# Cyclic Voltammetry & Chronoamperometry of p-Phenylbenzophenone

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Electrochemical reduction of p-phenylbenzophenone has been investigated in 50% solvent-water mixtures in acidic, neutral and basic media using cyclic voltammetry and chronoamperometry at hanging mercury drop electrode. The nature of the reduction is discussed. Diffusion coefficients and heterogeneous rate constants are reported.

In continuation of our earlier studies[1,2] on the electrochemical reduction of organic depolarizers, the present study deals with the electrochemical reduction of p-phenylbenzophenone in 50% aq. isopropanol, 50% aq. dimethylformamide and 50% aq. dioxane in acidic (0.1 M hydrochloric acid), neutral (0.1 M potassium chloride) and basic (0.1 M sodium hydroxide) media using cyclic voltammetry and chronoamperometry at hanging mercury drop electrode (HMDE).

The solution of p-phenylbenzophenone (Aldrich Chemicals) was prepared in the supporting electrolyte solutions containing 50% solvent-water (v/v) mixtures. Isopropanol, dimethylformamide (DMF) and dioxane, were purified by standard methods[3]. Hydrochloric acid, potassium chloride and sodium hydroxide (AR) were used as supporting electrolytes. Doubly distilled water was used to prepare all the solutions.

Electrochemical module and the cell assembly (model 370, Princeton Applied Research Corporation) were used to record the cyclic voltammograms and chronoamperometric curves. HMDE used as the working electrode had an area of 0.01542 cm². The experimental procedure employed has been described elsewhere[4].

p-Phenylbenzophenone undergoes irreversible reduction in all the media employed as revealed by the absence of peak in the reverse scan and variation of peak potentials, $E_p$, with voltage scan rate, $v$ [For example, $E_p$ varied from $-1.51$ V to $-1.56$ V (vs SCE) for a change in $v$ from 0.02 Vs$^{-1}$ to 0.50 Vs$^{-1}$ in 50% aq. isopropanol with 0.1 M sodium hydroxide as the supporting electrolyte]. Linear plots of $i_p$ (peak current) versus $v^{1/2}$ passed through the origin indicating the diffusion-controlled nature of the electrode process. Table 1 gives cyclic voltammetric data of p-phenylbenzophenone.

Table 1—Cyclic Voltammetric Data of p-Phenylbenzophenone in Different Supporting Electrolytes & Solvent-Water Mixtures

[Voltage sweep rate = 0.1 Vs$^{-1}$; depolariser conc. = 1.2 m$M$]

| Parameter | Supporting electrolyte | | |
|---|---|---|---|
| | 0.1 M HCl | 0.1 M KCl | 0.1 M NaOH |
| | 50% Aq. isopropanol | | |
| $-E_p$ (V, vs SCE) | 0.910 | 1.320 | 1.530 |
| $i_p$ ($\mu$A) | 12.98 | 25.25 | 29.55 |
| $\alpha n_a$ | 0.96 | 0.87 | 1.20 |
| $D \times 10^5$ C.V.: (cm² s$^{-1}$) | 6.12 | 5.79 | 6.13 |
| C.A.: | 5.83 | 4.28 | 5.83 |
| $k_{f,h}^{\circ}$ (cm s$^{-1}$) | $1.27 \times 10^{-17}$ | $2.28 \times 10^{-22}$ | $7.41 \times 10^{-34}$ |
| | 50% Aq. DMF | | |
| $-E_p$ (V, vs SCE) | 0.920 | 1.465 | 1.380 |
| $i_p$ ($\mu$A) | 13.42 | 29.51 | 28.76 |
| $\alpha n_a$ | 0.96 | 1.20 | 1.20 |
| $D \times 10^5$ C.V.: (cm² s$^{-1}$) | 6.39 | 5.77 | 5.35 |
| C.A.: | 4.82 | 3.78 | 4.82 |
| $k_{f,h}^{\circ}$ (cm s$^{-1}$) | $8.87 \times 10^{-18}$ | $1.49 \times 10^{-32}$ | $7.28 \times 10^{-31}$ |
| | 50% Aq. dioxane | | |
| $-E_p$ (V, vs SCE) | 0.880 | 1.370 | — |
| $i_p$ ($\mu$A) | 12.79 | 27.55 | — |
| $\alpha n_a$ | 0.96 | 1.20 | — |
| $D \times 10^5$ C.V.: (cm² s$^{-1}$) | 6.05 | 6.51 | — |
| C.A.: | 5.10 | 4.68 | — |
| $k_{f,h}^{\circ}$ (cm s$^{-1}$) | $3.86 \times 10^{-17}$ | $1.35 \times 10^{-30}$ | — |

The number of electrons ($n$) taking part in the electroreduction of p-phenylbenzophenone was calculated by comparing the experimental and theoretical current function values, i.e. $i_p/v^{1/2}C$ using the diffusion coefficient of p-phenylbenzophenone in borate buffer of pH 9.2 (ref. 1); $n$ was found to be two in 50% aq. isopropanol with 0.1 M sodium hydroxide as the supporting electrolyte. By comparing the $i_p/v^{1/2}C$ values in other media, the values of $n$ were found to be two in 0.1 M potassium chloride and 0.1 M sodium hydroxide and one in 0.1 M hydrochloric acid in all the solvent-water mixtures employed. The one-electron reduction in acid mediium may be due to the fact that because of high proton availability the reduction leads to the formation of pinacol[2] by dimerisation following the one-electron addition, whereas in neutral and alkaline media the two-electron reduction yields diphenylcarbinol[1].

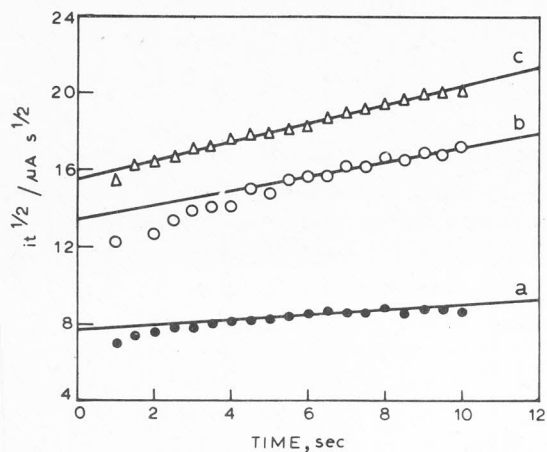The diffusion coefficients, $\alpha n_a$ values and heterogeneous rate constants ($k_{f,h}^{\circ}$) have been

Fig. 1—Plots of $it^{1/2}$ versus $t$ for the reduction of $p$-phenylbenzophenone in 50% isopropanol-water (v/v) in (a) 0.1 $M$ hydrochloric acid (b) 0.1 $M$ potassium chloride and (c) 0.1 $M$ sodium hydroxide at [depolariser] = 1.2 m$M$

evaluated and the data are presented in Table 1. The equation given earlier[1] was used for the evaluation of $k^{\circ}_{f,h}$. The rate constants are almost same in 0.1 $M$ hydrochloric acid and 0.1 $M$ sodium hydroxide. However, in neutral medium (0.1 $M$ potassium chloride), the rate constants are higher in aq. isopropanol than in aq. DMF and aq. dioxane. This is attributed to the protic nature of isopropanol; DMF and dioxane are aprotic in nature (in isopropanol the reaction involves the addition of proton). The rate constants are also found to decrease with increase in $p$H as reflected in the shift of $E_p$ values.

Step potentials for the chronoamperometric studies were chosen from diffusion-limited regions of the corresponding cyclic voltammograms. The reduction process was found to be a clean one, without any adsorption complication as can be seen from $it^{1,2}$ versus $t$ plots (Fig. 1) in the reduction of $p$-phenylbenzophenone in 50% aq. isopropanol. Similar plots have been obtained in 50% aq. DMF and 50% aq. dioxane. Diffusion coefficients evaluated from chronoamperometric data using Cottrell equation are given in Table 1.

### References

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