COMMUNICATION

In situ FTIR studies on the electrochemical reduction of halogenated phenols

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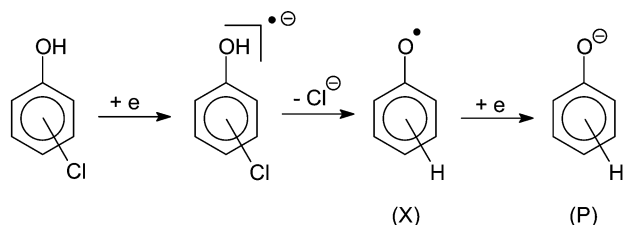
Electrochemical reduction of a variety of mono- and dichloro- and bromo- phenols at a palladised titanium electrode afforded phenolate in all cases according to *in situ* FTIR studies, with the same intermediate species being observed in some cases.

In 1994, Gillham and O'Hannesin[1] reported the application of zero valent metals, and particularly iron, to the dehalogenation of organic contaminants in groundwater. Since then, a number of papers have appeared concerning the kinetics and mechanism of both chemical[2,3] and electrochemical[4,5] dehalogenation.

As part of our research programme on the development of novel electrochemical reactors for the hydrodehalogenation of organic species in waste and wastewater,[6] we employed *in situ* Fourier Transform Infrared Spectroscopy (FTIR) to study the electrochemical reduction of a range of chlorophenols (CP) and bromophenols (BP) at a palladised titanium electrode. We have found that, for a wide range of substitution patterns, complete dehalogenation occurs to give phenolate through the same intermediate, which was observed in some cases. The mechanism of the reduction may be represented as a sequence of electron additions and chloride expulsions leading *via* an intermediate radical to product (see Scheme 1 for chlorophenols). This is the first such observation for aqueous media and has important implications for the remediation of toxic halogenated streams.

The *in situ* FTIR spectroscopic cell was of a standard, three electrode type[7] in which a thin layer of electrolyte (*ca.* 1 µm) was trapped between the reflective working electrode and the CaF_2 cell window. The palladised titanium working electrode (0.5 mg Pd cm^{-2}, 0.64 cm^2) was prepared by electrodeposition, as described elsewhere.[8] The counter electrode was Pt gauze and a commercial Ag/AgCl electrode (Sentek) was used as the reference. The electrochemistry in the cell was controlled by a Sycopel AEW2 potentiostat. A BioRad FTS-40 spectrometer fitted with a narrow-range MCT detector was employed in the *in situ* spectroscopic experiments; 100 scans at 8 cm^{-1} resolution were co-added and averaged to give each spectrum. The potential was stepped from −200 mV to a preset value, and the reference spectrum, (S_R), collected; further spectra (S_S) were taken as a function of time. These spectra were manipulated according to the equation: Absorbance = $Log_{10} (S_S/S_R)$. Peaks pointing *up* (to + Abs.) in the difference spectra that result are attributed to the loss of absorbing species as the reaction proceeds, peaks pointing *down* (to − Abs.) to the gain.

Cyclic voltammograms recorded in the spectroelectrochemical cell with the Pd/Ti working electrode pulled back from the

window are shown in Fig. 1 for various concentrations of 2,4-dichlorophenol (2,4-DCP), and are representative of those obtained with all the substrates studied in showing an increase in the cathodic current on adding the organic substrate to the pH 3 H_2SO_4–0.1 M Na_2SO_4 base electrolyte. Representative *in situ* FTIR spectra collected as a function of time during the reduction of 2,5-DCP at −1400 mV *vs.* Ag/AgCl are shown in Fig. 2. As may be seen from the figure, the spectra are dominated by a loss feature near 1100 cm^{-1} which may be attributed[9] to HSO_4^-, and gain features near 1169, 1268, 1480 and 1584 cm^{-1} due to the product P. The same product peaks were observed for the reduction of 2-CP, 4-CP, 2-BP, 4-BP, 2,3-DCP, 2,4-DCP, 2,5-DCP, 2,6-DCP, 3,4-DCP and 2,4-DBP.†

Diffusing phenol into the thin layer at pH 3 did not give absorptions that matched those in Fig. 2; however, the reduction of protons undoubtedly takes place at the same time as the
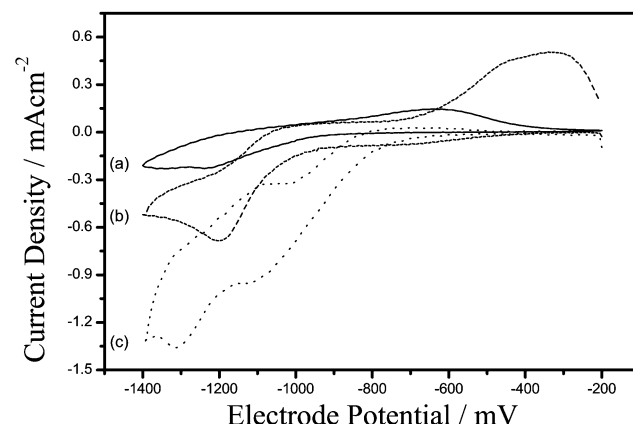
Fig. 1 Cyclic voltammograms for the reduction of 2,4-DCP in 0.1 M Na_2SO_4–H_2SO_4 at a palladised titanium electrode for no DCP (a), 1 mM DCP (b) and 20 mM DCP (c). The scan rate was 5 mV s^{-1} and the reference electrode was Ag/AgCl in KCl$_{(sat)}$ solution.
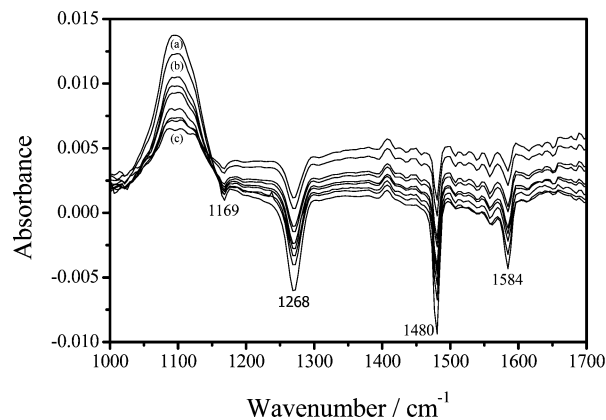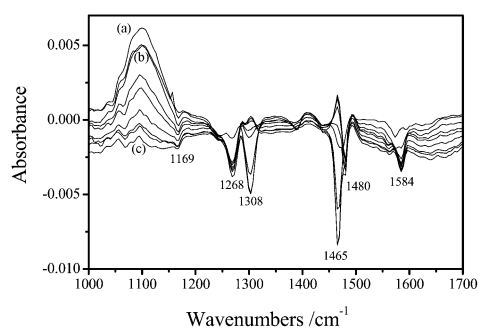
Fig. 2 FTIR spectra for the dehalogenation of 2,5-DCP at palladised titanium electrode. The electrode was set to −1400 mV and the spectra are presented with respect to the reference spectrum taken at 0 min; (a) 2 min; (b) 5 min, then every 5 min to 40 min (c).

Scheme 1 Mechanism of reduction of a chlorophenol to phenolate (all species are surface bound).

reduction of the 2,5-DCP (see representative cyclic voltammograms in Fig. 1) resulting in the pH of the thin layer rising. Diffusing phenol into the thin layer at pH 11 using Ti or Pd/Ti electrodes gave IR absorptions that exactly matched the gain features in Fig. 2, but not those of free phenol; using a Pt electrode did not result in matching absorptions. Sciré and co-workers[10] observed bands near 1276, 1492 and 1597 cm^{-1} in the IR spectra of phenol adsorbed at Al_2O_3, which they attributed to adsorbed phenolate. The features observed in Fig. 2 are very similar to those reported for phenolate on Al_2O_3 and also to those reported for thallous phenolate.[11] The data suggest that P is due to adsorbed phenolate ($C_6H_5O^-$), with the bands in Fig. 2 assigned as: 1268 cm^{-1} C–O stretch;[10] 1169, 1480 and 1584 cm^{-1} C–C stretching and C–H rocking.[11] P was not observed at a Ti electrode in the absence of Pd.

That the product was adsorbed is further supported by the data in Figs. 3 and 4, which show plots of the intensities of the features observed during the reduction of 2,4-DCP at -1400 mV: the features due to the product P reach a constant value, and do not subsequently decrease, as would be expected if the product diffused out of the thin layer into solution.

Adsorbed phenolate was the only species observed on reducing 4-CP, 4-BP and 2,3-DCP, 2,5-DCP and 2,6-DCP at potentials < -1200 mV; however, an intermediate X having

Fig. 3 FTIR spectra for the dehalogenation of 2,4-DCP at palladised titanium electrode. The electrode was set to -1400 mV and the spectra are presented with respect to the reference spectrum taken at 0 min; (a) 2 min; (b) 5 min, then every 5 min to 40 min (c).
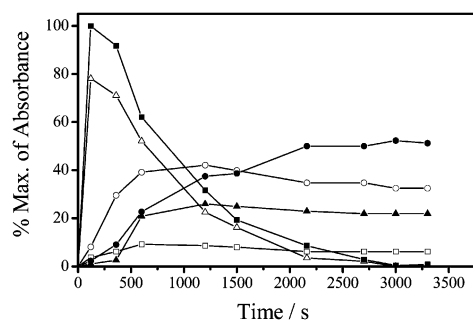
Fig. 4 Plot of the peak intensities observed for 20 mM 2,4-dichlorophenol at -1400 mV as a function of time for wave numbers 1169(□), 1268(○), 1308 (△), 1465(■), 1480 (●), 1584(▲) cm^{-1}.

absorptions near 1308 and 1465 cm^{-1} (see Figs. 3 and 4) was observed at potentials $E \le -1300$ mV on reducing 2-CP, 2-BP, 2,4-DCP, 3,4- DCP and 2,4-DBP. At -1300 mV in acid solution, X was stable, its absorptions decreasing slowly due to diffusion out of the thin layer; at lower potentials, the absorptions due to X decreased significantly faster than could be attributed to diffusion due to conversion to phenolate, the rate of loss of X being mirrored by the gain of P. As well as being insensitive to the number or identity of the halogen atoms on the aryl ring of the reactant, the absorptions of X (and P) did not change significantly when reduction was carried out in D_2O. Diffusing CP or BP into the thin layer at pH 11 and -200 mV, gave rise to X clearly suggesting that the conversion of halogenated phenol to X occurs at significantly higher potentials at elevated pH. Carrying out the experiments depicted in Figs. 2 and 3 in pH 3-citrate buffer showed no conversion of 2,4-DCP, suggesting that the pH needs to rise prior to the HDH reaction taking place.

Given the data above, the possible identities of X are limited: it does not contain a halogen or an OH group, but does appear to be of the form C_6H_5O. One possibility, and a working hypothesis for design of future experiments, is that X corresponds to a phenoxy radical stabilised by interaction with the electrode surface, with the 1308 cm^{-1} feature being attributable to the C–O stretch and the 1465 cm^{-1} band to an aromatic stretch;[12] the possibility of polymer formation is ruled out by the absence of a strong feature near 1188 cm^{-1} due to the C–O–C stretch[12] or of any other evidence for film formation (*e.g.* a decline in electroactivity with time).

Notes and references

† CP: chlorophenol, BP: bromophenol, DCP: dichlorophenol, DBP: dibromophenol.

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