

# Electrosyntheses from Aromatic Aldehydes in a Flow Cell. Part I. The Reduction of Benzaldehyde

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**Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday**

Guena, T. and Pletcher, D., 1998. Electrosyntheses from Aromatic Aldehydes in a Flow Cell. Part I. The Reduction of Benzaldehyde. – Acta Chem. Scand. 52: 23–31. © Acta Chemica Scandinavica 1998.

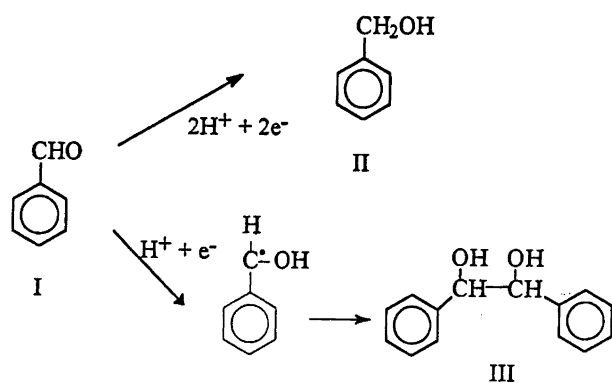
The reduction of benzaldehyde in acidic water–methanol mixtures has been re-investigated in a membrane flow cell with a lead cathode with the objective of defining conditions where  $1e^-$  reduction occurs and the  $C_6H_5CH^{\bullet}OH$  radical intermediate is formed in high selectivity. It is shown that it is the cathode potential which controls the ratio of  $1e^-/2e^-$  product (i.e. hydrobenzoin to benzyl alcohol) and a high rate generation of the radicals is also favoured by an efficient mass transport regime.

The cathodic reduction of aldehydes and ketones has been studied extensively, and it is generally agreed that products are usually a mixture of the alcohol and the pinacol.<sup>1–3</sup> At least under some conditions, these products are considered to arise by the routes shown in Scheme 1 (written for reduction of benzaldehyde). Thus, the pinacol results from the dimerisation of a radical intermediate formed by the addition of  $1H^+ + 1e^-$  to the carbonyl compound. The purpose of this programme is to demonstrate that such radicals derived from benzaldehyde, acetophenone and their derivatives may be used in the synthesis of larger, polyfunctional molecules. It was considered important to employ a medium where scale-up is possible, and this led to the selection of alcohol/water mixtures.

There is also a large body of literature which considers the influence of parameters such as solvent, pH, reactant concentration, electrode material and electrode potential

(or current density) on the mechanism, kinetics and products of the electrochemical reduction of aromatic aldehydes and ketones. While the conclusions of such studies using, for example, polarography or cyclic voltammetry,<sup>1,4–7</sup> provide helpful background information, the conditions are sufficiently removed from those in an electrosynthesis cell that it is often difficult to relate the data from the two types of study. Moreover, the results from different studies can appear contradictory. We have also noted that a Japanese group have also reported that the ratio of pinacol–alcohol from the reduction of acetophenone also depends very strongly on the mass transport regime (varied via rotation of the electrode, electrolyte flow rate or ultrasound) and temperature.<sup>8–12</sup> In these circumstances where the product selectivity clearly depends on many experimental parameters, it was considered essential to understand the selection of conditions in order to maximise the yield of the desired radical intermediates. Hence in this paper we describe a study of the reduction of benzaldehyde in acidic water–methanol using both preparative scale electrolyses and voltammetry in closely related conditions.

Many of these experiments were carried out in a FM01 laboratory electrolyzer. This is a plate and frame reactor supplied by ICI,<sup>13,14</sup> and it allows electrolysis in conditions of variable and controlled mass transport; in the experiments described here, it was used with flat plate electrodes, a polymer mesh turbulence promoter and a Nafion<sup>®</sup> membrane separator and is readily capable of the conversion of several grams of benzaldehyde per hour.



Scheme 1.

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## Experimental

**Chemicals.** Benzaldehyde (Aldrich, 99+%), benzyl alcohol, (±)-hydrobenzoin, (R,R)-(+)-hydrobenzoin,

(*S,S*)-(-)-hydrobenzoin and meso-hydrobenzoin (all Aldrich, 99%) were used as received although their purity was checked by HPLC or GC. Electrolyte solutions were prepared with deionised water and methanol (Fisons, Technical grade) as well as salts supplied by BDH or Aldrich. The catholytes were based on methanol–water and, depending on the pH required, were (i) LiCl (1 M), citric acid (0.2 M) with Li<sub>2</sub>CO<sub>3</sub> or NaOH added to give the required pH or (ii) Li<sub>2</sub>SO<sub>4</sub> (0.5 M) or LiCl (1 M) with added H<sub>2</sub>SO<sub>4</sub> or HCl to give the required pH. Freshly made solutions of organics were sonicated for at least 10 min to ensure that all the material was dissolved.

*Electrochemical cells.* Voltammograms at the rotating Pb disc electrode were recorded in a three-compartment, glass cell. The disc electrodes ( $d=0.32$  cm) were fabricated from lead rod (Goodfellow, purity 99.95%); a short length of rod was attached with silver loaded epoxy resin onto a threaded steel stud and then glued into a PTFE sleeve using epoxy resin. The counter electrode was a platinum gauze which was placed in a chamber separated from the solution under study by means of a glass frit. The reference electrode was a saturated calomel electrode (Radiometer type K401 SCE) mounted within a Luggin capillary. The tip of the Luggin capillary was positioned immediately below the rotating disc, which was in a compartment with a volume of 100 cm<sup>3</sup>. The temperature of the cell was maintained constant by pumping water from a thermostat through a water jacket. A bifurcated gas inlet (controlled via a glass tap) allowed either deoxygenation of the solution by bubbling nitrogen through the frit, or the maintenance of a nitrogen atmosphere during the experiments.

Flow cell voltammetry and electrolyses were carried out using a FM01-LC cell from ICI Chemicals & Polymers Ltd. The cell was used with a lead cathode and coated Ti anode (catalytic for O<sub>2</sub> evolution) also supplied by ICI Chemicals & Polymers Ltd. Normally, the electrode areas in this cell are 64 cm<sup>2</sup> (16 × 4 cm). Because of current limitations on the potentiostat, for controlled potential electrolyses, the cathode area was reduced to 10 cm<sup>2</sup> (i.e. 2.5 × 4 cm) at the centre of the channel by coating the unwanted area with Alcomit (W. Canning Materials Ltd.). The cell was also modified to allow a fine plastic tube to act as a Luggin capillary; it entered the catholyte chamber through a 2-mm hole drilled through the wall of the electrolyte compartment. The cell was always operated in the divided configuration and was set up with standard components placed in the following order: backplate/gasket/flat plate lead cathode/gasket/electrolyte compartment with turbulence promoter (fine polyethylene mesh)/gasket/membrane (Nafion 417 cation-exchange permeable membrane)/gasket/electrolyte compartment with turbulence promoter/gasket/plate anode/gasket/backplate. The stack was compressed together using 8 tie bolts to a torque of 25 N m. The interelectrode gap was 0.55 cm.

Electrolyte solutions were fed to each compartment

from glass reservoirs (500 cm<sup>3</sup>) through flow circuits containing a flow meter (GEC Elliot Process Instruments Ltd, model metric 14X), a valve (glass) and a pump (Totton Pumps, model EMP4014). The catholyte temperature was controlled by pumping water from a thermostat into a water jacket surrounding the catholyte reservoir. The catholyte was deoxygenated prior to electrolysis by bubbling nitrogen through the catholyte reservoir. During electrolyses with catholytes pH < 3, a nitrogen atmosphere was maintained above the reservoir. The anolyte reservoir was always aqueous nitric acid (0.1 M).

*Instrumentation.* Most electrochemical experiments were carried out using a Hi-Tek Potentiostat, model DT2101, and a waveform generator, model PPR1. When required, current potential curves were recorded on a Gould 60000 X–Y recorder. The charge passed was measured with a home-built integrator while cell voltages were measured with a DVM (PM2519 Automatic Multimeter, Philips). For constant current electrolyses with currents > 1 A, the current control was achieved using a power supply (Labornetzgerat, Regulated Power Supply Lab 505). Rotating disc experiments were performed using an EG&G Parc, model 616. pH was measured with a Mettler Delta 340 pH meter and the viscosity was measured with an Ostwald viscometer (type U-tube BS188).

High-pressure liquid chromatography was performed using a Perkin–Elmer series 400 liquid chromatograph with spectrophotometric detector (LC95 UV–VIS) and integrator (LC100) and a ODS column (such as Econosil analytical column, 25 cm, from Alltech). The detector was operated at a wavelength of 210 nm. A 65/35 water–acetonitrile mixture was used as eluent. A 5- $\mu$ l loop was fitted to the injector. Gas chromatography was performed using a Varian gas chromatograph model 3700 connected to a Trio chromatography integrator. The Carbowax 20M packed column was temperature programmed between 445 and 500 K in 25 min. The carrier gas was N<sub>2</sub>.

Proton and carbon NMR spectra were recorded on a Bruker AM 300 MHz FT instrument. Each sample was prepared in deuterated acetonitrile and tetramethylsilane was used as internal reference. The frequency used was 300 MHz for the proton and 75.42 MHz for the carbon.

*Product identification and quantification.* Products were identified and quantified by comparison of the HPLC retention times and peak areas with those of standard samples. In general, samples of electrolyte were analysed directly but when reactant concentration were > 20 mM, the samples were diluted with a known volume of 50/50 methanol–water. On several occasions, the result obtained by HPLC analysis were checked by GC; trimethylphenol was used as internal standard for the GC analyses.

On some occasions, products were extracted for spectroscopic examination. The catholyte was neutralised with Na<sub>2</sub>CO<sub>3</sub> and evaporated in vacuum to a small

volume (about 100 cm<sup>3</sup>) in order to eliminate any trace of methanol. Water (ca. 250 cm<sup>3</sup>) was then added to dissolve all the inorganic salt and the solution was extracted with ether (3 × 50 cm<sup>3</sup>). The organic phase was washed with saturated solution of NaCl, dried over MgSO<sub>4</sub> and the ether removed by evaporation in vacuum. When only the dimers were required, evaporation under high vacuum was sufficient to eliminate the alcohols and aldehydes. When all products were required, they were separated on a flash silica column (Rhone Poulenc, Sorbsil, C60/H 40–60 mesh) with 50/50 hexane–ether.

## Results

### *Voltammetric studies at a rotating Pb disc electrode.*

*Preliminary experiments.* The potential range for syntheses at a Pb electrode is rather restricted. The negative limit is caused by hydrogen evolution; the potential for this reaction becomes more positive with decreasing pH but in the methanol–water media, pH 0.5–6.0, it occurs in the range from –1.4 to –1.9 V vs. SCE. The positive limit results from the oxidation of the lead itself. In sulfate and chloride solutions, this reaction occurs at ca. –0.5 V vs. SCE and leads to the irreversible formation of lead salts on the electrode surface; thereafter only very poor voltammetry for the reduction of organic compounds was observed. Hence, it was essential to maintain the potential of a lead electrode well negative to this potential region, and –0.8 V was selected as a safe limit. In addition to leading to a competing cathode reaction, traces of oxygen in solution were found to cause passivation of the lead surface. At pH < 3, currents for the reduction of benzaldehyde at a Pb RDE were found to decrease by as much as 50% in 20 min when the solutions were in equilibrium with air but were relatively stable when thoroughly deoxygenated. This effect was particularly noticeable in the stronger acid solutions and occurred even when the potential was maintained negative to –0.8 V. Thorough deoxygenation was therefore essential to obtaining reproducible data. It must also be recognised that lead is a soft metal, and all mechanical polishing could result in particles of the polishing material being imbedded in the surface. For this reason, alumina powders were avoided and the surface was prepared by gentle rubbing on a fine Emery paper.

The chemical stability in the acidic methanol–water mixtures of benzaldehyde and its common reduction products, benzyl alcohol, II, and hydrobenzoin, III, were confirmed. HPLC analysis showed no change in their concentration over a minimum of a 3-day period. In addition, benzyl alcohol and hydrobenzoin were electroinactive over the whole of the potential range available at the lead electrode. A fivefold excess of benzoic acid was also found to have no effect on the response for benzaldehyde in these acidic methanol–water mixtures.

*Reduction of benzaldehyde.* Figure 1 reports voltammograms recorded at a Pb RDE for benzaldehyde (10 mM) in aqueous solutions of three different pH. At pH 0.5, the response shows two cathodic waves of equal height while with increasing pH, the waves tend to coalesce. Indeed, at pH 4.7, the voltammogram shows only a single wave, although it is rather drawn out along the potential axis and may still consist of two overlapping processes. Throughout, the overall limiting current remains the same. The separation, in fact, occurs due to a positive shift in  $E_{1/2}$  for the first reduction step as the solution becomes more acidic ( $dE_{1/2}/dpH = -70$  mV) while the  $E_{1/2}$  for the second wave is independent of the pH. Figure 1 also shows that the shapes of the responses are independent of the rotation rate of the Pb disc, while the limiting currents, measured at –1.50 V vs. SCE, are proportional to the square root of the rotation rate of

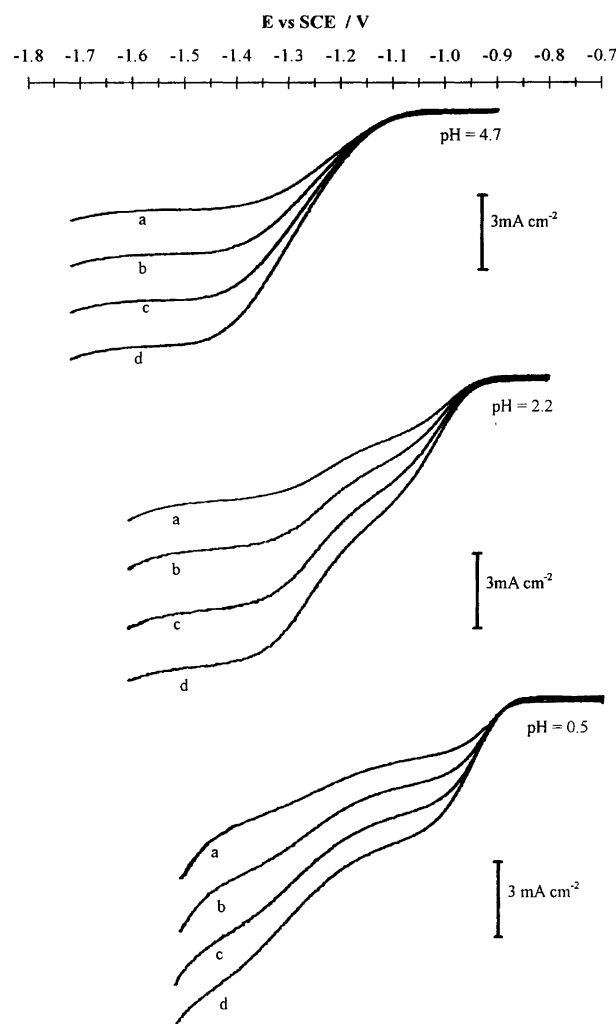
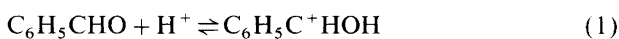


Fig. 1. Voltammograms for the reduction of benzaldehyde (10 mM) in aqueous citrate buffer (0.2 M) containing LiCl (1 M) as a function of pH and rotation rate of the Pb disc electrode. Rotation rates: (a) 400, (b) 900, (c) 1600 and (d) 2500 rpm. The solution pH were adjusted with NaOH or HCl.

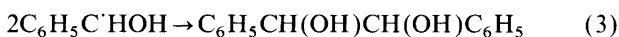
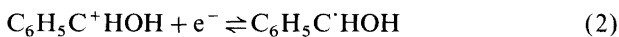
the disc, as expected for a reaction which is mass-transport controlled. The Levich equation shows that these limiting current are consistent with  $n=2$  and  $D=4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . At low pH,  $E_{1/4} - E_{3/4} \approx 60 \text{ mV}$  indicating that the first  $1e^-$  reduction is a reversible process.

Further experiments confirmed that the shape of the voltammograms were independent of the concentration of benzaldehyde (1–21 mM), solvent composition (0–50% methanol), choice of inert electrolyte and temperature (291–313 K). The half-wave potentials for both waves were also insensitive to these parameters. On the other hand, the magnitude of the currents are proportional to benzaldehyde concentration, decrease slightly with increasing methanol content of the solvent (due to increased viscosity) and also increase with temperature. In the plateau regions, the currents double over the temperature range studied. Moreover, a plot of  $\log I_L$  vs.  $1/T$  is linear, and the energy of activation is  $20 \text{ kJ mol}^{-1}$ , again typical of a mass transport controlled process.

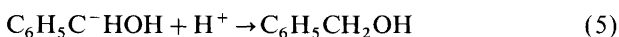
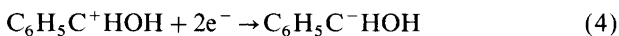
The voltammetry of benzaldehyde at a Pb RDE is therefore very similar to the responses at a mercury drop electrode,<sup>1,4–7</sup> and the mechanism of reduction appears to remain



followed at the potential of the first wave by



and at the potential of the second wave by



A consequence of this mechanism is that a radical intermediate is formed at the potential of the first wave and it is stable to reduction until more negative potentials. This was also the conclusion of Andrieux *et al.*<sup>7</sup> although they used buffered ethanol solutions with a higher pH (7–12).

*Voltammetric studies in the FM01 flow cell.* Figure 2 illustrates the voltammetry of benzaldehyde in the FM01 flow cell where the area of the lead cathode exposed to the electrolyte solution was limited to  $10 \text{ cm}^2$  at the centre of the compartment. It can be seen that, as at the disc, a single reduction wave is seen at pH 4.9 and that the response splits into two waves as the solution is made more acid. At each pH, it can be seen that the voltammograms show no significant change in shape with the flow rate. The shape of the voltammograms were also invariant with the concentration of benzaldehyde and the ratio of methanol to water.

Moreover, it is clear that in the plateau regions, the limiting currents show a strong dependence on the mean linear flow rate of the electrolyte,  $v$ . For solutions in 50/50 methanol–water containing citrate buffer, pH 5.2, voltammograms were recorded for several benzaldehyde

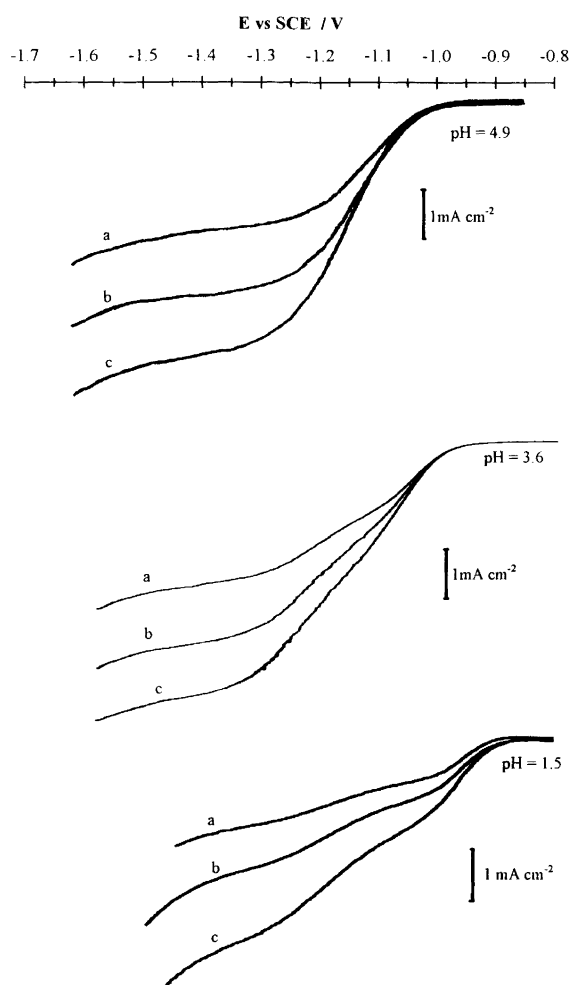


Fig. 2. Voltammograms for the reduction of benzaldehyde as a function of pH and mean linear catholyte flow rate in the FM01-LC flow cell. The cell was divided with a Nafion membrane, and the area of the Pb plate cathode was decreased to  $10 \text{ cm}^2$ . The mean linear flow rates are: (a) 3.5, (b) 6.7, (c)  $9.9 \text{ cm s}^{-1}$ . The solutions, pH 3.6 and 4.7, were benzaldehyde (10 mM) in aqueous citrate buffers containing LiCl (1 M), while the solution of pH 1.5 was benzaldehyde (6 mM) in 80%/20% water–methanol containing LiCl (1 M) with added HCl.

concentrations (5–40 mM) and at constant flow rates. The limiting currents were proportional to benzaldehyde concentration. Also at each concentration, plots of  $\log I_L$  vs.  $\log v$  are linear with slopes close to 0.5. This behaviour is characteristic of a mass transport controlled reaction in the FM01 cell.<sup>14,15</sup> The current densities observed at  $-1.50 \text{ V}$  are also very similar to those expected for a mass transport controlled  $2e^-$  reduction estimated from

$$j_L = 2Fk_m c \quad (6)$$

where  $k_m$  is the mass transfer coefficient and  $c$  the concentration of benzaldehyde. The mass transfer coefficients were taken from earlier studies,<sup>14</sup> although corrected for the change in the catholyte properties.<sup>15</sup> Overall, the voltammetry in the flow cell mirrored that at the rotating disc electrode and, as expected, there is

no reason to suspect a change in the mechanism of the cathode reaction with the cell design. It should, however, be recognised that good quality voltammetry is more difficult to achieve in the flow cell than in a RDE cell. The positioning of the tip of the Luggin capillary close to the cathode surface cannot be monitored visually. Also, maintaining oxygen free solutions without losing benzaldehyde by evaporation was a particular problem in the flow experiments, and this explains why few experiments were carried out at a  $\text{pH} < 1$ .

*Controlled potential electrolyses in the FM01 flow cell.* Controlled potential reductions of benzaldehyde at a Pb cathode were carried out in a range of conditions in the FM01 flow cell. A relatively low benzaldehyde concentration (5–10 mM) was employed in most experiments, since this minimised practical problems associated with uncompensated IR drop. Also, in general, the yields and selectivities are quoted at conversions of  $< 50\%$ , since this minimises the changes in conditions during the electrolysis as well as reducing the timescale of experiments. Current efficiencies were calculated from the amount of product formed and assuming that the diol and alcohol were formed in  $1e^-$  and  $2e^-$  reactions, respectively.

Table 1 reports the results from electrolyses carried out at several pH and cathode potentials. The current densities at the commencement of the electrolyses are reported to confirm that the  $j/E$  relationship obtained in this way is similar to the voltammogram in similar conditions. The amounts of benzaldehyde(I), benzyl alcohol(II) and hydrobenzoin(III) in the catholyte after the passage of a charge equivalent to 0.6 F are quoted as percentages of the benzaldehyde in the initial solution. The current efficiencies are also quoted in percent for the two reaction products, II and III. It will be seen that there is always a small shortfall in the mass balance, generally most marked when the current is low and the electrolysis therefore takes longer. It is thought that this

arises due to the slow evaporation of the more volatile components, benzaldehyde and benzyl alcohol, from the reservoir.

It is clear from the data in Table 1 that benzyl alcohol(II) is readily formed with a high selectivity and with a good current efficiency by electrolysis at a potential in the limiting current at high negative potential reported above in all voltammograms. It is also apparent that hydrobenzoin(III) becomes the major product at potentials of the first wave in the more acidic solutions or the lower half of the single wave seen at higher pH. Figure 3 shows the product distribution as a function of charge for an electrolysis at pH 1.5 and a potential of  $-1.0$  V and it can be seen that the ratio of the two products changes little during the electrolysis. The molar ratio of hydrobenzoin to benzyl alcohol is  $\approx 7:1$ . Moreover, this

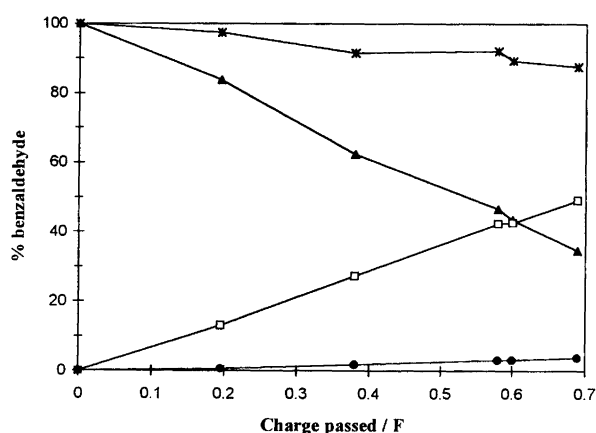


Fig. 3. Product distribution as a function of charge passed for a controlled potential electrolysis at  $E = -1.00$  V vs. SCE for benzaldehyde (7 mM) in 80%/20% water-methanol containing  $\text{Li}_2\text{SO}_4$  (0.5 M) with added  $\text{H}_2\text{SO}_4$  to pH 1.5. FM01-LC flow electrolyser with Nafion membrane and  $10\text{ cm}^2$  Pb plate cathode and turbulence promoter. Mean linear flow rate of the catholyte  $9.9\text{ cm s}^{-1}$ . The results are expressed in terms of the percentage of the initial benzaldehyde. ▲, Benzaldehyde; □, dimer; ●, alcohol; \*, total.

Table 1. The influence of cathode potential on the products from the reduction of benzaldehyde at several pH.<sup>a</sup>

pH	$E/\text{V vs. SCE}$	$j_{t=0}/\text{mA cm}^{-2}$	Product distribution <sup>b</sup> after 0.6 F (%)			Current efficiency (%)	
			I	II	III	II	III
4.3	-1.10	2.0	53	7	18	29	40
	-1.15	3.9	60	18	23	59	37
	-1.25	5.6	63	23	4	81	7
	-1.35	6.3	65	28	0	93	0
3.0	-1.15	3.0	60	8	15	26	26
	-1.35	6.0	63	32	1	103	2
1.5	-1.00	2.0	49	3	39	9	64
	-1.05	2.4	45	9	35	28	56

<sup>a</sup>FM01 cell with  $10\text{ cm}^2$  Pb cathode and turbulence promoter. Initial benzaldehyde concentration  $\approx 7$  mM. Room temperature. Mean linear electrolyte flow rate  $9.9\text{ cm s}^{-1}$ . Electrolyte compositions: pH 1.5,  $\text{Li}_2\text{SO}_4$  (0.5 M) +  $\text{H}_2\text{SO}_4$  in 20/80 MeOH/ $\text{H}_2\text{O}$ ; pH 3.0 and 4.3, Li citrate (0.2 M) + LiCl (1 M) in 40/60 MeOH/ $\text{H}_2\text{O}$ . <sup>b</sup>Based on  $\text{C}_6\text{H}_5\text{CHO}$  used in reaction. I,  $\text{C}_6\text{H}_5\text{CHO}$ ; II,  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ ; III,  $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}(\text{OH})\text{C}_6\text{H}_5$ .

selectivity can be maintained to a high conversion. On the other hand, it can be seen from Table 1 that the selectivity for the dimeric product is always significantly below 100%, and this is surprising in view of the good separation of the two cathodic waves in voltammograms at low pH. The ubiquitous formation of benzyl alcohol may indicate that the mechanism of Scheme 1 is not a complete picture. For example, benzyl alcohol could also be formed by hydrogen abstraction by the radical intermediate. Alternatively, electron transfer reactions between species in solution could be responsible for the formation of the benzyl alcohol.

Tables 2–4 report the influence of the benzaldehyde concentration, temperature and rate of mass transport

(the mean linear electrolyte flow rate) on the product distribution. Neither the benzaldehyde concentration nor the temperature has a significant effect on the ratio of hydrobenzoin to benzyl alcohol at  $-1.05$  V, where the dimer is the predominant product. The mass transport regime appears to have a small influence; this is most evident at intermediate potentials, e.g.  $-1.20$  V at pH 4, where the ratio of hydrobenzoin to benzyl alcohol increases with increase in the flow rate (in a cell with a turbulence promoter). This may imply that efficient local mixing close to the electrode surface aids the dimerisation of the radical intermediates.

In several electrolyses, the ratio of the DL and *meso* isomers in the hydrobenzoin product was checked by

Table 2. The influence of electrolyte flow rate on the products from the reduction of benzaldehyde at several pH. FM01 cell with  $10\text{ cm}^2$  Pb cathode and turbulence promoter.<sup>a</sup>

pH	[C <sub>6</sub> H <sub>5</sub> CHO]/mM	E/V vs. SCE	Mean linear electrolyte flow rate/cm s <sup>-1</sup>	$j_{t=0}$ /mA cm <sup>-2</sup>	Product distribution <sup>b</sup> after 0.6 F (%)		
					I	II	III
1.5	7	-1.05	5.6	2.0	51	6	27
			9.9	2.4	45	9	35
			14.1	3.4	60	6	30
4.0	37	-1.20	3.6	3.4	47	13	20
			9.9	5.5	52	9	31
			15.1	5.7	48	8	31
		-1.90	3.6	12.4	67	18	2
			9.9	16.0	78	19	0
			15.1	18.4	69	23	0

<sup>a</sup>Room temperature. Electrolyte compositions: pH 1.5, Li<sub>2</sub>SO<sub>4</sub> (0.5 M)+H<sub>2</sub>SO<sub>4</sub> in 20/80 MeOH/H<sub>2</sub>O; pH 4.0, Li citrate (0.2 M)+LiCl (1 M) in 40/60 MeOH/H<sub>2</sub>O. <sup>b</sup>Based on C<sub>6</sub>H<sub>5</sub>CHO used in reaction. I, C<sub>6</sub>H<sub>5</sub>CHO; II, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH; III, C<sub>6</sub>H<sub>5</sub>CH(OH)CH(OH)C<sub>6</sub>H<sub>5</sub>.

Table 3. The influence of initial benzaldehyde concentration on the products from the reduction of benzaldehyde at several pH.<sup>a</sup>

Initial benzaldehyde concentration/mM	Product distribution <sup>b</sup> after 0.6 F (%)			Current efficiency (%)	
	I	II	III	II	III
2.3	56	8	24	27	42
4.0	46	8	33	27	54
8.0	45	8	31	25	50
22.0	51	4	33	16	64

<sup>a</sup>FM01 cell with  $10\text{ cm}^2$  Pb cathode and turbulence promoter. Potential  $-1.05$  V vs. SCE. Mean linear electrolyte flow rate  $9.9\text{ cm s}^{-1}$ . Room temperature. Electrolyte compositions: Li<sub>2</sub>SO<sub>4</sub> (0.5 M)+H<sub>2</sub>SO<sub>4</sub> in 50/50 MeOH/H<sub>2</sub>O, pH 1.5. <sup>b</sup>Based on C<sub>6</sub>H<sub>5</sub>CHO used in reaction. I, C<sub>6</sub>H<sub>5</sub>CHO; II, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH; III, C<sub>6</sub>H<sub>5</sub>CH(OH)CH(OH)C<sub>6</sub>H<sub>5</sub>.

Table 4. The influence of temperature on the products from the reduction of benzaldehyde at several pH. FM01 cell with  $10\text{ cm}^2$  Pb cathode and turbulence promoter.<sup>a</sup>

T/K	$j_{t=0}$ /mA cm <sup>-2</sup>	Product distribution <sup>b</sup> after 0.6 F (%)			Current efficiency (%)	
		I	II	III	II	III
290	2.3	40	7	40	25	66
298	3.7	44	8	37	28	62
313	4.0	45	7	38	23	64
328	4.7	43	7	38	23	64

<sup>a</sup>Potential  $-1.05$  V vs. SCE. Mean linear electrolyte flow rate  $9.9\text{ cm s}^{-1}$ . Electrolyte compositions: Li<sub>2</sub>SO<sub>4</sub> (0.5 M)+H<sub>2</sub>SO<sub>4</sub> in 20/80 MeOH/H<sub>2</sub>O, pH 1.5. <sup>b</sup>Based on C<sub>6</sub>H<sub>5</sub>CHO used in reaction. I, C<sub>6</sub>H<sub>5</sub>CHO; II, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH; III, C<sub>6</sub>H<sub>5</sub>CH(OH)CH(OH)C<sub>6</sub>H<sub>5</sub>.

Table 5. The influence of electrolyte flow rate on the products from the reduction of benzaldehyde by constant current electrolysis.<sup>a</sup>

Mean linear electrolyte flow rate/cm s <sup>-1</sup>	$(j/j_L)_{t=0}^b$	$E_{t=0}/$ vs. SCE	Product distribution <sup>c</sup> after 0.6 F (%)			Current efficiency (%)	
			I	II	III	II	III
3.6	0.75	-1.38	68	28	2	96	4
15.1	0.34	-1.17	54	12	29	40	48

<sup>a</sup>FM01 cell with 10 cm<sup>2</sup> Pb cathode and turbulence promoter. Current density 6 mA cm<sup>-2</sup>. Electrolyte compositions: Li citrate buffer, pH 4 + LiCl (1 M) in 40/60 MeOH/H<sub>2</sub>O. Benzaldehyde concentration 37 mM. <sup>b</sup> $j_L$  estimated from  $j_L = 2Fk_m$ . <sup>c</sup>Based on C<sub>6</sub>H<sub>5</sub>CHO used in reaction. I, C<sub>6</sub>H<sub>5</sub>CHO; II, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH; III, C<sub>6</sub>H<sub>5</sub>CH(OH)CH(OH)C<sub>6</sub>H<sub>5</sub>.

Table 6. The influence of current density on the products from the reduction of benzaldehyde.<sup>a</sup>

pH	$j_L/\text{mA cm}^{-2}$	$(j/j_L)_{t=0}^b$	Product distribution <sup>c</sup> after 0.5 F (%)			Current efficiency (%)	
			I	II	III	II	III
5.2	16	0.17	48	3	38	12	76
	39	0.43	55	4	28	16	56
	63	0.66	64	6	16	24	32
0.9	8	0.24	70	5	25	20	50
	31	0.97	78	3	12	12	24
	78	2.42	80	10	1	40	1

<sup>a</sup>FM01 cell with 64 cm<sup>2</sup> Pb cathode and turbulence promoter. Electrolytes: Li citrate buffer, pH 5.2 + LiCl (1 M) in 50/50 MeOH/H<sub>2</sub>O with a flow rate of 15.2 cm s<sup>-1</sup> or H<sub>2</sub>SO<sub>4</sub> (0.25 M) in 80/20 MeOH/H<sub>2</sub>O with a flow rate of 3.7 cm s<sup>-1</sup>. Benzaldehyde concentration 200 mM. <sup>b</sup> $j_L$  estimated from  $j_L = 2Fk_m$ . <sup>c</sup>Based on C<sub>6</sub>H<sub>5</sub>CHO used in reaction. I, C<sub>6</sub>H<sub>5</sub>CHO; II, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH; III, C<sub>6</sub>H<sub>5</sub>CH(OH)CH(OH)C<sub>6</sub>H<sub>5</sub>.

NMR and on all occasions it was close to 1 : 1 as expected for simple electrolysis conditions.<sup>16</sup>

*Controlled current electrolyses in the FM01 flow cell.* On a preparative scale, controlled current electrolysis is a more convenient way to employ a parallel plate flow cell. Hence, the study of the product selectivity was extended to these conditions. Table 5 reports data from two electrolyses carried out with a constant current density of 6 mA cm<sup>-2</sup> but different catholyte flow rates; the product selectivity can be seen to be quite different. At the low flow rate, the major product is clearly benzyl alcohol, while at the higher flow rate hydrobenzoin is formed in higher amounts. The measured initial cathode potential is also reported in Table 5. As the electrolyses proceed, in both cases the cathode potential shifts negative but, below 50% conversion, the potentials remain close to the initial values and the ratio of products is almost independent of charge past. On the other hand, it can be seen that the effect of increasing the flow rate is to shift the measured potential from the region of the second reduction wave in a voltammogram to that of the first. In contrast, in other controlled current electrolyses, the product selectivity varied little with flow rate. The reason is clear if the cathode potential is monitored; in these cases the cathode potentials for the different flow rates were not in different regions of the current/potential characteristic.

Table 6 reports the results from truly preparative scale electrolyses where the concentration of benzaldehyde was increased to 0.2 M and the full cathode area of 64 cm<sup>2</sup>

was employed. In these conditions the conversion of 10 g of benzaldehyde in well under 2 h becomes possible. At both sets of conditions, the trend is for hydrobenzoin to be the major product at low current density and benzyl alcohol to dominate at high current densities. Indeed, the products are readily predicted from a knowledge of  $j/j_L$ , the ratio of the current density to the mass transport limited current density calculated from the known mass transport coefficient for the cell conditions (13). This ratio also determines the extent of H<sub>2</sub> evolution (a major competing cathode reaction when  $j/j_L > 1$ ) and hence the current efficiency for the organic conversion. Figure 4 shows the product distribution during an electrolysis where initially  $j/j_L = 0.46$ . Of course, during the electrolysis the concentration of benzaldehyde drops and this ratio increases and the influence of this ratio can be seen; with charge passed, the major product changes from hydrobenzoin to benzyl alcohol. This is the inherent drawback in controlled current electrolysis when the product distribution depends on the reaction conditions, e.g. potential. It should, however, again be emphasised that very satisfactory yields of hydrobenzoin can be achieved at pH 5.2 despite the observation of only a single wave on the voltammogram, provided  $j/j_L$  is maintained < 0.5.

## Discussion

Voltammetry at a Pb rotating disc electrode and in the flow cell with a Pb cathode are essentially identical and indicate that the mechanism of the reduction of benz-

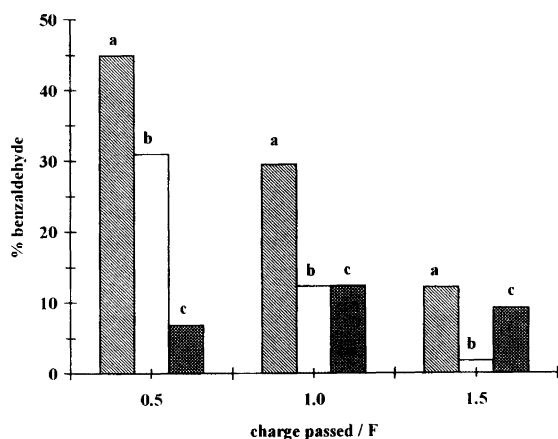


Fig. 4. Incremental selectivity for 0.5 F intervals during constant current electrolysis at  $i = 63 \text{ mA cm}^{-2}$  of benzaldehyde (200 mM) in 50%/50% water-methanol containing citrate buffer (0.2 M), pH 5.2. FM01-LC flow electrolyser with Nafion membrane and  $64 \text{ cm}^2$  Pb plate cathode and turbulence promoter. Mean linear flow rate of the catholyte  $15.2 \text{ cm s}^{-1}$ . (a) Percentage of benzaldehyde (present at the commencement of charge interval) consumed during the 0.5 F interval. (b) Percentage of benzaldehyde consumed during 0.5 F interval and converted into hydrobenzoin. (c) Percentage of benzaldehyde consumed during 0.5 F interval and converted into benzyl alcohol.

aldehyde in acidic methanol-water mixtures is similar to that deduced earlier for a mercury drop electrode,<sup>1,4-7</sup> see Scheme 1 and eqns. (1)–(5). In one sense, the voltammetry is, however, misleading, since it clearly shows two  $1e^-$  reduction waves at low pH and only a single  $2e^-$  wave at  $\text{pH} > 4$ . In contrast, if the purpose of the electrolysis is to prepare the  $1e^-$  product, the electrolyses seem to show no advantage of using more acid media pH compared to pH 4–6, since the same selectivity can be achieved by working at a potential in the lower half of the  $2e^-$  wave. Hence, it must be concluded that the single  $2e^-$  wave at  $\text{pH} > 4$  consists of two overlapping  $1e^-$  waves and, at least in this pH range, the reduction really still occurs in two, well defined  $1e^-$  steps. Moreover, even when the voltammetry appears to show two well separated  $1e^-$  reduction waves, it remains impossible to prepare hydrobenzoin without some benzyl alcohol. This must reflect some complication in the mechanism, not shown in Scheme 1 and not evident in the voltammetry. This could be hydrogen abstraction by the radical intermediate or solution electron transfer reactions. Overall, the observed behaviour does, however, largely have the chemistry expected for a radical intermediate which is reducible at more negative potentials.

The results demonstrate clearly that it is the cathode potential which is the over-riding parameter in determining the ratio of hydrobenzoin to benzyl alcohol in the product from the cathodic reduction of benzaldehyde. Parameters such as reactant concentration, temperature and mass transport regime have little influence on the products from controlled potential electrolysis and

during controlled current electrolyses, they effect the product distribution<sup>8-12</sup> principally in an indirect way through changing the cathode potential. These conclusions are perhaps not surprising but are important to electrosyntheses, where the objective is to use the radical intermediates in other reaction. Finally, it should be noted that the mass transport regime does appear to have a small influence on selectivity of controlled potential electrolyses, particularly at low rates of mass transport. This presumably indicates a role for some reaction in homogeneous solution, and efficient mass transport favours the formation of hydrobenzoin.

The objective of the work was to identify those conditions where the radical intermediate was formed with good selectivity. It has been shown that there are a range of conditions where hydrobenzoin is the major product and accounts for  $> 70\%$  of the benzaldehyde consumed. In contrast to earlier workers,<sup>8-12</sup> however, we have not quoted our results in tables or graphs in terms of a ratio of hydrobenzoin to benzyl alcohol; in our experience this ratio is subject to substantial experimental error (requiring accurate determination of minor products) and, anyway, does not contain information about the overall mass balance, equally important in the assessment of conditions. Even so, it has to be stressed that we have been unable to reproduce the very high molar ratios of hydrobenzoin/benzyl alcohol reported by the Japanese group<sup>8-12</sup> or the strong influence of temperature and mass transport regime on the selectivity. In this paper, the isolation of hydrobenzoin is used to infer the presence of the radical intermediate. While this is reasonable and consistent with the voltammetry, more definitive proof of radical intermediates will appear in the following paper.<sup>17</sup>

*Acknowledgements.* This work was supported by the European Commission through the Human Capital & Mobility Scheme, contract no. ERBCHRXCT920073. We also gratefully acknowledge the interest and advice of other members of the Network *Activation of Organic Molecules by Electron Transfer*. Finally we thank ICI Chemicals & Polymers Ltd. for the loan of the FM01 LC Electrolyser.

## References

1. Evans, D. H. In: Bard, A. J. and Lund H., Eds., *Encyclopedia of Electrochemistry of the Elements – Organic Section*, Part XII, Marcel Dekker, New York 1978.
2. Fry, A. J. *Synthetic Organic Electrochemistry*, 2nd Edn., Wiley Interscience, New York 1989, p. 174.
3. Baizer, M. M. In: Lund, H. and Baizer, M. M., Eds., *Organic Electrochemistry – An Introduction and a Guide*, 3rd Edn., Marcel Dekker, New York 1991, Chaps. 10 and 22.
4. Zuman, P., Barnes, D. and Ryvolová-Kejharová, A., *Discuss. Faraday Soc.* 45 (1968) 202.
5. Zuman, P. *Substituent Effects in Organic Polarography*, Plenum, New York 1967.
6. Laviron, E. and Lucy, J.-C. *Bull. Chim. Soc. Fr.* (1966) 202.



7. Andrieux, C. P., Grzeszczuk, M. and Saveant, J. M. *J. Am. Chem. Soc.* **113** (1991) 8811.
8. Cheng, P. C., Nonaka, T. and Chou, T. C. *Bull. Chem. Soc. Jpn.* **64** (1991) 1911.
9. Cheng, P. C. and Nonaka, T. *Bull. Chem. Soc. Jpn.* **64** (1991) 3500.
10. Cheng, P. C. and Nonaka, T. *Bull. Chem. Soc. Jpn.* **68** (1995) 378.
11. Cheng, P. C. and Nonaka, T. *J. Electroanal. Chem.* **269** (1989) 223.
12. Nonaka, T., Atobe, M., Chen, P., Matsuda, K. and Fujiwara, H. In: Torii, S., Ed., *Novel Trends in Electroorganic Synthesis*, Kodansha, Tokyo 1995, p. 251.
13. Robinson, D. In: Genders, J. D. and Pletcher, D. *Electrosynthesis – From Laboratory to Pilot to Production*, The Electrosynthesis Co, Lancaster, NY 1990, p. 219.
14. Hammond, J. K., Robinson, D., Brown, C. J., Pletcher, D. and Walsh, F. C. *J. Appl. Electrochem.* **23** (1993) 38.
15. Guena, T. *Ph.D. Thesis*, University of Southampton, Southampton 1997.
16. Nonaka, T. In: Lund, H. and Baizer, M. M., Eds., *Organic Electrochemistry – An Introduction and a Guide*, 3rd Edn., Marcel Dekker, New York 1991, Chap. 27.
17. Guena, T. and Pletcher, D. *Acta Chim. Scand.* **52** (1998) 32.

Received January 8, 1997.