

## ORIGINAL PAPER

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## Reactions at solid-liquid interfaces: contrasting chemistry at different crystal faces in the hydroxide-induced reactive dissolution of *p*-chloranil as revealed by channel flow cell voltammetry

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**Abstract** The (100), (010) and (001) faces of monoclinic crystals of the organic solid *p*-chloranil display contrasting reactivities towards hydrolytic dissolution induced by aqueous hydroxide ions. The differing behaviour is rationalised in terms of the functional groups exposed in the different faces.

**Key words** *p*-Chloranil · Channel flow cell · Solid/liquid interface

### Introduction

The fundamental study of reactions between solids and liquid phase species is the subject of rapidly growing attention [1, 2], particularly given their synthetic, environmental and industrial importance. In general, two mechanistic limits may be recognised: either the solid dissolves and then reacts with the solution phase species homogeneously or alternatively the latter may react directly with the solid reagent at the solid/liquid interface. Whilst the former type of behaviour is relatively common [3], examples of interfacial reaction have been much less frequently unambiguously characterised [4, 5]. Nevertheless, authentic interfacial solid/liquid reactions have, for example, been demonstrated for the reaction of triphenylmethyl chloride with water [4] and for the reactive dissolution of *p*-chloranil with hydroxide ions [5–7] using the methodology of channel flow cell voltammetry. If such true interfacial reactions are conducted using single crystals, it is natural to enquire as to whether different crystal faces show contrasting reac-

tivity both qualitatively in terms of the mechanism of reaction, and/or quantitatively in terms of relative interfacial rate constants. This paper reports differing behaviour of both types for the reaction of a solute ( $\text{OH}^-$ ) with an organic crystal (*p*-chloranil) as revealed by kinetic measurements obtained using the channel flow cell (CFC) method [1, 6, 7]. Figure 1 shows the crystallographic unit cell of *p*-chloranil, from which it may be deduced that the three faces (010), (100) and (001) have significantly contrasting structures with different functional groups exposed, as shown schematically in Fig. 2. Previous work [5] using polycrystalline samples has suggested that, in aqueous base, reactive dissolution of *p*-chloranil may be initiated via reaction of  $\text{OH}^-$  ions with the C=O functionality in the (010) plane. Accordingly, differential reactivity of the three faces may be anticipated as is shown, in the following, to be experimentally observable via the CFC technique.

### Experimental

Commercially available *p*-chloranil (Aldrich, 99%) was employed without further purification. Monoclinic crystal of *p*-chloranil were grown in seeded saturated solutions of *p*-chloranil in toluene cooled slowly from ca. 60 °C to 20 °C over a period of 150–200 h [5] and were characterised crystallographically on the basis of literature parameters [8]. Crystals as large as 8 mm × 13 mm × 5 mm could be obtained in this manner with the face of greatest area corresponding to the (010) plane [8].

A diagram of the CFC is given in Fig. 3; the cell is composed of a rectangular duct (about 4.5 cm long, 0.1 cm deep and 0.6 cm wide) cut in a perspex block and closed by a cover plate. The solid substrate, in the form of a single crystal, was embedded into the cover plate together with a downstream platinum foil detector electrode for the amperometric monitoring of the amount of products released. Solutions were made up using deionized water of resistivity 18 MΩ cm. The ionic strength was adjusted to the desired value by adding AR grade potassium chloride. Solution pH was modified with volumetric standard potassium hydroxide (Aldrich). Solution flow rates were obtained in the range  $10^{-3}$ – $10^{-1}$  cm<sup>3</sup> s<sup>-1</sup> using gravity feed [1, 6, 7]. In every experiment the temperature of the flow system was maintained at  $25 \pm 0.5$  °C using an air thermostat.

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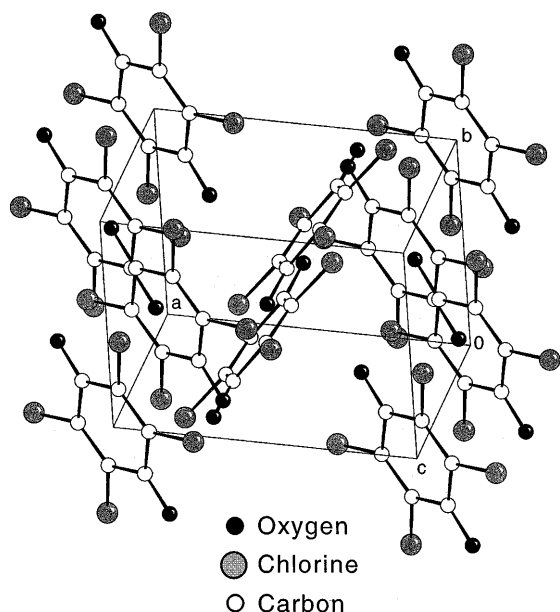


Fig. 1 The crystallographic unit cell of *p*-chloranil

The cover plate was a block of perspex with a circular hole (see Fig. 3) which supported a single crystal selected from batches grown as above according to size. The solid substrate was masked with thin Teflon tape so that a known area of the solid was exposed to the solution. A platinum amperometric detector was located downstream of the crystal so as to monitor products released from the *p*-chloranil surface. The precise geometry of the assembled crystal/detector system was measured to  $\pm 0.002$  cm with a travelling microscope. Exposed crystal lengths investigated were in the range 0.21–0.30 cm, the detector electrode length in the direction of flow was 0.30 cm whilst the gap between the crystal and the detector varied between 0.23 and 0.37 cm. Typically several cell geometries were employed to characterise each crystal face. Individual cover plates were used for 2–3 experiments before being replaced.

The surfactant dodecyltrimethylammonium bromide (C12TAB) (Aldrich, 99%) was used as received. A precise measure of solution pH was made using a pre-calibrated glass combination electrode (ABS) and meter (model 7020, Electronic Instruments). All solutions were thoroughly purged with argon (B.O.C 99.99%) prior to use.

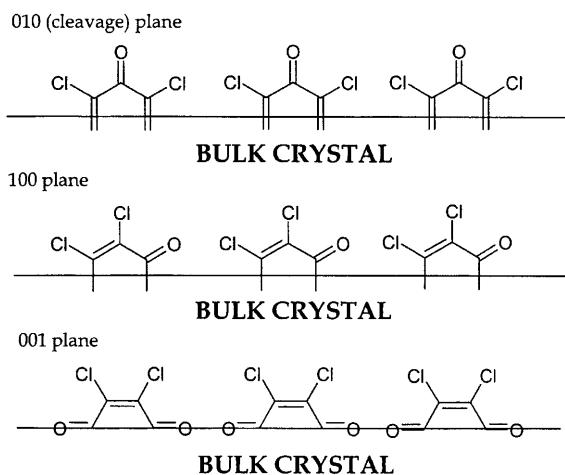


Fig. 2 A schematic diagram showing the functional groups exposed at the three faces of *p*-chloranil

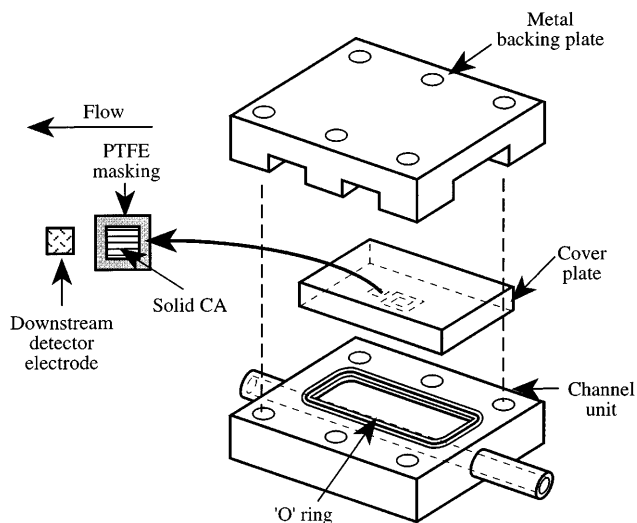


Fig. 3 Diagram of a practical channel flow cell

## Results and discussion

Channel flow cell experiments were conducted on the dissolution of each crystal face in turn using aqueous solutions containing both 0.2 M KCl and varying concentrations of KOH in the range 15–50 mM. In addition, a small concentration (7 mM) of the surfactant dodecyltrimethylammonium bromide was present to ensure full wetting of the organic surface [5].

Following reactive dissolution, *p*-chloranil is known to react via the homogeneous chemistry summarised in Fig. 4 with the intermediacy of species A, B and C; species E is discussed below. For all three crystal faces, two distinct signals were seen at the downstream detector electrode, as in the case of the dissolution of polycrystalline samples [5], consistent with the reduction (1) of species A and (2) of species B and C together [5]. A typical voltammogram is shown in Fig. 5. In all cases the transport limited current for the two voltammetric signals was recorded as a function of electrolyte volume flow rate in the range  $10^{-4}$  to  $0.26 \text{ cm}^3 \text{ s}^{-1}$ . Figures 6 and 7 show representative data recorded for the reactive dissolution of the (100) and (010) faces of *p*-chloranil in the presence of 15 mM and 30 mM potassium hydroxide.

A diversity of possible interfacial mechanisms were considered to interpret the observed current-flow rate data: a saturated concentration of *p*-chloranil at the surface followed by homogeneous hydrolysis by  $\text{OH}^-$ ; the dissolution of *p*-chloranil followed by re-precipitation in parallel with hydrolysis by  $\text{OH}^-$ ; heterogeneous reaction of solid *p*-chloranil with  $\text{OH}^-$ . The necessary kinetic modelling required to assess the different rate laws has been described fully elsewhere [5, 11], together with the protocols for differentiating between the various mechanistic possibilities. All the available data suggested, given the higher hydroxide concentrations present compared to previous studies [5, 6, 11], that the homogeneous chem-

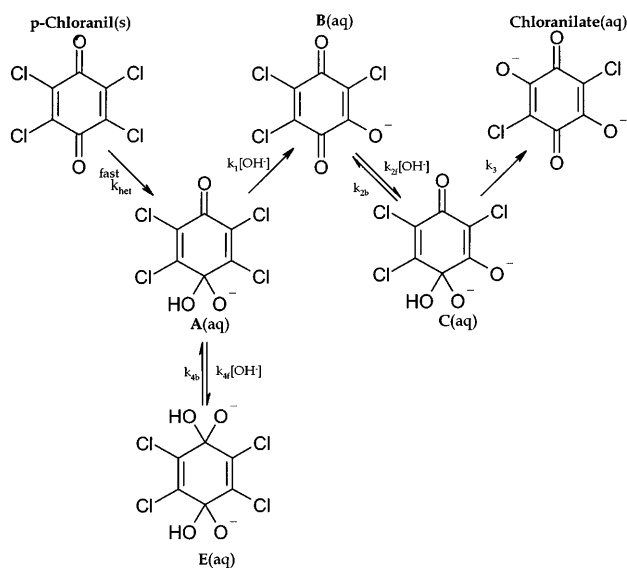


Fig. 4 The homogeneous chemistry subsequent to reactive dissolution of *p*-chloranil [5, 9, 10]

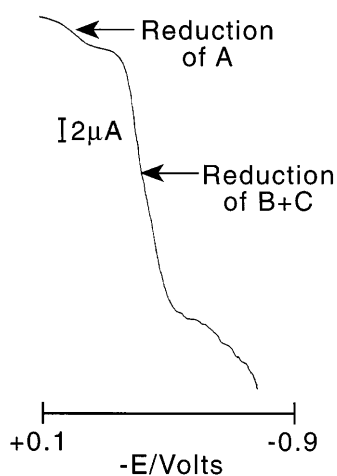


Fig. 5 Channel flow cell voltammogram recorded at a flow rate of  $0.06 \text{ cm}^3 \text{ s}^{-1}$  for the reactive dissolution of *p*-chloranil in  $0.01 \text{ M KOH}/0.2 \text{ M KCl}$ . The reduction waves are attributed to species A and B + C, respectively (see Fig. 4). Note that the voltage scan starts at a value corresponding to zero current flow

istry (Fig. 4) needed to be modified by the addition of an equilibrium between species A and species E with an equilibrium constant  $K_4 = 2.35 \times 10^5$  and a forward rate constant  $k_{4f} = 2 \times 10^6 \text{ mol}^{-1} \text{ cm}^3 \text{ s}^{-1}$ .

Turning next to the simulation of the data shown in Figs. 6 and 7, the various possible interfacial mechanisms identified above were systematically investigated. In the case of the (010) face, dissolution was concluded to be induced via heterogeneous reaction of  $\text{OH}^-$  at the solid-liquid interface. The following rate law was inferred:

$$\text{rate} = k_{(010)}[\text{OH}^-]_o$$

where  $[\text{OH}^-]_o$  is the concentration of  $\text{OH}^-$  local to the reacting interface [11] and  $k_{(010)}$  has a value of

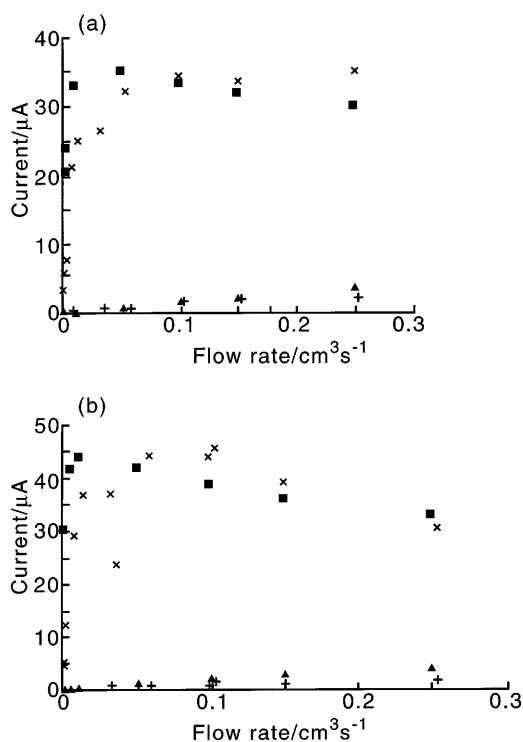


Fig. 6 Comparison between experiment (x) and simulation (■ and ▲) for the reactive dissolution of the (100) face of *p*-chloranil in a  $15 \text{ mM}$  and b  $30 \text{ mM KOH}$ . The lower curves relate to species A whilst the upper curves to species B + C

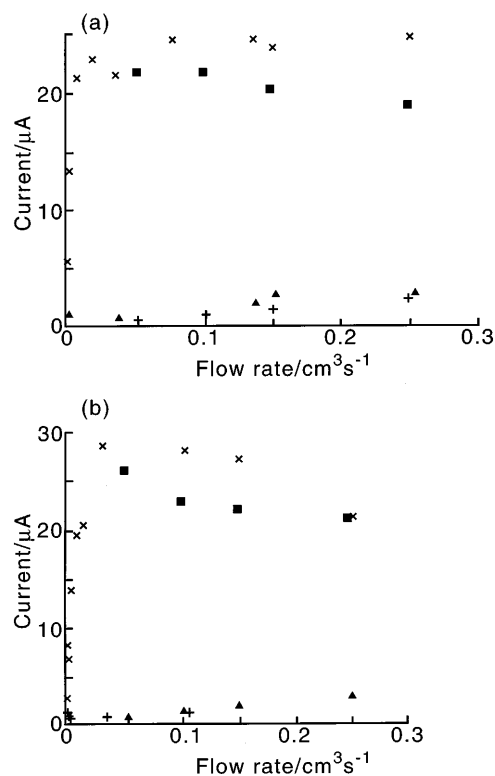
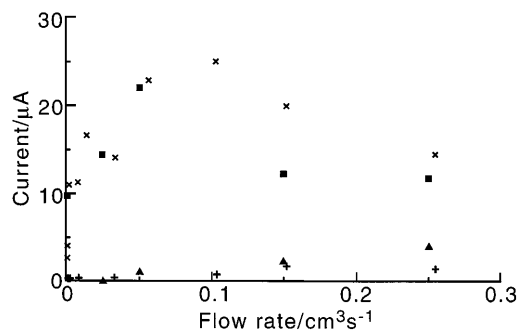


Fig. 7 Comparison between experiment (x) and simulation (■ and ▲) for the reactive dissolution of the (010) face of *p*-chloranil in a  $15 \text{ mM}$  and b  $30 \text{ mM KOH}$ . The lower curves relate to species A whilst the upper curves to species B + C



**Fig. 8** Comparison between experiment (x) and simulation (■ and ▲) for the reactive dissolution of the (010) face of *p*-chloranil in 15 mM KOH. The lower curves relate to species A whilst the upper curves to species B + C

$1.8 \times 10^{-3} \text{ cm s}^{-1}$ . For the (100) face a similar dissolution mechanism was deduced to take place but with a heterogeneous rate constant  $k_{(100)}$  of  $3.25 \times 10^{-3} \text{ cm s}^{-1}$ . Figures 6 and 7 show that the simulated behaviour for these rate laws is in satisfactory agreement with experiment.

In the case of the (001) face the experimental data showed a *significantly reduced* dissolution rate compared to that seen for the other two faces. Additionally, the flow rate corresponding to maximum current for the B + C wave was shifted to higher flow rates. Modelling indicated that a heterogeneous hydroxide-induced dissolution was implausible but that the observed current-flow rate data were consistent with a saturated surface dissolution mechanism model in which a maximum concentration of ca.  $1.25 \times 10^{-5} \text{ mol cm}^{-3}$  of species A is generated at the interface. Figure 8 shows the simulated and experimental behaviour. The modelling therefore suggests that this face reactively dissolves via a qualitatively different mechanism to the other faces.

It follows that the two faces (010) and (100) in which there are exposed C=O groups at the interface reactively dissolve via a similar mechanism involving the interfacial attack of  $\text{OH}^-$ , suggesting that the process may be

triggered by addition of hydroxide to the carbonyl groups. The markedly slower rates seen for the (001) face are consistent with the observation that this is a face rich in exposed chlorine atoms but lacking carbonyl groups adjacent to the surface. The modelled behaviour in this case may suggest that dissolution is initiated via dissolution/re-precipitation of the organic solid together with rapid homogeneous hydrolysis of *p*-chloranil. The different faces have been shown to have qualitatively and quantitatively different behaviour towards interfacial reaction.

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## Conclusions

The hydroxide-induced reactive dissolution of *p*-chloranil, which is known to occur via reaction at the solid/liquid interface, is highly sensitive to the structure of the crystal face(s) available for reaction. The (100) face shows greatest reactivity and the (001) face the least, with (010) displaying intermediate behaviour.

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## References

- Atherton JH (1994) *Res Chem Kinet* 2: 93
- Macpherson JV, Unwin PR (1995) *Prog React Kinet* 20: 185
- Compton RG, Harding MS, Atherton JH, Brennan CM (1993) *J Phys Chem* 97: 4677
- Tam KY, Compton RG, Atherton JH, Brennan CM, Doherty R (1996) *J Am Chem Soc* 118: 4419
- Booth J, Sanders GHW, Compton RG, Atherton JH, Brennan CM (1997) *J Electroanal Chem* 440: 83
- Hill E, Compton RG (1997) *Res Chem Kinet* 4: 203
- Prieto F, Hill E, Coles BA, Compton RG, Atherton JH (1999) *J Solid State Electrochem* (in press)
- Van Weperen KJ, Visser GJ (1972) *Acta Crystallogr Sect B* 28: 338
- Veltsisitas PG, Karayannis MI, Koupparis MA (1994) *Talanta* 41: 1725
- Veltsisitas PG, Karyannis MI (1987) *Analyst* 112: 1579
- Hill E (1998) D Phil thesis. Oxford University