vinyl discs were inserted between the electrodes and glass beads, and a ring-shaped Teflon spacer (1 cm thick) was placed between the anode and cathode. Electrical contacts were made from the top and bottom of the cell (Fig. 2). In both cells current flow was parallel to the electrolyte flow.

2.5. *Auxiliary equipment*

Electrode voltages were controlled, when desired, by a Magna Corp. Model Anotrol 4200 M potentiostat. The constant d.c. current power supply was a Harrison 6201B. An electrometer (Keithley Model 602) and a coulometer (Electrosynthesis Co. Model 64) were used to measure electrode potentials and the quantity of charge passed, respectively. A schematic arrangement of the equipment for experiments in continuous flow cells is shown in Fig. 3.

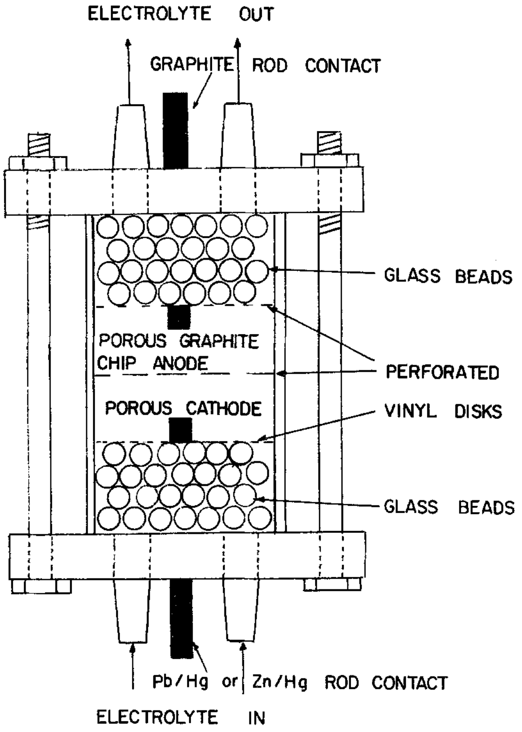

Fig. 2. A schematic diagram of the packed bed flow cell B.

2.6. *Procedures*

2.6.1. In H-cells. These cells were used in order to

(a) obtain *I–E* relationships for the direct and indirect oxidation of *1* and its oxidation products *2* and *4* and the reduction of *1*, *2* and *4* and

(b) determine (separately) the distribution of products obtained on a macro-scale in the oxidation and reduction of the solution constituents to be expected in a continuous paired synthesis.

In all cases aqueous solutions containing *ca.* 10% of *1* were used*.

2.6.2. In continuous flow cells. Fig. 3 shows the reaction loop of the flow-cell electrolyser. The solution was introduced at the bottom of the cell and flowed upwards, and the H_2 gas generated inside the cell was removed in the reservoir before the solution was passed into the glass-coil reactor (0.4 cm diameter and 10 m long). The tube reactor was immersed in the water bath for temperature control. The reservoir was a 50 cm^3 three-necked

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* Obtained in *ca.* 10% concentration in aqueous media by appropriate fermentation of xylose.

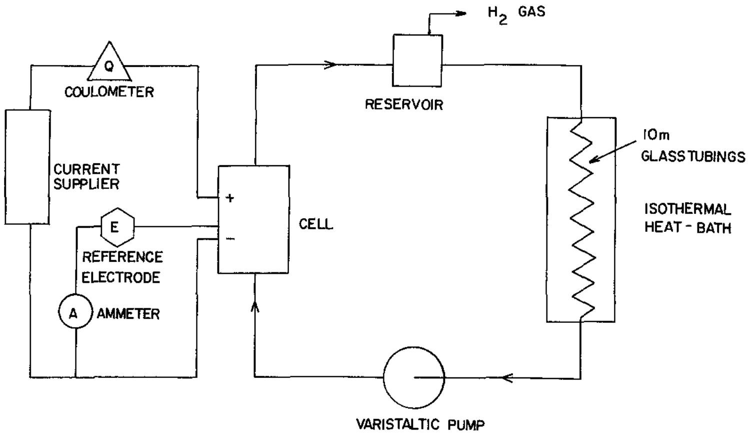

Fig. 3. Schematic for operation in continuous flow cells.

flask. A Liebig water condenser was placed on it to minimize the evaporation of 2-butanone. A varistaltic pump (Manostat model 1073) was used and during electrolysis flow rate was about 20 cm^3 min^{-1}. Tygon tubes were used for connections between the elements of the reaction loop.

First, electrolyses were carried out mainly in cell A, for the operation was relatively simple and less reaction was required than in cell B. After some of the conditions appropriate for the paired reaction were determined using cell A, electrolyses were then carried out in cell B. The experimental variables studied here include pH, temperature and residence time; these are particularly important in determining the efficiency of the oxidation. The reduction part of the paired reaction, on the other hand, is more dependent on pH, current density or electrode potential and supporting electrolytes. The effects of these variables are, as will be discussed later, closely related to one another, and so they should be optimized to yield the best results in the paired reaction.

3. Results and discussion

3.1. *Experiments in H-cells*

The *I–E curves* obtained for the direct oxidation of *1* and its derived oxidation products are shown in Fig. 4. Although *1* may clearly be oxidized before oxygen evolution occurs, a direct oxidation of *1* in a paired continuous system is not feasible because *2* is even more easily oxidized. Therefore oxidation of *1* by mediators was examined. Hypervalent metal ions and hypohalites were candidate mediators; the former were eliminated from trials because they are effective only in acidic media and therefore would lead to excessive H$_2$ production in an undivided cell.

Fig. 5 shows *I–E* curves of the three halide ions (Cl^-, Br^- and I^-) at pH values of 5 and 12. As can be noted here, the Cl^-/Cl_2 redox system may not

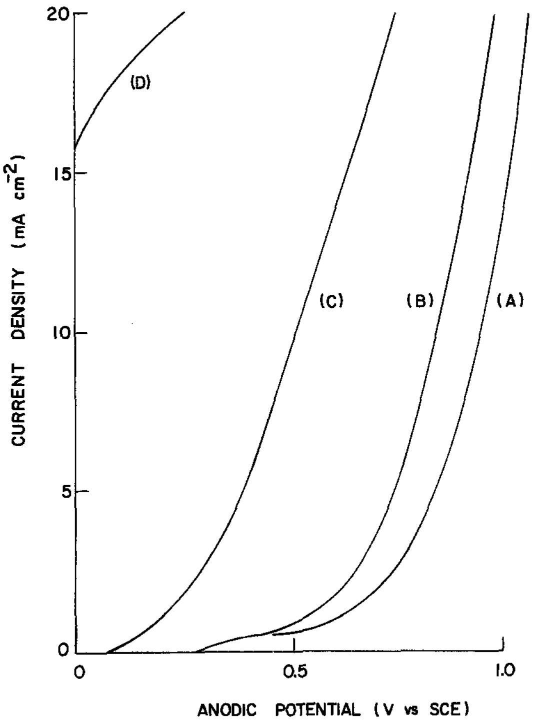

Fig. 4. *I–E* curves of 2,3-butanediol and its oxidation products at a graphite anode in pH 14 solution: (a) Background; (B) 0.2 mol dm^{-3} 2,3-butanediol; (C) 0.2 mol dm^{-3} acetoin; (D) 0.2 mol dm^{-3} 2,3-butanedione.

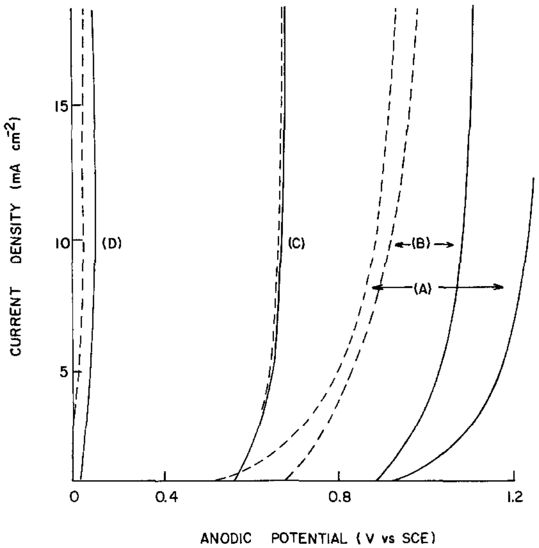

Fig. 5. *I–E* curves of halide ions at a graphite anode at pH 5 (——) and pH 12 (– – –): (A) background; (B) 0.5 mol dm^{-3} NaCl; (C) 0.5 mol dm^{-3} NaBr; (D) 0.5 mol dm^{-3} NaI.

be suitable for the oxidation, because the oxidation potential of the Cl$^-$ ion is too close to that of oxygen evolution (background). In alkaline solution (pH 14), I$^-$/I$_2$ would seem to be the only choice as oxidation mediator, for acetoin can be preferentially oxidized over Br$^-$ ions (Fig. 4c.) As will be shown later, however, the paired reaction should not be run at such a high pH, because the high pH can increase the formation of easily-reducible 2,3-butanedione.

Both I$^-$/I$_2$ and Br$^-$/Br$_2$ seem to be good redox systems in near neutral solutions (pH 4 and 5) as iodide and bromide ions are much more easily oxidized than are 2,3-butanediol and its oxidation products (data not shown). However, the oxidizing power of electrogenerated iodine (I$_2$ or HIO$^-$ ion) may be so weak that unreacted iodine can be circulated and reduced at the cathode in a flow-cell electrolysis.

It must be concluded that the Br$^-$/Br$_2$ redox system in neutral media is the best among various combinations of halide ions and pH values. Fig. 6 shows *I–E* curves for Br$^-$, 2,3-butanediol, acetoin and 2,3–butanedione at a graphite anode in neutral solutions. It is clear that Br$^-$ ion can be oxidized to an active bromine species at much lower anodic potentials (about 500 mV) than 2,3-butanediol and its oxidation products.

I–E curves for the *reduction* of *1*, *2* and *4* are displayed in Fig. 7. They show that *2* can be easily reduced and that the reduction product *3* is stable under these conditions. This was one of the *sine qua non* requirements for the planned paired synthesis.

The high reactivity of 2,3-butanedione toward reduction (Fig. 7c) as well as oxidation (Fig. 6d) is a clear indication that its presence may substantially decrease the total current efficiency of the paired reaction. Hence, the electrolyte conditions should be chosen so that further oxidation of acetoin to 2,3-butanedione is prevented.

Preparative electrolytes were carried out separately in the anodic or cathodic chamber of the cells using appropriate substrates in order to confirm the identity of the products. Typical results of an oxidation are shown in Table 1. Although the current efficiency was fairly high, the selectivity for acetoin had to be improved to eliminate the

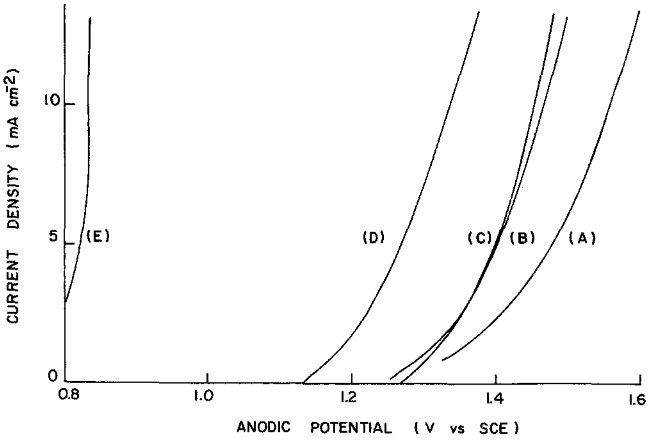

Fig. 6. *I–E* curves of 2,3-butanediol, its oxidation products, and bromide ion at a graphite anode in neutral solution: (A) background (phosphate buffer solution); (B) 0.2 mol dm^{-3} 2,3-butanediol; (C) 0.2 mol dm^{-3} acetoin; (D) 0.2 mol dm^{-3} 2,3-butanedione; (E) 0.5 mol dm^{-3} NaBr.

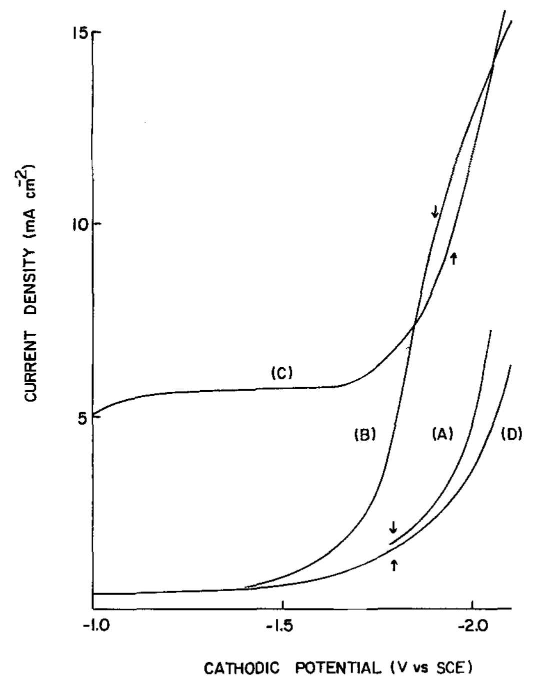

Fig. 7. Cathodic polarization of (A) 2,3-butanediol (1 mol dm^{-3}); (B) acetoin (20 mmol dm^{-3}); (C) 2,3-butanedione (20 mmol dm^{-3}) at Pb/Hg cathode in neutral solution containing (D) sodium bromide (1 mol dm^{-3}). The arrows indicate the onset of the hydrogen evolution reaction.

formation of 2,3-butanedione. The drastic decrease in the total current efficiency during the electrolysis was clear evidence that 2,3-butanedione is oxidized more readily than 2,3-butanediol.

The *reduction* of acetoin was carried out at a Pb/Hg cathode in Na_2HPO_4/H_3PO_4 buffer solution (pH 3). The current efficiency was only 20% due to vigorous H_2 evolution, while the selectivity was so high that 2-butanone was the sole product.

The results of preliminary preparative electrolyses confirmed that *1* could be selectively oxidized to *2* and *2* could be reduced to *3* thus encouraging the hypothesis that a paired reaction scheme could be designed. It was assumed that with proper pH control, more easily achieved in undivided than in divided cells, the current efficiency could be improved.

*Table 1. Oxidation of 2,3-butanediol**

Electricity passed (F mole^{-1})	*Current efficiency (%)*	
	Acetoin	*2,3-Butanedione*
0.21	48	–
0.38	35	3
0.78	12	6

* Anode solution: 30 cm^3 of Na_2HPO_4–H_3PO_4 buffer solution (pH 3) including 30 mmole of 2,3-butanediol and 1.5 mmole of KBr.
Anode: graphite (surface area 3.5 cm^2 × 2).
Anodic current: 80 mA (constant).

3.2. *Experiments in flow cell A*

3.2.1. Effect of pH and residence time. The pH of the electrolyte solution is one of the crucial factors than can influence the overall current efficiency. High pH, as mentioned before, can greatly increase the formation of 2,3-butanedione resulting from further oxidation of acetoin, which decreases the current efficiency due to the parasitic reduction of 2,3-butanedione. Hence, it was first required to determine the highest pH at which the formation of 2,3-butanedione did not occur.

Table 2 shows the results of electrolysis using flow cell A. One important conclusion can be drawn from the results: when the pH of the electrolyte is higher than 7, considerable amounts of 2,3-butanedione are formed, which leads to lower current efficiency and selectivity for 2-butanone. On the other hand, no 2,3-butanedione was formed at pH 7 and the conversion of 2,3-butanediol was very close to the theoretical.

Electrolyses, shown in Table 2, were run at 333 K; the glass tubing outside the cell was immersed in the heating bath at 333 K. At this temperature the yellow colour of molecular bromine seemed to disappear when the electrolyte solution entered the inlet of the cell. At room temperature, however, there still remained unreacted bromine in the solution at the cell inlet. As the rate of the oxidation can also be increased at a longer reaction time (longer residence time outside the cell), one electrolysis was carried out using a longer glass coil, and the residence time increased to 2 min from the previous 1 min.

As can be seen in Table 2, the current efficiency increased to 52% from 42% with longer residence time without any decrease in the initial acetoin concentration and without the formation of 2,3-butanedione.

3.2.2. Effects of temperature and current density. These were studied under appropriate electrolyte conditions. As shown in Table 3, it is apparent

*Table 2. Effect of pH and residence time on the current efficiency of the paired reaction**

Electrolyte	*Current density ($mA\ cm^{-2}$)*	*Current passed ($F\ mole^{-1}$)*	*Conversion of 2,3-butanediol (%)*	*Concentration of products ($mmol\ dm^{-3}$)*			*Current efficiency (%)*	*Residence time (min)*
				Acetoin	*2,3-Butanedione*	*2-Butanone*		
0.5 mol dm^{-3} Na_2HPO_4/ NaH_2PO_4 (pH 8) 1 mol dm^{-3} NaBr 1 mol dm^{-3} 2,3-butanediol 20 mmol dm^{-3} acetoin (pH 7)	12	0.5	14 (25)†	30	15	37	15	~ 1
1 mol dm^{-3} NaBr 1 mol dm^{-3} 2,3-butanediol 20 mmol dm^{-3} acetoin (pH 7)	3	0.18	9 (9)†	35	0	38	42	~ 1
1 mol dm^{-3} NaBr 1 mol dm^{-3} 2,3-butanediol 20 mmol dm^{-3} acetoin (pH 7)	3	0.5	25 (25)†	32	0	130	52	2

* Anode, graphite; cathode, Pb/Hg; $T = 333$ K.

† Indicates theoretical conversion.

*Table 3. Effects of temperature and current density on current efficiency for the paired reaction with 2,3-butanediol**

Temperature (° C)	*Current density ($mA\ cm^{-2}$)*	*Cathodic potential*† *(V vs SCE)*	*Current efficiency (%)*
65	2	− 1.85	52
65	1	− 1.70	51
21	2	− 2.07	58
22	1	− 1.80	60

* Cathode, Pb/Hg; Anode, graphite; pH 7.0–7.5; flow rate, 20 cm^3 min^{-1}; initial concentration of *1*, 1 mol dm^{-3}; initial concentration of *2*, 20 mmol dm^{-3}; final concentration, 25–38 mmol dm^{-3}; charge passed, 0.2 F mole^{-1}; supporting electrolyte, 1 mol dm^{-3} NaBr.

† Changed 0.05–0.06 V during electrolysis.

that the current efficiency was unaffected by the change in the current density at a given temperature. Further increase in the current density (above 2 mA cm^{-2}) caused more H_2 evolution and resulted in poor current efficiency as well as high cell voltage due to the gas trapped inside the cell. Therefore, it seemed that the paired reaction should be run at a low current density (1 or 2 mA cm^{-2}) to obtain relatively high current efficiencies.

The effect of temperature seemed peculiar in that higher current efficiencies were obtained at lower temperature. It was first suspected that the volatile 2-butanone might have escaped at higher temperature. However, 2-butanone was not found in a cold-trap (dry ice and acetone), and our cooling system seemed effective in preventing the 2-butanone evaporation. Another hypothesis was then put forth to explain these experimental results: since high temperature enhances the rate of bromate formation, current could be wasted in reducing the bromate ions, with overall lower current efficiencies. To check this possibility, experiments were carried out to determine the presence and concentration of bromate ions.

3.2.2.1. Determination of bromine species present. An iodometric titration method [14] was used to determine the concentration of both Br_2 and BrO_3^-. Titre solutions were obtained from the flow-cell electrolyses without recirculation of electrolytes (single path). Normally 500 cm^3 of electrolyte solution was passed through the cell and a single titre volume was about 100 cm^3.

Bromate concentrations in the electrolysed solution varied significantly so that no quantitative conclusion could be drawn from data regarding the percentage of total charge used for bromate formation. It was, however, always less than 10%. One of such experimental results is shown in Table 4.

As can be seen in Table 4, the bromate concentration became very small in the presence of 2,3-butanediol indicating that the formation of bromine and bromate are competitive. It should be also noted in Table 4 that part of the active bromine species remained unreacted toward 2,3-butanediol suggesting that the oxidation of 2,3-butanediol with bromine is a slow reaction. In an effort to estimate the necessary residence time for

*Table 4. Determination of Br_2 (or BrO^-) and BrO_3^- formed in anodic oxidation of Br^- (1 mol dm^{-3} NaBr) at pH 7**

	Br_2 (or BrO^-) (mmol dm^{-3})	*BrO_3^- (mmol dm^{-3})*
In the absence of 2,3-butanediol†	0.577	0.153
In the presence of 2,3-butanediol	0.032	0.006

* Anode, graphite; anodic potential, 1.1–1.2 V vs SCE; current density, 4.0 mA cm^{-2}; current, 70 mA; flow rate, 18 cm^3 min^{-1} (single pass).

† Overall current efficiency for oxidation of Br^- *ca.* 81%.

*Table 5. Electrolytic results in solutions of ammonium bromides**

Supporting electrolyte	*Cathodic potential (V vs SCE)*	*Charge passed ($F\,mole^{-1}$)*	*pH*	*Final concentration of acetoin ($mmol\,dm^{-3}$)*	*Current efficiency for 2-butanone (%)*
1 mol dm^{-3} Et_4NBr	– 2.35	0.20	9–10	9	27
1 mol dm^3 NH_4Br	– 1.72	0.19	7	0	17

* Experimental conditions are same as in Table 3 unless stated otherwise.

the oxidation, a kinetic measurement of the oxidation of 2,3-butanediol with bromine was attempted.

3.2.2.2. Kinetics of the oxidation with bromine species. According to the kinetic parameters obtained, 5 min was required for 70% conversion, whereas about 50 min was required for 99% conversion. Although these results may not be precise quantitatively, they are a clear indication that a substantial increase in the residence time is required for more complete oxidation in order to yield higher current efficiencies in the paired reaction.

Residence time can be increased by lowering the flow rate. At a very low flow rate, however, significant back-mixing can occur inside the cell that results in low current efficiencies. Residence time can also be increased either by using a longer glass coil or by using a larger reservoir. This aspect will be one of the subjects for further study.

3.2.3. Effect of supporting electrolytes. H_2 evolution was always observed during electrolyses. In order to decrease this reaction at the cathode, Et_4NBr and NH_4Br were used as supporting electrolytes instead of NaBr. As is shown in Table 5, a much higher rate of hydrogen evolution was observed, and the concentration of acetoin became negligible at the end of the electrolyses. These facts may suggest that the use of ammonium bromides is less advantageous for both cathodic and anodic reactions.

3.2.4. Mass and charge balances. In order to determine the mass and charge balances between the initial and final states of the electrolyses, the electrolysis was continued to such an extent that a substantial decrease in the concentration of 2,3-butanediol could be detected by gas chromatography (GC); the hydrogen gas generated during the electrolysis was also collected in a gas-burette. Table 6 shows the results of the electrolysis that was carried out under the best conditions.

As shown in Table 6, the mass balances were approximately 90%. This fact combined with 60–85% of selectivity for 2-butanone, suggests the formation of unknown products. Although the identification of possible by-products has not been complete, preliminary work indicated that the by-products may include hydrodimers of acetoin and 2-butanone.

On the other hand, the charge balance was 74%. The remaining charge has probably been used to reduce the unreacted bromine and/or bromate ions at the cathode.

As can be noted in Table 6, the current efficiencies for 2-butanone decreased in the course of the electrolysis. This tendency is, however, not a general one. In fact, most electrolyses resulted in rather consistent current efficiencies throughout. One example of such a case is shown in Fig. 8.

The current efficiencies of the electrolytes varied slightly between electrolyses, but they were always between 50 and 60%. The slight variation might be due to the error involved in the GC analysis. Although the amalgamated cathodes becomes dull losing their original shiny surface after electrolyses, the cathode did not seem to deteriorate since the current efficiencies were fairly constant.

3.3. *Results in packed bed flow cells B*

The paired reaction with 2,3-butanediol was carried out in the packed bed flow cell. Pb/Hg and Zn/Hg chips were used as cathodes and cylindrical graphite chips were used as anodes. In the electrolyses the current was increased until the total cell voltage reached 3 V, which is the same as that

*Table 6. Mass and charge balances in 2,3-butanediol paired reaction**

Charge passed ($F\,mole^{-1}$)	Concentration ($mol\,dm^{-3}$)			Conversion of 2,3-butanediol (%)	Selectivity for 2-butanone (%)	Current efficiency (%)		Balance (%)	
	2,3-butanediol	Acetoin	2-butanone			2-butanone	Hydrogen	Mass	Charge
0	1.00	0.020	0	0	0	0	0	–	–
0.22	0.91 ± 0.08	0.030	0.07	9	77	64	10	99	74
1.10	0.60 ± 0.05	0.027	0.27	40	61–77	50	–	88	–
1.32	0.59 ± 0.04	0.023	0.32	41	70–85	48	–	91	–

* Experimental conditions are same as in Table 3 unless stated otherwise.

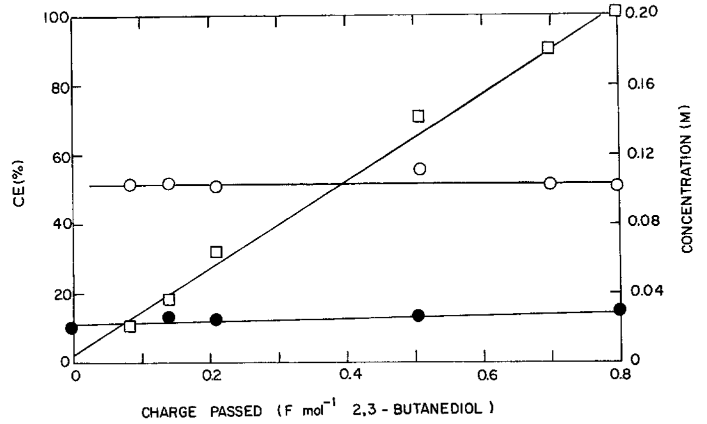

Fig. 8. Performance of the paired reaction of 2,3-butanediol in a flow cell A. Pb/Hg cathode, perforated graphite anode, pH 7, temperature = 337 K, residence time in heat-bath = 2 min. 1 mol dm^{-3} NaBr supporting electrolyte, and 1 mol dm^{-3} (9 wt %) initial 2,3-butanediol concentration. ○ CE, ● acetoin, □ 2-butanone.

observed using the cell A. Experimental results are shown in Table 7. Results using the Cell A (Experiment 1) are also shown for comparison.

In Experiment 2 the cell voltage steadily increased from 3 to 8 V due to the build up of H_2 gas. In contrast, H_2 gas evolution was almost negligible with Zn/Hg shot in Experiment 3, and the cell voltage remained constant at 3 V. Slightly lower current efficiencies resulted with Pb/Hg cathode due to the higher rate of H_2 gas evolution. It may seem surprising that Experiment 3 did not result in a significant increase in current efficiency. This may be explained by the fact that the current efficiency of oxidation was only 68%, due possibly to parasitic reduction of either unreacted bromine or bromate ions.

Electrolyses were then carried out at higher temperatures and longer residence times in order to increase the oxidation reaction and decrease the concentration of unreacted bromine. As Table 8 shows, neither experiment resulted in any significant increase in the overall current efficiency. It was disappointing not to see any improvement at a longer residence time. This again points out the very slow bromine oxidation of 2,3-butanediol. As high temperature should enhance the oxidation reaction to some degree, it is possible that increased bromate formation could have obscured such an effect. Other means for suppressing BrO_3^- formation are:

(a) The anodic potential should be as small as possible, since the formation potential of BrO_3^- is less positive than that of Br_2 from Br^- (1.1 V vs NHE [15])

(b) The reaction temperature should be low as possible to suppress the formation of BrO_3^- by chemical reaction

(c) The pH should be at 7, for some of chemical formation of BrO_3^- is favoured at higher pH's

(d) BrO_3^- itself has no oxidizing power, but it can be changed in acidic solution to Br_2 which is a strong oxidizing reagent

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

For this purpose, the combined use of cation and anion exchange-resins in the outside circuit of the flow cell system may be effective.

*Table 7. Performance of paired synthesis of 2-butanone in a packed bed flow cell (Cell B)**

Experiment	*Temperature (K)*	*Cell voltage (V)*	*Flow rate (cm³ min⁻¹)*	*Overall CE (%)*	*Oxidation CE (%)*	*Cathode material*
1†	293	3	20	60	70	planar Pb/Hg
2	293	3.8	45	57	64	Pb/Hg chip
3	293	3	45	64	69	Zn/Hg shot

* Anode, graphite; pH, 7.5; initial concentration of *1*, 1 mol dm^{-3}; initial concentration of *2*, 20 mmol dm^{-3}; charge passed, 0.2 F mole^{-1}; supporting electrolyte, NaBr.

† In cell A for comparison.

*Table 8. Performance of paired synthesis of 2-butanone in packed bed flow cell B. Increased temperature and residence time**

Experiment	*Temperature (K)*	*Flow rate* ($cm^3 min^{-1}$)	*Residence time (min)*	*Overall CE (%)*	*Oxidation CE (%)*
a	293	45	~ 4	64	69
b	333	45	~ 4	60	68
c	293	10	~ 16	64	68

* Anode, cylindrical graphite chips; cathode, Zn/Hg chips; pH, 7.5; initial concentrations, 1 mol dm^{-3} of *1* and 20 mmol dm^{-3} of *2*; supporting electrolyte, 1 mol dm^{-3} NaBr; charge passed, 0.2 F $mole^{-1}$.

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