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SHORT COMMUNICATION

Effect of surface protonation on the voltammetric behaviour of para chlorobenzophenone on glassy carbon

M. CHANDRASEKARAN, M. NOEL, V. KRISHNAN
Central Electrochemical Research Institute, Karaikudi-623006, India

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1. Introduction

The electrochemical responses on carbon surfaces depend greatly on the surface structure, surface chemistry and pretreatment procedures [1, 2]. Recently the effect of acidic functional groups present on the glassy carbon electrode (GCE) surface on the voltammetric behaviour of aromatic carbonyl compounds was investigated [3]. In addition to the voltammetric peaks noted on mercury electrodes under identical experimental conditions, benzaldehyde [4], vanillin [5], benzophenone [6] and benzil [7] gave rise to an additional prepeak on GCE due to the reduction of the adsorbed surface protonated carbonyl group. The adsorption process was also found to correlate well with the basicity of the carbonyl compounds involved [3–7]. In this work one further question on the surface protonation effect is addressed. What happens if the aromatic carbonyl compounds contain another reducible function, which itself will not exhibit a protonation effect, such as an aromatic C–X function? Will this compound still exhibit the surface protonation effect?

p-Chlorobenzophenone is a good candidate for addressing these questions. The voltammetric behaviour of this compound in aprotic solvents such as DMF on mercury is well documented [8]. Saveant *et al.*, for example, have observed three distinct cathodic peaks at slow sweep rates [8]. Constant potential electrolysis beyond the first reduction potential region established the dehalogenation reaction. The second and the third one-electron stages correspond to the formation of anion radicals and dianions of benzophenone formed during the first reduction stage [8]. At high sweep rates, *p*-chlorobenzophenone itself formed anion radicals and dianions in two 1e steps without C–Cl bond cleavage [8].

2. Experimental details

The electrochemical cell, electrode fabrication and other experimental procedures are presented elsewhere [4, 6]. The electrode activity in aqueous solution was evaluated using the cyclic voltammetric response of the ferricyanide–ferrocyanide redox couple in 0.1 M KCl [9]. In nonaqueous solvents, the voltammetric response depended greatly on the level of polishing and pretreatment. From a number of experiments it was found that a 'perfectly polished' GCE surface for nonaqueous studies was obtained by polishing the GCE with 1/0 to 4/0 emery paper for 10 min each, washing with water, trichloroethylene and the solvent supporting electrolyte (SSE) solution and introducing it into the cell in a wet condition then activating it electrochemically by cycling in the potential region of interest at $10\,\mathrm{mV\,s^{-1}}$ for 15 min, without adding the compound. An electrode activated according to this procedure produces the voltammetric response of anthracene (An) reported in the literature for mercury [10] and platinum [11] electrodes in the same potential region. Any electrode not polished to this level (eg. 40 min of polishing) gives rise to a small decrease in the peak current for An-reduction and a ΔE_p value of the $\mathrm{An/An^{\dot{-}}}$ couple greater than 59 mV. Such electrodes are referred to as 'partially polished electrodes' in the present work.

Some attempts were also made to carry out constant potential electrolysis using a 5 cm × 20 cm GC plate. During these experiments the cell current dropped substantially within a very short time and reached very low values. Hence, no detectable quantities of reduction product were obtained under the present experimental conditions, probably due to the filming effect of ketone on the GC surface.

3. Results and discussion

At very low concentrations (< 0.5 mM) *p*-chlorobenzophenone gives a single voltammetric peak at potentials less negative than −1.5 V (Fig. 1(a)–(c)) on glassy carbon. The peak current increases with concentration. At slightly higher concentrations (> 0.5 mM), in addition to this prewave, three additional peaks are observed around −1.6, −1.8 and −2.2 V, respectively (Fig. 1(d)–(e)), whereas the peak heights of these waves increase with concentration, the peak height of the first wave (hereafter denoted as the prewave) becomes almost independent of concentration. At constant sweep rate all three peak heights, other than prewave, increase with concentration and the peak potentials also shift slightly in the cathodic direction. At constant concentration, however, all four peak currents are found to increase with sweep rate.

Except for the prewave, the voltammetric response of *p*-chlorobenzophenone on the GCE in DMF is qualitatively similar to the voltammetric pattern observed on mercury [8]. The three voltammetric peaks (denoted as I, II, III in Fig. 1) are observed

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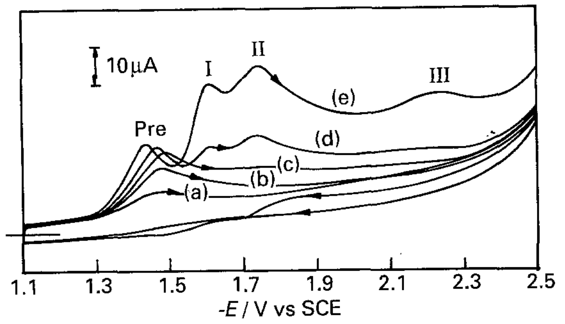

Fig. 1. Cyclic voltammograms for the reduction of *p*-chlorobenzophenone on GCE in 0.1 M TBAI/DMF at various concentrations at 20 mV s^{-1}: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.5 and (e) 1.0 mM.

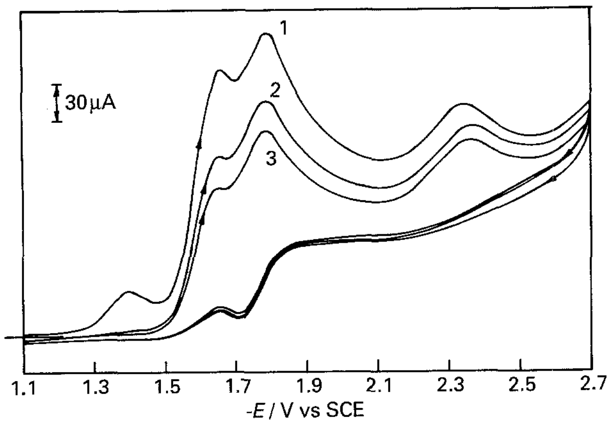

Fig. 2. Cyclic voltammograms for the reduction of *p*-chlorobenzophenone on GCE in 0.1 M TBAI/DMF in multisweeps. [*p*-chlorobenzophenon] = 5 mM at 40 mV s^{-1}. (Numbers indicate the sweeps).

on both these electrodes. On mercury the three waves were ascribed to three 1e reduction steps of *p*-chlorobenzophenone, benzophenone (formed from the cleavage of *p*-chlorobenzophenone anion radical and subsequent proton abstraction from the solvent) and benzophenone anion radical, respectively. On GCE the first reduction peak may also be ascribed to the reductive cleavage of the C–Cl bond of *p*-chlorobenzophenone. The second and third reduction peak potentials on GCE are identical with those of benzophenone reported earlier on the same electrode surface [6].

There is, however, one important difference with regard to these main waves themselves between mercury and GCE. On mercury all the three cathodic peaks correspond to a 1e processes, since the peak currents for all the three peaks were found to be almost equal [8]. However, on GCE the first cathodic peak height is more than twice the peak heights of the second and third cathodic peak. This suggests a 2e, 1e, 1e reduction sequence on GCE, since the i_p value under identical charge transfer conditions is proportional to $n^{3/2}$ rather than n. The reductive cleavage of the C–Cl bond may be represented in the following reaction scheme:

$$C_6H_5COC_6H_4Cl + e^- \rightleftharpoons [C_6H_5COC_6H_4Cl]^{\overline{\cdot}} \quad (1)$$

$$[C_6H_5COC_6H_4Cl]^{\overline{\cdot}} \xrightarrow{\text{rds}} [C_6H_5COC_6H_4]^{\cdot} + Cl^- \quad (2)$$

$$[C_6H_5COC_6H_4]^{\cdot} + e^- + H^+ \longrightarrow C_6H_5COC_6H_5 \quad (3)$$

The 2e against 1e pathway for reductive dehalogenation reactions depend on whether the free radical formation (Equation 2) occurs close to the electrode surface or far from it. In the case of GCE, it appears that the reactant and/or the 1e reduction intermediate weakly interacts with the electrode surface and, hence, C–Cl bond cleavage and further reduction also proceed through electron transfer rather than abstraction of a hydrogen atom from the solvent [8].

The prewave observed for *p*-chlorobenzophenone on GCE (Fig. 1) is again due to the surface protonation process discussed for other carbonyl compounds earlier [3]. At very small concentration of *p*-chlorobenzophenone, the electroreduction probably takes place only through surface protonation giving rise to the prewave alone (Fig. 1). Only after the surface peak current reaches a maximum value and becomes independent of concentration, are the main peaks corresponding to the bulk diffusion controlled processes observed. The surface sensitive nature of the prewave is further confirmed by multisweep cyclic voltammetric experiments. The peak current in the prewave region is noticed only in the first sweep and disappears in all subsequent sweeps suggesting the time dependent nature of this wave (Fig. 2). The peak currents of all the other three cathodic peaks persist even after many sweeps with a slight decrease in the peak current values, suggesting diffusion controlled solution phase processes in these regions.

Some cyclic voltammetric experiments were also carried out in the prepeak region alone, ie with a cathodic limit of 1.5 V. Some time effects were also noticed in these experiments. At least a time interval of 3 min is essential between each CV experiment to ensure reproducible peak potential and peak current values in this region. This is probably due to the time required for the slow surface protonation process mentioned above. However, when CV were recorded with such time intervals the peak current was found to increase linearly with sweep rate, indicating that this is indeed a surface process. Integration of the charge involved in the CV curve also showed that overall charge is much less than a monolayer charge. The results obtained for *p*-choloro-benzophenone were similar to those for benzophenone reported in greater detail [6, 12].

One further question arises regarding the prewave. Which is the reduction centre in the prepeak region? Since protonating agents in solution have practically no effect on the reductive dehalogenation of aromatic compounds, it would be difficult to presume that the C–Cl bond in *p*-cholorobenzophenone molecule is influenced by surface protonation. Hence the prewave should correspond to the reduction of surface protonated carbonyl group of *p*-choloro-benzophenone. However, this partial surface coverage by the reduction product does not inhibit direct reduction of the C–Cl bond at more negative potentials, as indicated above.

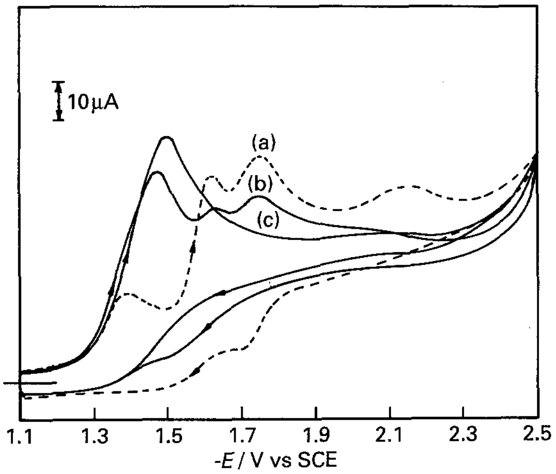

Fig. 3. Effect of benzoic acid on the reduction of *p*-chlorobenzophenone on GCE in 0.1 M TBAI/DMF at 40 mV s^{-1}. (a) - - - - 1 mM *p*-chlorobenzophenone; (b): (a) + 1 mM benzoic acid; (c): (a) + 2 mM benzoic acid.

However, in the presence of strong protonating agents like benzoic acid, the voltammetric pattern completely changes (Fig. 3). In the presence of excess benzoic acid, all the four peaks noted above merge into a single peak. The peak potential also shifts in the positive direction to a significant extent (Fig. 3). In this condition, the carbonyl group is easily protonated and, hence, this, rather than the C–Cl bond, becomes the reduction centre. Benzoic acid protonates the reactant *p*-chlorobenzophenone molecule itself.

$$C_6H_5COC_6H_4Cl + H^+ \rightleftharpoons C_6H_5\overset{+}{C}OHC_6H_4Cl \quad (4)$$

This protonated species probably undergoes a 2e transfer at carbonyl group leading to the formation of chlorocarbinol.

$$C_6H_5\overset{+}{C}OHC_6H_4Cl + 2e^- + H^+ \longrightarrow C_6H_5CHOHC_6H_4Cl \quad (5)$$

This is responsible for the disappearance of all the three main waves of *p*-chlorobenzophenone reduction in the presence of benzoic acid and the appearance of a single (probably 2e) wave in the prewave region. The reduction of the carbonyl group in the presence of benzoic acid supports the view that the reduction in the prewave region due to the surface protonation should occur at the carbonyl group.

4. Conclusion

Two major differences between the voltammetric behaviour of *p*-chlorobenzophenone on GC and mercury electrodes are apparent. The dehalogenation process follows a 2e pathway on GCE when compared to a 1e pathway on mercury. A prewave due to the reduction of surface protonated carbonyl functions is noticed prior to the reduction of the C–Cl bond itself on GC.

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