JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 645–651

Electroreduction of hexachlorobenzene in protic solvent at Hg cathodes

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Received 2 June 1997; revised 8 September 1997

The electrochemical reduction of hexachlorobenzene (HCB) to lower chlorinated benzenes has been studied in methanol solution. Differential pulse voltammetry at a sessile mercury drop cathode showed four reduction waves at $E = -1.13$, -1.33, -1.57 and -1.84 V vs the standard hydrogen electrode, corresponding to sequential reduction to penta-, tetra-, tri- and dichlorobenzenes, respectively. The formation of these products was followed with time using a recirculating flow-through cell; the isomer distributions of the lower chlorinated benzenes were as predicted from a mechanism involving chloride elimination from radical anion intermediates. A maximum current efficiency of 60% was achieved in single-pass experiments in which the potential was controlled near the peak of the first reduction peak (−1.2 V) and the initial concentration of HCB was 1 mM.

Keywords: *hexachlorobenzene*, *electroreduction*, *methanol solution*, *mercury electrode*, *flow-through cell*

1. Introduction

Highly chlorinated aromatic compounds are recalcitrant towards disposal; biological treatment of low concentrations of such materials in aqueous waste streams often leaves the chloro compounds untreated or causes toxicity problems in the biological reactor. Electrochemical technologies show promise for treating these materials on grounds such as their promise of high energy efficiency compared with thermal and photochemical processes, relative simplicity of the equipment, and environmental friendliness [1, 2]. The low chemical reactivity of chlorinated aromatic compounds is reflected, however, in the need for very negative potentials (in case of reduction) or very positive potentials (for oxidation). The low solubility of hydrophobic chloro compounds in water also limits the applicability of electrolytic destruction, although attempts to overcome this limitation have been made by using surfactant media to increase solubility [3–6]. Besides direct electrolysis, the possibility of mediated electrolysis has also been investigated. This approach involves electrolytic generation of a 'catalyst' as a reactive oxidant or reductant. Under these conditions the destruction process of the chloro compound is a chemical reaction with the reactive oxidant or reductant which is simultaneously reconverted to its original form for a further catalytic cycle [7].

The electroreduction of aryl halides in nonaqueous, aprotic solvents such as DMF, DMSO, and acetonitrile is a stepwise process in which two electrons are transferred for each chlorine atom removed as chloride ion [8–10]. Initially, a single electron is transferred, with the formation of a radical anion whose chief reaction channel is ejection of Cl^-. The resulting aryl radical $Ar^{\bullet}$ is readily reduced to Ar^-, which protonates immediately. The regioselectivity of dechlorination of polychlorinated benzenes observed by Farwell *et al.* [8] is consistent with the intermediacy of radical anion intermediates, as shown by Freeman *et al.* [11], who compared the regioselectivity of homolytic against electron-donor-assisted photochemical dechlorination of pentachlorobenzene:

$$ArCl + e^- \rightarrow ArCl^{\bullet -} \rightarrow Ar^{\bullet} + Cl^-$$
$$Ar^{\bullet} + e^- \rightarrow Ar^-$$
$$Ar^- + H^+ \rightarrow ArH$$

Highly chlorinated benzenes are reduced at less negative potentials than lower chlorinated ones (e.g., half-wave reduction potentials for HCB and monochlorobenzene in DMF are −1.08 V and −2.2 V vs SHE, respectively) [8]. These data suggest that total electrochemical dechlorination of HCB would not be feasible, because of both the large electrical requirement and the highly negative potential needed to remove the last chlorine atoms [12].

The ultimate goal of our research is to evaluate electrolytic methods for the removal of hexachlorobenzene (HCB), a pesticide intermediate, from aqueous waste streams, with a view to implementing this technology for partial dechlorination of the contaminant ahead of a biological treatment unit. In this paper, we report fundamental investigations of the electroreduction of HCB in methanol at mercury cathodes. Electrochemical reduction of several chlorinated benzenes in this solvent had previously been demonstrated using a Pb cathode and tetramethylammonium bromide as the supporting electrolyte; the products were less chlorinated benzenes [12].

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2. Experimental methods

2.1. *Chemicals*

Chlorinated benzenes were obtained from Aldrich and their purities checked by HPLC and GC-MS. Tetrabutylammonium bromide (TBAB), tetraethylammonium chloride (TEACl), lithium perchlorate and sodium chloride (Aldrich) were used as supporting electrolytes (0.05 M TBAB, 0.05 M TEACl, 0.1 M $LiClO_4$ and 0.05 M NaCl). HPLC grade solvents were obtained from Fisher. HCB solutions in 0.05 M TBAB in ethanol or 60/40 by volume methanol/water were prepared by sonication.

2.2. *Chromatography*

HPLC analyses were performed on a Waters system, comprising a model 486 tunable absorbance detector, U6K injector, and 600 E system controller; this was connected to a PC computer and controlled by Millenium chromatographic software. Absorbances were monitored at $\lambda = 227$ nm. Analytical separations were performed on a Waters μBondapack C_{18}, 3.9×300 mm column, which was eluted with 90/10 methanol/water, at flow rate of 2 mL min^{-1}. Solvents were HPLC grade and were filtered before use through 0.45 μm Nylon 66 membranes to remove microparticulates.

Analytical CG-MS was performed on a Hewlett Packard 5971 Series mass selective detector interfaced to a Hewlett Packard 5890 Series II gas chromatograph equipped with a J&W DB5 capillary column (0.25 mm i.d., 30 m length, 0.25 μm film thickness), using helium as the carrier gas. The temperature program was 60 °C (3 min); 60 to 150 °C at 6 °C min^{-1}; 150 to 250 °C at 8 °C min^{-1}; 250 to 300 °C at 10 °C min^{-1}; 300 °C (5 min). The tetra-, tri-, and dichlorobenzene isomers were identified by comparison with authentic standards supplied by Aldrich.

2.3. *Reference electrodes*

An internal Ag/AgCl reference electrode was used when the supporting electrolyte contained chloride ion. The electrode was prepared by anodic polarization of a Ag wire (diameter 0.15 cm and length 1 cm) in 0.1 M NaCl for 2 h at 1 mA. For the experiments involving single flow at an Fe cathode, the reference electrode was an external SCE with flexible luggin capillary. All potential data were corrected to the standard hydrogen electrode as a common point of reference.

2.4. *Differential pulse polarography*

An EG&G, Princeton Applied Research (PAR) (model 264A) polarographic analyser with an EG&G, PAR (model 303A) static mercury drop electrode was controlled through a 486 PC computer. A 'drop knocker' and solenoid valve were used to produce mercury drops of uniform size and lifetime. A saturated calomel electrode (SCE) was used as the reference electrode and a Pt wire as the counter electrode. A 10.00 mL sample of the solution to be investigated was transferred into the reagent cell and was purged with ultrapure nitrogen for 10 min before recording the polarogram. Differential pulse polarograms were recorded using the following parameters: initial potential, −1200 mV; final potential, −1800 mV; scan rate, 5 mV s^{-1}; pulse height, 25 mV; pulse width, 50 ms; current range on the potentiostat, 0.010 mA.

2.5. *Differential pulse voltammetry on sessile drop mercury electrodes*

The electrochemical cell was a glass container, volume 50 cm^3, with a Teflon lid which had four openings for electrodes and an argon purging tube. The sessile Hg drop was supported on a J-shaped glass tube, closed at the short end, with a Pt wire ($d = 0.02$ mm) contact passed through the tube. The Hg drop (1.8 μL ± 5%) was dispensed into the hollow end of the J-tube by means of a syringe. Ag/AgCl was used as the reference electrode and a Pt foil, $A = 2$ cm^2, as the counter electrode. For the experiments that were performed above room temperature, the glass cell assembly was immersed into a circulating water bath. The cell was connected to an EG&G, PAR (model 273) potentiostat/galvanostat interfaced with a PC computer and operated by M270, version 4.1 electrochemical software, using the following parameters on the potentiostat: scan rate, 1 mV s^{-1}; pulse height: variable; pulse width, 50 ms; current, autoranging.

2.6. *Exhaustive electrolysis*

A sandwich flow-through cell was made of high density polypropylene (Fig. 1). The cathode and anode compartments were interior channels of dimensions 4 mm × 15 mm × 55 mm. The cathode and anode were 0.2 cm apart and separated by a Nafion®

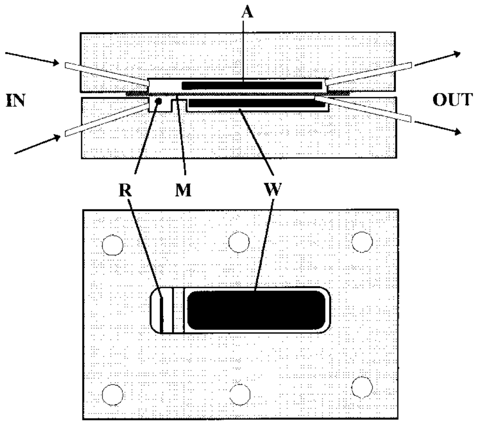

Fig. 1. Schematic of the flow cell: (R) reference electrode; (M) Nafion® membrane; (W) working (mercury pool) cathode; (A) Ti/IrO_2 anode.

417 membrane (DuPont) in the K^+ form. The cathode was a Hg pool with area ~5 cm^2 (or Fe wire (0.5 mm × 2 m, $A = 30\,\text{cm}^2$); the auxiliary electrode was made of Ti/IrO_2 with $A = 27\,\text{cm}^2$; an internal Ag/AgCl reference electrode or an SCE with flexible salt bridge was used. The cell was connected to an EG&G, PAR (model 273) potentiostat/galvanostat interfaced with a PC computer and operated with Head Start (EG&G) electrochemical software.

2.7. *Polarization of the working electrodes*

Potentiostatic control of the cell was used for experiments in which the potential of the working electrode was not enough to cause significant hydrogen evolution. Voltage loss due to uncompensated resistance was measured with the potentiostat by using a built-in current interrupt unit. When hydrogen evolution was significant, the hydrogen bubbles that accumulated at the surface of the electrode interfered with the measurement of potential, and galvanostatic control of the cell was employed to increase the polarization range in which the potential could be correctly determined.

2.8. *Continuous flow experiments*

Both potential-controlled and current-controlled experiments were carried out. In both cases, a 20.0 mL sample of 1 mM HCB solution in 0.05 M TEACl/MeOH was continuously recirculated through the cathodic compartment by a peristaltic pump, and 20.0 mL of electrolyte (0.05 M TEACl in MeOH) was pumped through the anodic compartment. The catholyte was deaerated by purging with argon for 20 min before electrolysis, and a slow Ar flow was maintained throughout the experiment. Samples were analysed by HPLC at intervals during electrolysis, and the reaction rates were corrected for the consequent change in the volume of the solution.

2.9. *Single flow experiments*

A solution of 1 or 0.1 mM HCB in electrolyte (0.05 M TEACl/MeOH or 0.05 M NaCl/MeOH) was pumped from a 0.5 L container through the cathodic compartment at 0.6 mL min^{-1}, and the output from the cathode was directed to waste. Approximately 20 mL of electrolyte solution was circulated through the anodic compartment, as in continuous flow experiments. The cathodic solution containing HCB was deaerated by purging with argon for 20 min before electrolysis. The potential of the working electrode was varied from −1.1 to −2.1 V vs SHE controlling either the potential or the current. Potentiostatic control was used to polarize the working electrode up to −1.7 V; beyond this potential the rate of hydrogen evolution is higher and galvanostatic technique was used for a better control. The output of the cathodic compartment was monitored by HPLC; samples for analysis were not collected until the solution had flowed through the cell for 20 min so as to achieve a steady state (flow rate 0.6 mL min^{-1}, system volume 2.0 mL).

3. Results and discussion

3.1. *Reduction of HCB at mercury drop electrodes*

Differential pulse polarography (DPP) was used to characterize analytical aspects of the electroreduction of HCB. In experiments using dropping Hg electrodes (DME), ethanol and methanol/water mixtures as solvents, and 0.05 M tetrabutylammonium bromide as the supporting electrolyte, a single maximum at −1.32 V in ethanol and at −1.38 V in 60:40 methanol:water was assigned to the reduction of HCB to pentachlorobenzene (PeCB). Detection limits for HCB under these conditions were $\sim 8 \times 10^{-6}$ M in EtOH and $\sim 2 \times 10^{-5}$ M in 60/40 MeOH/H_2O. The useful range of concentration of HCB in the methanol:water mixtures was severely limited by the solubility of HCB (1×10^{-4} M in 60/40 MeOH/H_2O). In addition, results with the DME were difficult to reproduce in alcoholic solvents, because of their low surface tension compared with water. In consequence, the mercury drop lifetime was irreproducible at the negative potentials required to reduce HCB. Subsequent voltammetric experiments were performed using a sessile Hg drop electrode (SMDE) in the three-electrode cell described in the experimental section. The solvent was methanol and the supporting electrolyte was either tetraethylammonium chloride (TEACl) or NaCl (0.05 M).

Using 0.05 M TEACl in MeOH as supporting electrolyte, we observed four reduction maxima at E ~−1.13, −1.33, −1.57 and −1.84 V vs SHE (Fig. 2). These were attributed to the stepwise reduction of HCB to PeCB, tetrachlorobenzene (TeCB), trichlorobenzene (TrCB) and dichlorobenzene (DCB), and confirmed by showing that the latter three maxima corresponded to the first reduction maximum of PeCB, TeCB and TrCB, respectively. The current was

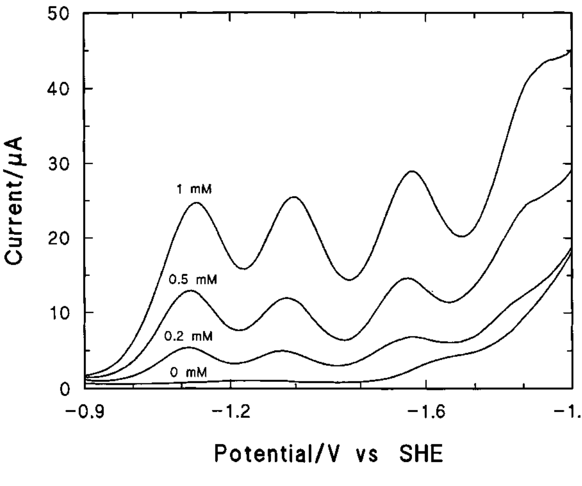

Fig. 2. Differential pulse voltammograms of HCB at concentrations ranging from 0 to 1 mM; supporting electrolyte: 0.05 M TEACl in MeOH; pulse height 100 mV.

proportional to the concentration of the analyte in solution (Fig. 3); consistent with stepwise reduction, the calibration sensitivities of the four peaks were similar (~25 μA mM^{-1}). The background currents were small at the potentials corresponding to the first three peaks and these calibration curves intersect the ordinate close to the origin. This was not the case for the peak at −1.84 V for which a significant background current was observed.

Because of the low solubility of HCB in partly aqueous solvents we examined whether these experiments could be made at higher temperatures, to improve the solubility of the substrate. Figure 4 shows the effect of increasing the temperature upon reduction potentials of HCB, using 0.05 M TEACl in MeOH as supporting electrolyte. The reduction maxima shifted slightly to less negative potential, and at constant concentration the amplitude of the peak maximum approximately doubled for a 30 °C rise in temperature. The practical significance of this observation is that the electrolytic reduction of HCB can be carried out above ambient temperature. The magnitude of the larger peak amplitude is too large to be explained by an increase in the rate of diffusion and indicates that the reduction currents are at least partially controlled by the kinetics of the electrode reaction.

When 0.05 M NaCl was used as supporting electrolyte, reduction of HCB showed only a single peak at $E \sim -1.35$ V, almost 200 mV more negative than with TEACl. In addition, hydrogen evolution shifted to less negative potentials, diminishing the useful potential range for electroreduction. Both observations suggest that TEACl is a much better supporting electrolyte than NaCl. Tetraethylammonium cations are known to modify the electrode surface by adsorption from non-aqueous solutions at negative electrode potentials, thereby changing the composition of the double layer and the potential distribution across the interface [13, 14]. The resulting change in the rate of the electrode reactions explains qualitatively the different behaviour of the two electrolytes, but more detailed investigations are needed to provide a quantitative explanation.

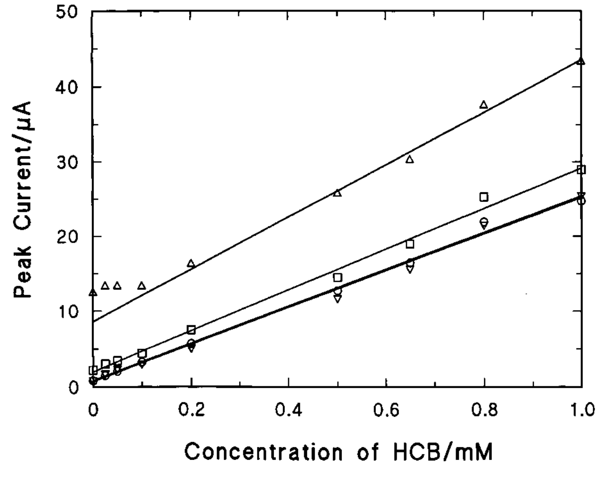

Fig. 3. Calibration curves of peak current against HCB concentration: same conditions as Fig. 2. Key (E/V, slope/μA mM^{-1}): △ (−1.84, 33.7); □ (−1.57, 27.2); ○ (−1.33, 24.5); ▽ (−1.13, 24.6).

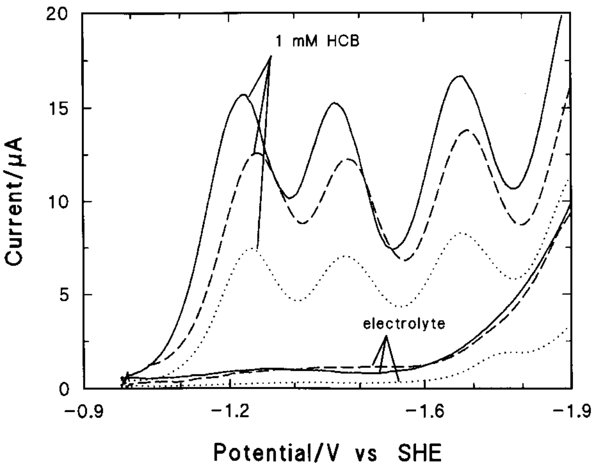

Fig. 4. Effect of temperature on the differential pulse voltammograms of electrolyte (0.05 M TEACl/MeOH) and of 1.0 mM HCB in 0.05 M TEACl/MeOH; pulse height 40 mV. Temperatures, T:(——) 55, (– – –) 40 and (······) 22 °C.

3.2. *Exhaustive electrolyses of HCB at Hg pool electrodes*

Having established approximate potentials for the sequential reduction of HCB to PeCB, TeCB, and TrCB, we carried out bulk electrolyses to confirm the identities of the reduction products, to determine a mass balance, and to follow the kinetics of sequential reduction. The bulk electrolyses employed a recirculating three-electrode, flow-through cell as described in the experimental section. Separate experiments were carried out at −1.27, −1.50 and −1.75 V, corresponding to the selective reduction of HCB, PeCB, and TeCB respectively (Fig. 2). Samples were removed at convenient time intervals to monitor the disappearance of starting material and appearance of products using HPLC analysis. Calibration curves with authentic standards were used for quantitation by HPLC; in all cases >98% of starting material, based on benzene residues, was present at all stages in the electrolysis.

Samples were extracted and analysed by GC/MS in order to complete the identification of the products, including their isomer distributions. PeCB is a single isomer; TeCB showed a single peak on GC/MS, but it was not possible to separate the 1,2,3,5- and 1,2,4,5-isomers. However, the latter were deduced to have been present in a 6:94 ratio, because this was also the ratio of 1,3,5-TrCB to 1,2,4-TrCB. The three DCB isomers were formed in a ratio *o*-:*m*-:*p*- of 8:19:73. The regioselectivity of dechlorination of PeCB thus strongly favours the formation of 1,2,4,5-TeCB, and the symmetrical 1,2,4,5-TeCB affords only 1,2,4-TrCB. This is consistent with the observations of Freeman *et al.* [11] in the context of chloride elimination from the polychlorobenzene radical anions. Finally, 1,2,4-TrCB dechlorinates to yield predominantly *p*-dichlorobenzene.

Figure 5 shows the rate of electrolysis in the recirculating flow experiments. At −1.27 V, the major reduction product was PeCB, although at long reaction times small concentrations of TeCB were also observed (Fig. 5(a)). At −1.50 V, TeCB was the major product at all reaction times (Fig. 5(b)); the concentration of PeCB remained low at all times, indicating that under these conditions most PeCB molecules are reduced to TeCB immediately upon formation. At −1.75 V TeCB can also be reduced; in this case TeCB and TrCB were major products, with PeCB again observed only in trace amounts. The time course of this reaction (Fig. 5(c)) makes clear that at this potential PeCB and TeCB behave differently; PeCB undergoes immediate further reduction as it is formed, but much of the TeCB enters the bulk solution, and is reduced to TrCB from the bulk solution. In an amperostatic experiment ($i = 20$ mA), with the working electrode kept at potential more negative than −2.0 V, both PeCB and TeCB underwent immediate sequential reduction (Fig. 5(d)), but much of the TrCB was reduced to DCB from the bulk solution.

In all continuous flow experiments the loss of HCB with time followed first order kinetics ($\ln c_0/c_t \propto$ time): Table 1. The apparent rate constant increased very weakly with increased applied potential: changing the electrode potential by ∼0.8 V increased the rate constant by only a factor of four. Separate experiments in which the flow rate of the electrolyte was varied showed that the rate constant is proportional to the flow rate. This behaviour suggests that the bulk electrolysis is predominantly a mass transfer-limited process, in contrast to the differential pulse voltammetric reduction of HCB, which was kinetically controlled. The explanation is that significant diffusion fluxes may be achieved during the 50 ms pulse time employed in the differential pulse voltammetry, whereas the small flow rate used in the bulk electrolysis results in a slow mass transport of HCB

Table 1. Pseudo-first order rate constants for reduction of 1 mM HCB in 0.05 M TEACl/MeOH

Potential V vs SHE	*Current* /mA	$(k \pm SE) \times 10^4$ /s^{-1}	r^2
−1.27	0.5–0.9	0.91 ± 0.02	0.992
−1.50	1.3–2.0	1.97 ± 0.09	0.973
−1.75	2.5–4.0	3.05 ± 0.04	0.997
∼−2.1	20	3.55 ± 0.08	0.995

Continuous flow electrolysis, $F = 0.6\,\mathrm{mL\,min^{-1}}$

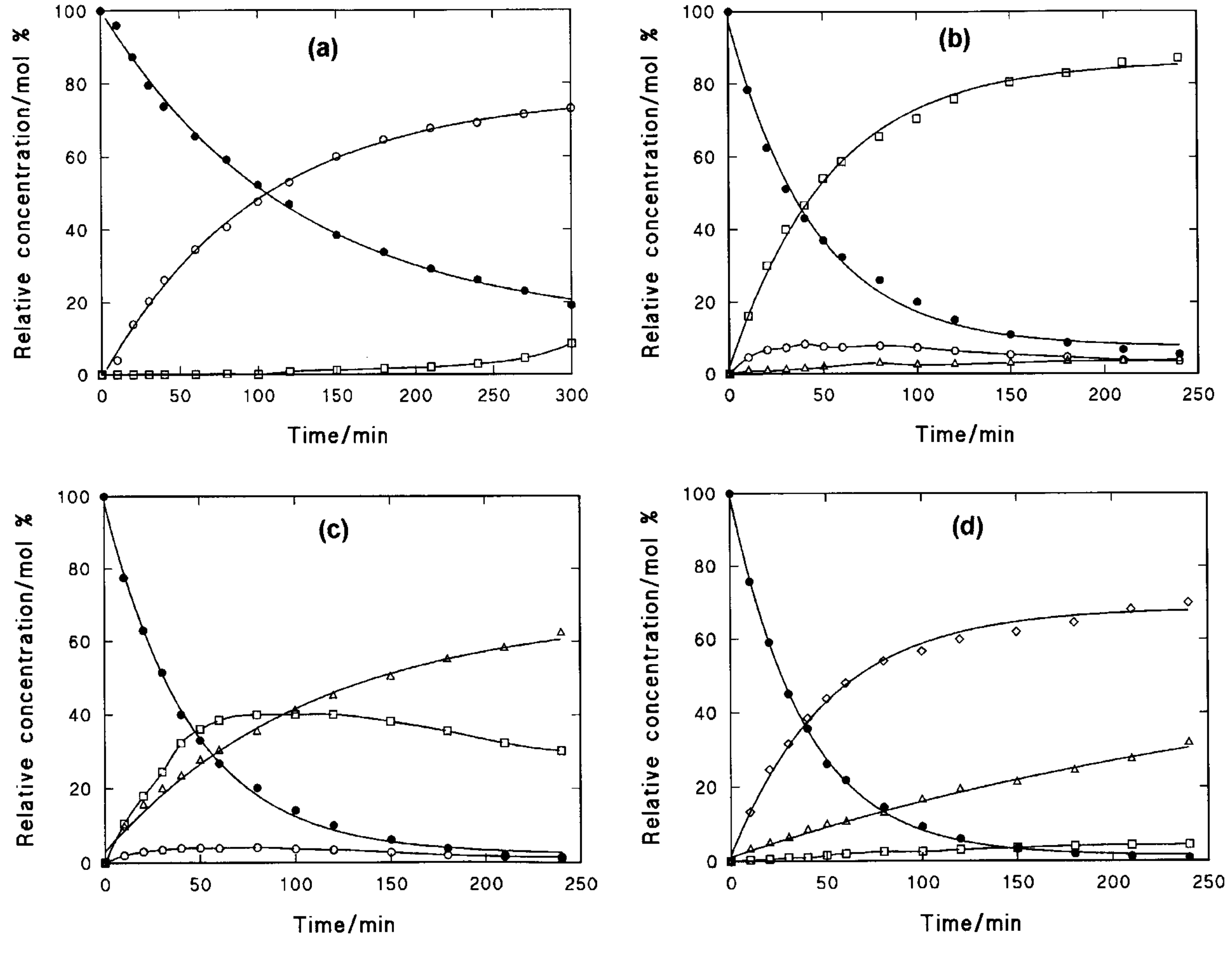

Fig. 5. Kinetics of electrolysis of HCB in the recirculating flow cell using a mercury pool cathode of area 27 cm^2 at a flow rate of 0.6 mL min^{-1}: (a) $E = -1.27$ V; (b) $E = -1.50$ V; (c) $E = -1.75$ V; (d) $i = 20$ mA. Key: (●) HCB, (○) PeCB, (□) TeCB, (△) TrCB and (◇) DCB.

towards the electrode surface. In the amperostatic electrolysis (Fig. 5(d)), the initial rate of formation of dechlorinated products during the first 1 h of electrolysis corresponded to an overall current efficiency of 13%.

3.3. *Single flow experiments*

These experiments employed the same three-electrode flow-through cell as used in continuous flow experiments, except that the HCB solution was passed by the cathode only once. These conditions approach more closely a prospective industrial application, and also allow both current efficiency for reduction and product distribution to be determined as a function of applied potential. The concentrations of products and unreacted HCB were determined by collecting a sample of the spent catholyte, once sufficient time had been allowed for the system to reach a steady state at the given flow rate and potential. Both TEACl and NaCl were used as supporting electrolytes. With TEACl/MeOH, stepwise dehalogenation of HCB to lower chlorinated benzenes was achieved by successively shifting the potential from −1.1 to −2.1 V. The concentrations of HCB and its reduction products are shown as a function of applied potential (Fig. 6). The potential at the electrode has been corrected for IR drop, using the current interrupt method. The current efficiency for two such reductions is presented in Fig. 7. At an initial HCB concentration of 1 mM, the current efficiency for removal of the first chlorine atom was ~60% near the maximum potential of the first reduction peak. The current efficiency dropped at more negative potentials because of competing evolution of hydrogen from the solvent, and the measurements were somewhat irreproducible because of the presence of hydrogen bubbles at the electrode surface. The current efficiency fell at lower HCB concentration, and the maximum efficiency was ~25% for the 0.1 mM solution. In experiments performed at more negative potentials than −1.6 V and at large HCB concentrations (1 mM), the current efficiency dropped after approximately 3 h of electrolysis, an effect attributed to poisoning of the mercury cathode. In separate experiments using NaCl as the electrolyte, the rate of reduction was much smaller, consistent with the results using the SMDE.

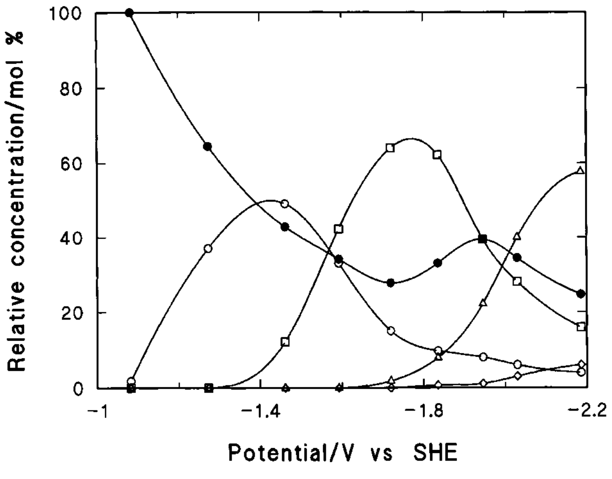

Fig. 6. Electrolysis of 0.1 mM HCB in 0.05 M TEACl/MeOH using the single flow system at a flow rate of 0.6 mL min^{-1}. Key: (●) HCB, (○) PeCB, (□) TeCB, (△) TrCB and (◇) DCB.

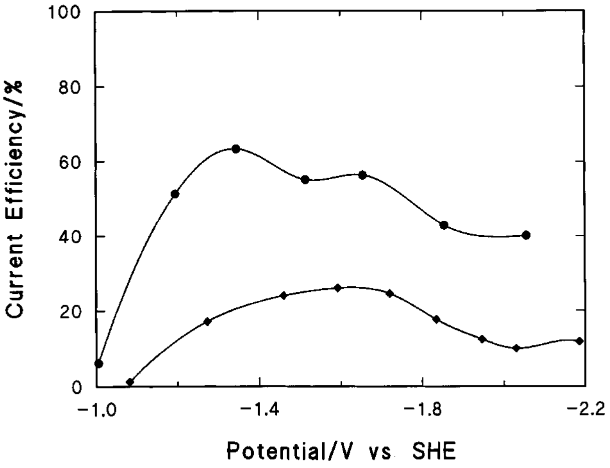

Fig. 7. Current efficiency of HCB reduction in 0.05 M TEACl/MeOH as a function of applied potential. Key: (●) 1 mM HCB and (◆) 0.1 mM HCB.

4. Conclusions and environmental significance

At present, there are no widely accepted technologies for the removal of chlorinated aromatic compounds from water, but several studies have shown electrolytic dechlorination to be a promising method. Reductive dechlorination by electrochemical catalysis has been used to selectively remove halogen from PCBs to yield biphenyl [3, 15].

Methanol was used in the present work because it is an environmentally friendly solvent; miscible with water, relatively inexpensive, in contrast to DMF and other aprotic solvents, and not toxic to microorganisms in biological treatment reactors. Fernando *et al.* had previously found that halogenated compounds rapidly dechlorinate in aqueous methanol solutions on the surface of palladized iron [16, 17]. The experiments described in this paper demonstrate proof of concept for the partial electrolytic reduction of highly chlorinated benzenes in methanol solutions, and the ongoing work in our laboratory is directed towards solving problems standing between proof of concept and a possible practical technology. Among these is the need to increase the aqueous content of the solvent. Electrochemical catalytic dehalogenation can also be employed in water-based surfactant media, which is providing an alternative to organic solvents [18–20], although no method is yet available for recovering the nonaqueous material from the emulsion after electrolysis.

Recognizing that mercury is inappropriate for use as a cathode for 'real world' environmental applications, we carried out some preliminary experiments in the flow cell using Fe wire as the cathode and $LiClO_4$

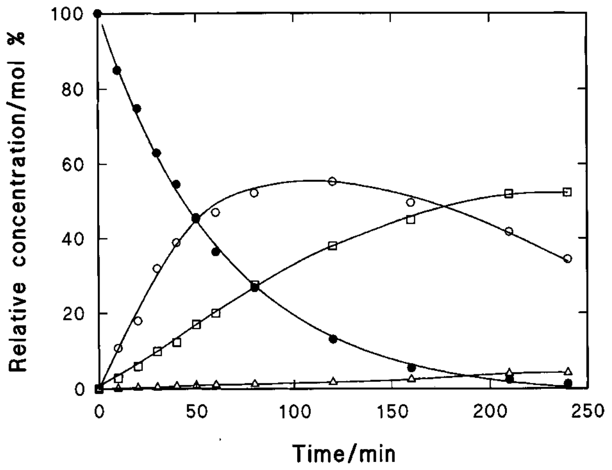

Fig. 8. Electrolysis of 1.0 mM HCB in the recirculating flow cell at an iron wire electrode of area 30 cm^2; 0.1 M $LiClO_4$/EtOH; constant current 50 mA; flow rate 2.5 mL min^{-1}. Key: (●) HCB, (○) PeCB, (□) TeCB and (△) TrCB.

as the supporting electrolyte. Under amperostatic conditions, the pseudo-first order rate constant for the disappearance of HCB was $3.0 \times 10^{-4}\,s^{-1}$ at $i = 50$ mA (Fig. 8). The current efficiency, based on product appearance after 1 h of electrolysis, was 1.4% at 50 mA and 0.5% at 190 mA, lower than attained at mercury (13%). In addition, there was very little evidence of reduction beyond TeCB at the iron cathode. Nevertheless, these experiments show qualitatively that partial reduction of HCB is possible using a non-polluting cathode material.

Much further research is needed to devise a practical scheme for environmental samples. Specific requirements include a mostly aqueous solvent, a cheaper supporting electrolyte than TEACl, environmentally friendly electrode materials, and the ability to work at reasonable current efficiencies at the low contaminant concentrations encountered in practical situations. Our ongoing experiments are directed towards evaluating different combinations of cathode materials and supporting electrolytes for their current efficiency in this respect. Suitable cathode materials must combine high overvoltages for hydrogen evolution, ruggedness and freedom from inactivation through poisoning, capability of being manufactured with large surface area, and no propensity to release toxic materials into the catholyte.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support through the Strategic Grants Program.

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