JOURNAL OF APPLIED ELECTROCHEMISTRY **27** (1997) 51–57

An investigation of the electrochemical reduction of pentachlorophenol with analysis by HPLC

N. C. ROSS, R. A. SPACKMAN, M. L. HITCHMAN*, P. C. WHITE

Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, Great Britain

Received 26 February 1996

A study has been made of the electrochemical reduction of pentachlorophenol (PCP) on a lead electrode in both water and propylene carbonate. A combination of voltammetric measurements and analysis of reaction products by high performance liquid chromatography (HPLC) have established that the reduction of PCP in propylene carbonate occurs by two different pathways, depending upon the electrode potential. At −1.9 V vs SCE, reduction is mediated by adsorbed hydrogen, whereas at −2.3 V vs SCE direct reduction of PCP also occurs. A similar approach has established that the reduction of PCP in water follows only one reaction pathway, namely, direct electron transfer from lead to PCP.

1. Introduction

Chlorinated organic chemicals have for sometime been causing much concern because of their toxicity, persistence and bioaccumulation in aquatic organisms and, for this reason, political and public groups have forced the introduction of legislation for their disposal. As early as 1976, the European Community introduced legislation to control their release into inland, coastal and territorial waters [1] and this necessitated the development of disposal methods for unwanted waste. However, in 1989 a report to the House of Commons Environmental Committee [2] expressed concern at the lack of new technologies to meet this need and, subsequently, interest in emerging technologies such as environmental electrochemistry has increased [3].

As part of a programme on the destruction of carbon–halogen bonds, we have begun to investigate the destruction of chlorophenols and, in particular, the electrochemical reduction of pentachlorophenol (PCP), an extensively used wood preservative which is both corrosive to the skin and highly embryotoxic [4]. In aqueous solutions, it has been reported that the cathodic reduction of water competes with PCP reduction [5] and, hence, we decided initially to study PCP reduction in a nonaqueous solvent. Propylene carbonate was selected because cathodic breakdown is known to occur typically at rather more negative potentials in this solvent than in water [6]. Studies in both dried and undried propylene carbonate were undertaken. Subsequently, the reduction of PCP in water was also undertaken.

In addition to considering the electrochemical characteristics of the reduction, HPLC was used to monitor the products formed. Previous studies showed that PCP was electrochemically degraded to less chlorinated phenols which were not identified individually [5, 7, 8]. In this study an HPLC system has been developed to separate variously chlorinated and even isomeric chlorophenols, and this method has been used to identify the PCP electrolysis products. The results obtained for reduction in both water and propylene carbonate are discussed and pathways for the dehalogenation processes are proposed.

2. Experimental details

2.1. *Electrochemical conditions*

Electrochemical investigations of PCP were made in a standard three-electrode cell, as shown schematically in Fig. 1. The cell incorporated a platinum mesh counter electrode separated from a lead disc working electrode (Oxford Electrodes, UK) by a Nafion™ membrane. Lead was chosen as a working electrode because of its high overpotential for the reduction of water. (Water was present as either an impurity in the propylene carbonate studies or as the solvent of choice in the aqueous studies.) The lead electrode, which was capable of rotation for steady state measurements, was brought into close proximity to the saturated calomel electrode (SCE) by using a luggin probe. All voltages are reported with respect to the SCE. The area of the lead electrode was 0.405 cm^2. The working compartment of the cell had an approximate volume of 15 cm^3 and was degassed with nitrogen.

Cyclic voltammetry was conducted with a scanning potentiostat (EG&G PARC model 362, New Jersey) to provide voltage sweeps from −1 V to −2.4 V vs SCE at 20 mV s^{-1}. The currents produced were recorded on a chart recorder.

---

* Author to whom correspondence should be addressed

0021-891X

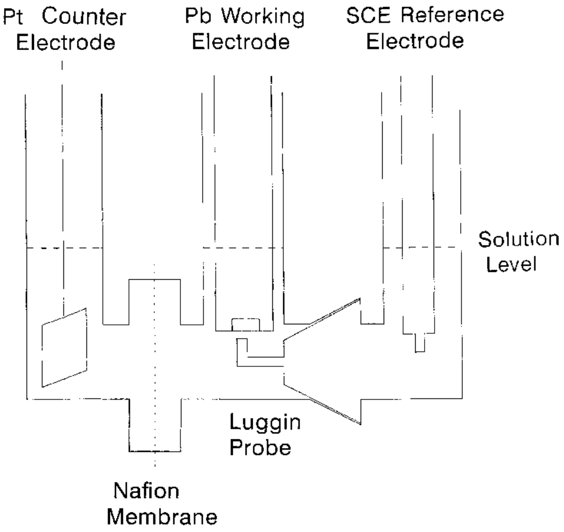


Fig. 1. Diagram of the three compartment cell used for studying electrochemical reduction of chlorinated phenols.

Steady state measurements were achieved by spinning the lead electrode at different rotation rates using a rotating disc apparatus and motor controller (Oxford Electrodes, Rochester, UK). Voltages were again swept between −1 V and −2.4 V vs SCE, but in this case at $2\,\mathrm{mV\,s^{-1}}$, and the currents produced were also recorded as before.

Controlled potential electrolysis measurements were performed using the same cell configuration with the lead electrode maintained at either −1.9 V or −2.3 V vs SCE and rotated at a constant speed of 9 Hz. The corresponding currents were recorded using a chart recorder over a timed period of electrolysis.

2.2. *Chromatographic conditions*

HPLC analyses were performed on a system which included a pump (Spectra Physics 8700XR, Burke Analytical, UK) used to deliver eluent at $1.5\,\mathrm{ml\,min^{-1}}$ through a 125 mm × 4.6 mm i.d. stainless steel tube packed with Exsil 80 ODS-1 (5μm, Exmere Ltd, UK). The eluent consisted of methanol/acetonitrile/water (30:30:40) containing $2\,\mathrm{g\,dm^{-3}}$ citric acid. Samples were introduced onto the column using an injection valve fitted with a 20μL loop (Negretti & Zambra, UK). Samples were monitored at a wavelength of 254 nm with a u.v. detector (Pye Unicam LC3, UK) coupled to a chart recorder.

2.3. *Reagents and sample solutions*

All reagents used were of analytical grade and the chlorophenols used were as follows: 2-, 3- and 4-chlorophenols, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dichlorophenols, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5- and 2,4,6-trichlorophenols and pentachlorophenol (Aldrich, UK); 2,3,4,6- and 2,3,5,6-tetrachlorophenols (TCl via Fluorochem Ltd, UK) and phenol (BDH, UK). All the chlorophenols were used as received. No supplier could be found for 2,3,4,5-tetrachlorophenol.

Prior to each electrochemical study a solution containing 20 mM PCP and 0.25 M tetraethylammonium chloride (TEACl) (< 2% water, Fluka, UK) in the appropriate solvent, propylene carbonate (Aldrich) or distilled water, was prepared. The supporting electrolyte of 0.25 M TEACl was used to reduce the effects of ion migration. A Karl Fischer water analyser was used to determine the water content of the propylene carbonate/TEACl electrolyte before and after drying over 0.3 nm molecular sieves. Water concentrations of 65 mM and 5 mM were obtained, respectively. Furthermore, analysis of the electrolyte after experimentation showed that the water content in the predried electrolyte had only risen to 9 mM, significantly lower than the value obtained for undried electrolyte.

For the chromatographic studies individual standards of the phenols were prepared at a concentration of $1\,\mathrm{mg\,mL^{-1}}$ in methanol/acetonitrile/water (40:20:40). Mixed standards were also prepared at the same concentrations.

3. Results and discussion

3.1. *Analysis by HPLC*

As a preliminary to studying the electrochemical reduction of PCP, an investigation of the separation by HPLC of possible products was made. From initial experiments with the octadecyl-silane (ODS) modified silica column and eluents containing methanol/water mixtures, separation of phenol from PCP could be achieved, but these conditions generated long retention times and poor peak shapes. Suppressing the ionization of these analytes by the addition of citric acid to the eluent yielded considerable improvements in column efficiency but failed to reduce the analysis times. The addition of acetonitrile to the eluent produced the desired reduction in retention times.

To optimize the eluent conditions, standard mixtures of the phenols were analysed using eluents containing varying amounts of acetonitrile and citric acid. The optimized eluent conditions were determined to be methanol/acetonitrile/water (30:30:40) containing citric acid at a concentration of $2\,\mathrm{g\,dm^{-3}}$ and provided retention time data which could be used to identify phenol and 15 of the 17 chlorophenols tested. Unfortunately, the separation between the 2,4- and 3,4-dichlorophenol isomers could not be achieved, as illustrated from the retention data recorded in Table 1. A chromatogram obtained for the analysis of a standard containing phenol and the 17 chlorophenols is shown in Fig. 2 and it can be seen that an analysis can be completed within 16 min. It is possible that gradient elution could have improved the separation. However, only isocratic conditions were investigated.

3.2. *Electrochemical reduction of PCP*

Initially the electrochemical reduction of PCP was studied by cyclic voltammetry. During a cathodic

Table 1. Retention time data for all available chlorophenol isomers

Compound		
Name	*Identifier* (*see Fig. 2*)	*Retention time* /min
phenol	**(1)**	1.1
2-chlorophenol	**(2)**	1.5
3-chlorophenol	**(3)**	1.6
4-chlorophenol	**(4)**	1.7
2,6-dichlorophenol	**(5)**	2.1
2,3-dichlorophenol	**(6)**	2.2
2,5-dichlorophenol	**(7)**	2.4
2,4-dichlorophenol	**(8)**	2.5
3,4-dichlorophenol	**(9)**	2.5
3,5-dichlorophenol	**(10)**	3.4
2,3,6-trichlorophenol	**(11)**	3.5
2,3,4-trichlorophenol	**(12)**	3.9
2,4,6-trichlorophenol	**(13)**	4.3
2,4,5-trichlorophenol	**(14)**	4.5
2,3,5-trichlorophenol	**(15)**	4.9
2,3,4,6-tetrachlorophenol	**(16)**	7.1
2,3,5,6-tetrachlorophenol	**(17)**	7.4
pentachlorophenol	**(18)**	13.3

voltage sweep from −1 V to −2.4 V vs SCE at 20 mV s^{-1}, two irreversible reductions, C_1 at −1.7 V and C_2 at −2.15 V, were observed prior to the onset of solvent breakdown at C_3, as shown in Fig. 3. It was noted that C_1 was broad and was therefore probably not a simple reduction process. To determine whether the presence of water, an impurity in the propylene carbonate and the tetraethylammonium chloride (discussed in Section 2.3), had affected the voltammetry, the measurements were then repeated using reagents that had been dried over 3A molecular sieves. A voltammogram identical to the one shown in Fig. 3 was obtained and, therefore, it was concluded that traces of water did not significantly alter the voltammetry.

Steady state measurements made at 9 Hz and 2 mV s^{-1} on the same solution of PCP showed two reduction processes (Fig. 4) and these occurred at potentials, taken at the centre of the voltammetric plateaus, of −1.9 V and −2.3 V vs SCE for C_1 and C_2 respectively. The nature of the two processes was investigated by varying the PCP concentration and electrode rotation rate.

For studies conducted at a potential of −2.3 V vs SCE, steady-state current–voltage curves were

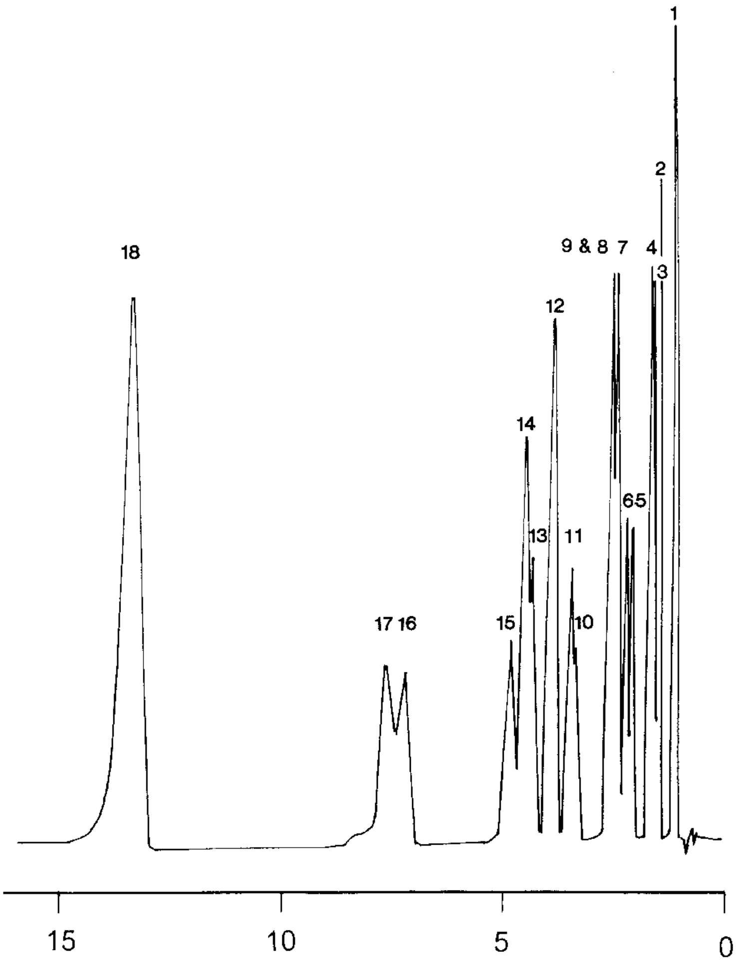


Fig. 2. HPLC separation (λ = 254 nm) for phenol (**1**) and seventeen chlorophenol isomers (**2**)–(**18**). For identification of components see Table 1.

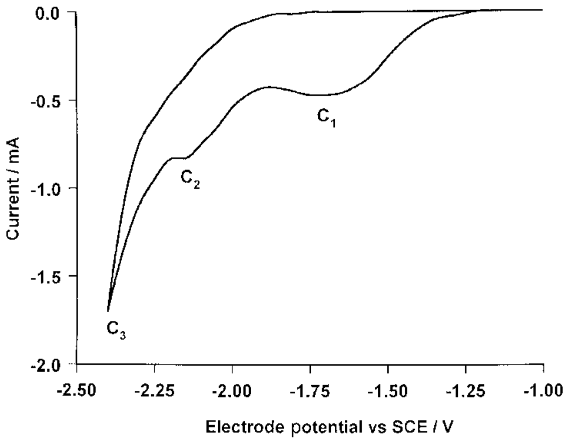


Fig. 3. Cyclic voltammogram for the reduction of 20 mM PCP in 0.25 M TEACl/propylene carbonate on a lead electrode at a voltage scan rate 20 mV s^{-1}. C_1 and C_2 are irreversible reductions at −1.7 V and −2.15 V, respectively, and C_3 is solvent breakdown.

obtained for PCP solutions of varying concentration in the range 1–30 mM and at electrode rotation rates of 4, 9, 16 and 25 Hz. Levich analyses [9] gave straight lines with gradients which scaled with PCP concentration. The conclusions drawn from these data were that the reaction was mass transport controlled at all concentrations tested and that the PCP was the only active molecule undergoing direct electroreduction.

HPLC analyses using a 20 mM PCP solution were conducted to confirm the direct electrochemical reduction suggested by steady state experimentation. Controlled potential electrolysis was carried out with the working electrode rotating at 9 Hz and the potential held at −2.3 V. The solution was sampled at 30 min intervals over a period of 3 h. Aliquots of these samples were analysed by HPLC and these results (illustrated in Fig. 5) indicated the destruction of PCP to a single product with a retention time of 7.1 min. Based upon retention time data obtained for the chlorophenol standards, the degradation peak was identified as 2,3,4,6-tetrachlorophenol (**16**) but in the absence of a standard for 2,3,4,5-tetrachlorophenol it is possible that this compound may have been produced and then coeluted with the 2,3,4,6-isomer. The presence of only one peak, though, suggested that direct electron transfer was responsible for the degradation, as shown below.

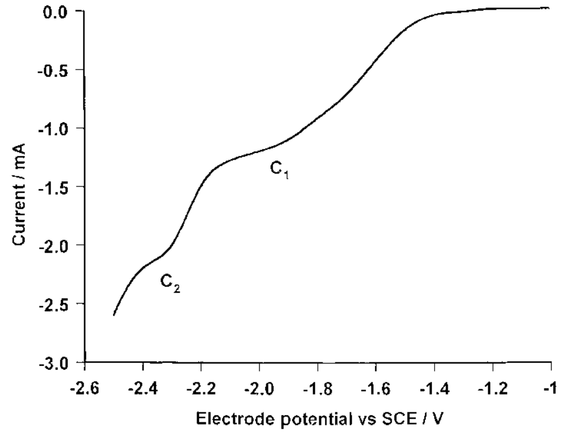


Fig. 4. Steady-state voltammogram for the reduction of 20 mM PCP in 0.25 M TEACl/propylene carbonate on a lead disc electrode rotating at 9 Hz and for a voltage scan rate of 2 mV s^{-1}. C_1 and C_2 at −1.9 V and −2.3 V vs SCE, respectively, are the centres of two current plateaus.

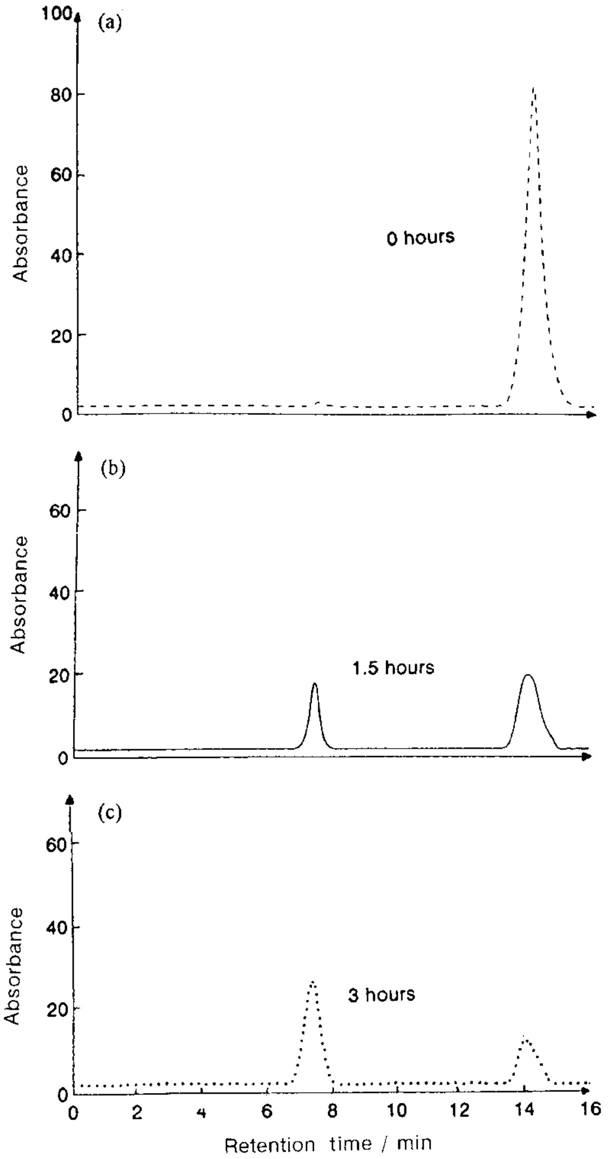
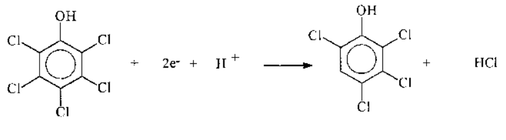


Fig. 5. Chromatograms monitoring the electrolysis of PCP (the peak at 14 min) on a rotating lead electrode at −2.3 V vs SCE at intervals of (a) 0 h, (b) 1.5 h and (c) 3 h.



For a similar controlled potential electrolysis study performed at a potential of −1.9 V vs SCE, HPLC analyses revealed the formation of three products (a)–(c) and if allowed to proceed for 7 h, a fourth product (d) was detected, but a significant quantity of PCP still remained. A chromatogram obtained after 7 h is shown in Fig. 6. From HPLC retention time data of the chlorophenol standards, components (b) and (c) were identified as 2,3,5,6-(**17**) and 2,3,4,6-

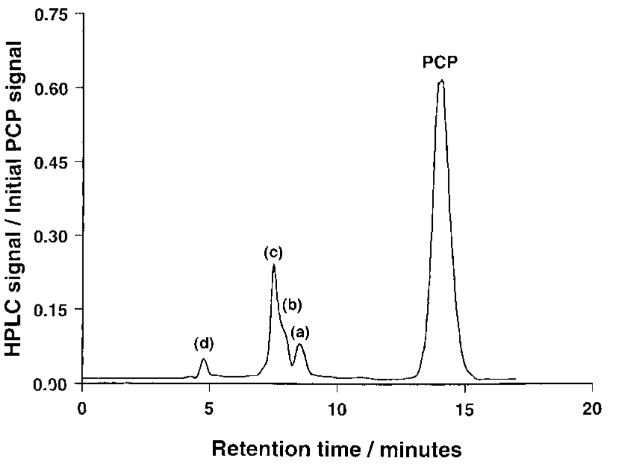


Fig. 6. Chromatogram monitoring the electrolysis of PCP after 7 h on a rotating lead electrode at −1.9 V vs SCE. (a) = 2,3,4,5-tetrachlorophenol. (b) = 2,3,5,6-tetrachlorophenol (**17**), (c) = 2,3,4,6-tetrachlorophenol (**16**), (d) = 2,4,5-trichlorophenol (**14**).

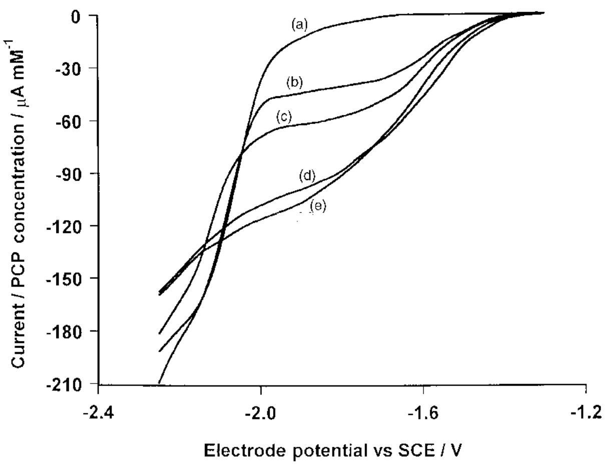
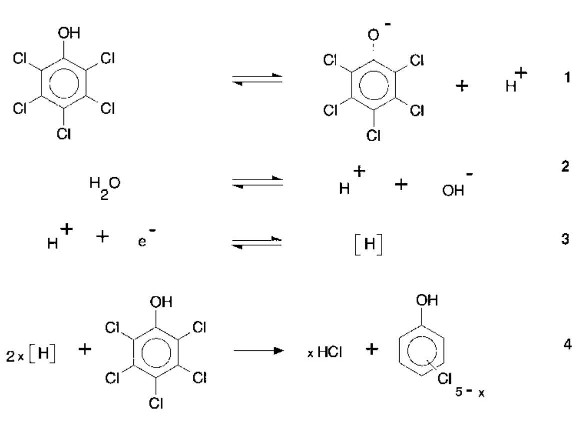


Fig. 7. Steady-state voltammograms for the reduction of PCP in propylene carbonate on a lead rotating disc electrode. Note that currents have been normalized with respect to PCP concentration and are shown for PCP concentrations of (a) 1, (b) 3, (c) 10, (d) 20 and (e) 30 mM.

tetrachlorophenol (**16**), respectively. Product (a) could possibly be the 2,3,4,5-tetrachlorophenol isomer. However, without being able to obtain a suitable standard this could not be confirmed. The compound which was produced over a longer timescale (d) was identified as 2,4,5-trichlorophenol (**14**).

To determine the mechanism for the reductive process taking place at −1.9 V, steady-state electrochemical measurements were again recorded over a concentration range of 1 to 30 mM PCP and Fig. 7 shows the current–voltage curves which were obtained after normalizing the current with respect to the PCP concentration. This figure shows that the reduction current did not scale with PCP concentration. At low concentrations ($\leq$ 1 mM) no wave was observed at all, but at higher concentrations plateaus were observed. Furthermore, for [PCP] $\geq$ 20 mM, Levich analysis demonstrated that these plateau currents were limited by the transport of PCP. It was concluded that PCP enhanced the rate of its own reduction and the following electrochemical pathway was tentatively proposed:



According to this mechanistic scheme, the electrode process is the reduction of a proton rather than of PCP. After initial acid dissociation of PCP (Reaction 1) and trace water (Reaction 2), present as an impurity in the solvent and the tetraethylammonium chloride electrolyte, the reduction of protons yields an adsorbed layer of hydrogen on the electrode surface (Reaction 3) which then can mediate the reduction of both PCP and its partially dechlorinated products, giving a mixture of chlorinated phenols and regenerating a proton for each released chloride anion (Reaction 4). It is proposed that a critical proton concentration is required to maintain the adsorbed hydrogen layer and the steady-state voltammetry suggests that this condition is only met by PCP concentrations greater than 1 mM. For higher PCP concentrations, significant mediated reduction of PCP occurs and, for [PCP] $\geq$ 20 mM, the process is so rapid that it is mass transport limited.

The electrochemical mechanism, defined by Reactions (1–4), accounts for the voltammetric data presented in Fig. 7. Evidence for the involvement of the proton was only established by some further electrochemical studies. Figure 8 shows the coincidence of the peak potentials for the reduction of PCP (C_I) and for the reduction of hydrochloric acid in propylene carbonate. This suggests that direct reduction of the proton rather than PCP is the electrode process at −1.9 V. Figure 9, a plot of unreacted PCP (as determined by HPLC analysis) against electrolysis time, shows that the rate and the yield of PCP reduction increases when the proton sources, acetic acid and hydrochloric acid, are added to the electrolyte. In particular, the rate of PCP reduction falls off sharply when only 30% of a 20 mM PCP solution has been reduced, but for a solution containing an added electrolyte of 0.2M HCl, the reduction is still proceeding at a significant rate even after 70% of the PCP has been reduced.

In contrast to the complex voltammetric behaviour which was obtained for the reduction of PCP in propylene carbonate (see Figs 3, 4 and 7), the cyclic voltammograms for the reduction in water showed only one reductive feature, a peak centred on −1.75 V vs SCE. Figure 10 shows steady-state voltam-

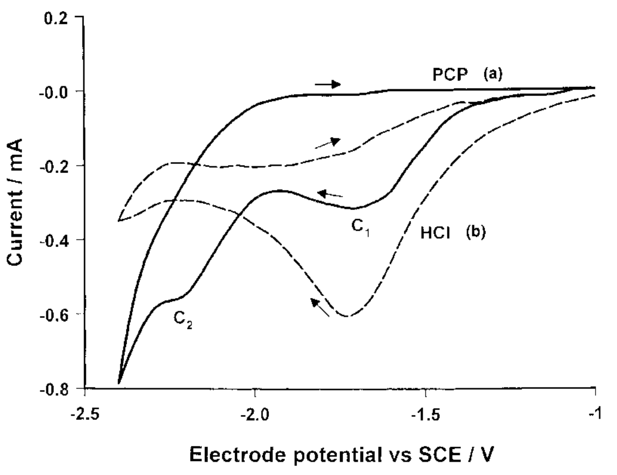


Fig. 8. Cyclic voltammograms for the reduction of (a) 0.2M hydrochloric acid and (b) 20 mM PCP in propylene carbonate.

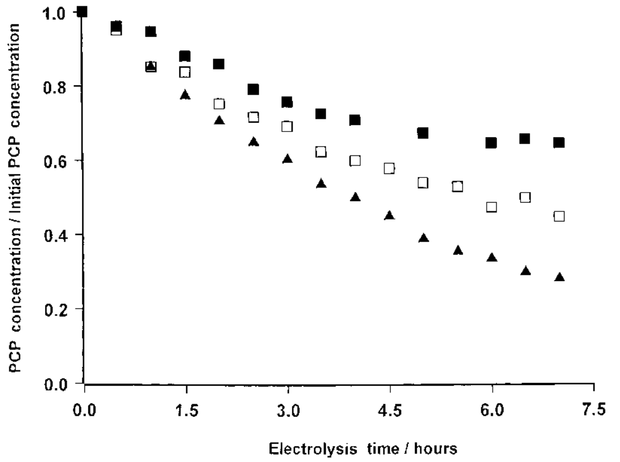


Fig. 9. Transient decay of PCP HPLC peak as a function of electrolysis time and for an electrode potential of −1.9 V vs SCE. Three curves are shown for the reduction of PCP in the presence of no additional proton source (■), 0.2 M acetic acid (□) and 0.2 m HCl (▲).

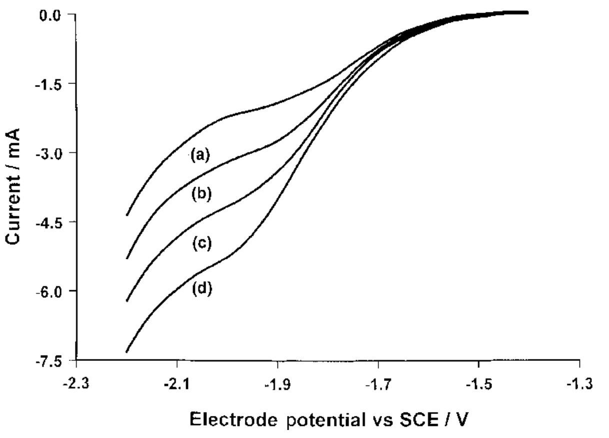


Fig. 10. Steady-state voltammograms for the reduction of 20 mM PCP in water at pH 12 on a lead rotating disc electrode. Frequency: (a) 4, (b) 9, (c) 16 and (d) 25 Hz.

mograms which were obtained at a lead rotating disc electrode for a 20 mM PCP solution. Data were obtained for 1 mM ≤ [PCP] ≤ 20 mM and Levich analysis of the plateau currents gave straight lines in each case such that the gradient of the plots scaled with the PCP concentration. Therefore, it was concluded that the reduction of PCP in water was by direct electron transfer.

To confirm the conclusions from the voltammetric measurements, an HPLC analysis of the products of the reduction was undertaken. A controlled potential electrolysis was performed at −1.95 V vs SCE for aqueous PCP solutions of 8 ≤ pH ≤ 13 (only in this pH range was PCP soluble). In all cases, only one product was identified, 2,3,4,6-tetrachlorophenol (**16**). This is the same product as was observed for the reduction of PCP in propylene carbonate when the electrode potential was −2.3 V vs SCE. Furthermore, a current efficiency of approximately 100% was obtained for the production of tetrachlorophenol in water, assuming that the reduction required 2 electrons.

4. Conclusions

This study has shown that an ODS modified silica HPLC column, when operated under isocratic and ion-suppressed conditions, can provide a stable chromatographic system for the analysis of phenol and chlorophenols. Phenol and 15 of the 17 chlorophenols tested could be identified from retention time data. Complete analyses were possible within 16 min and therefore the system was suitable for monitoring the electrochemical reduction of PCP.

From combined voltammetric measurements and HPLC analysis of the products of controlled potential electrolysis, it was concluded that the reduction of PCP on lead in propylene carbonate occurs by two different pathways at −1.9 V and −2.3 V vs SCE. At −1.9 V vs SCE the reduction is mediated by a layer of hydrogen adsorbed on the lead electrode, and at −2.3 V vs SCE the dominant reductive pathway is by direct electron transfer from lead to PCP. For −1.9 V > electrode potential > −2.3 V, these pathways compete for the reduction of PCP. HPLC analysis of the products of controlled potential electrolysis at −1.9 V vs SCE revealed that the hydrogen-mediated process gave a mixture of tetrachlorophenols and 2,4,5-trichlorophenol (**14**), but a similar analysis after controlled potential electrolysis at −2.3 V demonstrated that 2,3,4,6-tetrachlorophenol (**16**) was the only product of direct electron transfer from lead to PCP; in the absence of a standard for the 2,3,4,5-isomer it is possible that this compound might also have been co-eluted with the 2,3,4,6-isomer. The failure to produce less chlorinated products than trichlorophenols at −1.9 V vs SCE could be attributed to a decrease in the inductive effect of substituents on the phenolic ring after two chlorine atoms had been removed from PCP.

It was also shown that PCP could be reduced directly to 2,3,4,6-tetrachlorophenol on lead in water; a current efficiency of approximately 100% was obtained for this process. However, in this solvent hydrogen-mediated reduction and, hence, further dechlorination was not observed. Evidently, in the experimental pH range for which PCP is soluble in water, $8 \leq \mathrm{pH} \leq 13$, the proton concentration was too low for the adsorbed hydrogen layer to be maintained. Further dechlorination may only be achieved by direct reduction and, as has been demonstrated by Schmal [5], this requires electrode potentials within the hydrogen evolution region.

Acknowledgements

We acknowledge the financial and technical support from E.A. Technology, Capenhurst, Chester, UK for a studentship for NCR, and financial support from the European Union under the Environment Programme contract EV5V-CT92-0237 for RAS.

References

[1] Directive 76/464/EEC, European Community Law (1976).
[2] House of Commons Environmental Committee, 'Second Report on Toxic Waste', HMSO London (1989).
[3] D. Genders and N. Weinberg, 'Electrochemicstry for a Cleaner Environment', Electrosynthesis Company Inc., New York (1992).
[4] R. B. Clark, 'Halogenated Hydrocarbons in Marine Pollution', 2nd edn, Oxford Science publications (1989).
[5] D. Schmal, J. Van Erkel, A. M. C. De Jong and P. J. Van Duin, 'Electrochemical Treatment of Organohalogens in Process Waste Water', *in* 'Environmental Technology', vol. 103, Kluwers Academic Publishing Group (1987).
[6] C. K. Mann, 'Electoanalytical Chemistry', vol. 3, Marcel Dekker, New York (1969).
[7] D. Schmal, J. Van Erkel and P. J. Van Duin, *I. Chem. E. Symposium Series* **98** (1985) 281.
[8] J. Van Erkel, D. Schmal and P. J. Van Duin, 36th ISE Meeting, Spain (1985) 04040.
[9] A. J. Bard and L. R. Faulkner, 'Electrochemical Methods', Wiley, New York (1980).