# Cyclic Voltammetric Study of 4'-Chloro-2-Hydroxy-4-Methoxybenzophenone

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The electrochemical reduction of carbonyl group present in 4'-chloro-2-hydroxy-4-methoxybenzophenone has been studied employing cyclic voltammetric technique in 40% (v/v) ethanol-water and DMF-water mixures in the pH range 4.0–11.8. The reduction of keto group follows one electron irreversible reduction process in the pH range 4.0–8.2 and two electron irreversible reduction process in the above pH range studied. The effect of solvent on the reduction process is discussed. The diffusion coefficient and forward rate constant values have been evaluated and a suitable reduction mechanism is proposed.

## INTRODUCTION

Aromatic ketones resemble quite closely the aromatic aldehydes in their electrochemical behaviour. Benzophenone gives two polarographic waves in alkaline buffers on dropping mercury electrode[1]. Formation of benzpinacol in acidic media and benzocarbinol in more alkaline media was observed by Pasternak[2]. Benzophenones having different substituents in the phenyl ring were studied extensively by Jayarama Reddy and co-workers[3,4]. The amide group present in some heterocyclic drugs is studied by Ramachandraiah and co-workers[5,6]. In the present study, 4'-chloro-2-hydroxy-4-methoxybenzophenone has been studied under hanging mercury drop electrode (HMDE) where single cathodic peak is observed in the pH range 4.0–8.2 and two cathodic peaks in the above pH range where the second one is found to merge with buffer discharge.

## EXPERIMENTAL

The title compound supplied by Aldrich Chemical Co. Ltd. was recrystallised in ethanol and the purity was checked by melting point determination. AR grade chemicals were used for the preparation of supporting electrolytes. All experiments were carried out at 298 ± 1 K. Cyclic voltammograms and differential pulse

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polarograms were obtained by Polarographic Analyzer Model 264A and Static Mercury Drop Electrode Model 303 coupled with an X-Y Recorder Model RE 0150 (PARC). The HMDE of area 0.0096 cm$^2$ was used as working electrode and Ag/AgCl(s), Cl$^-$ as reference electrode. Elico Digital pH Meter was used for pH measurements.

## RESULTS AND DISCUSSION

The sample under consideration gave single well defined peak in the cyclic voltammogram under HMDE in the pH range 4.0–8.2. In more basic range a second peak is also observed at more negative potential which is found to merge with buffer discharge. A typical cyclic voltammogram obtained in ammonia buffer of pH 8.2 is shown in Fig. 1. The cathodic peak is attributed to the reduction of
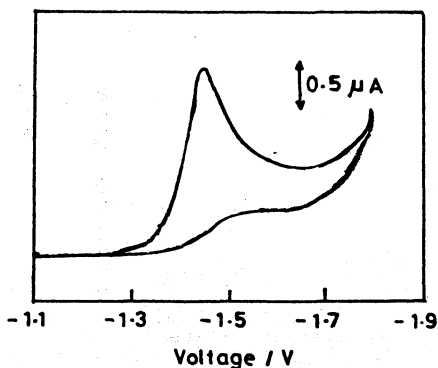


Fig. 1   Typical cyclic voltammogram of 4'-chloro-2-hydroxy-4-methoxybenzophenone in ammonia buffer of pH 8.2 at scan rate 50 mV s$^{-1}$, concentration 0.3 mM and solvent 40% ethanol.

carbonyl group present in the molecule. The reduction process of this group is found to be irreversible as seen from the absence of anodic peak in the reverse voltage scan (Fig. 1) and also from the shift of peak potential towards more negative side with increase of scan rate and concentration. It is also found to be diffusion controlled and adsorption free in the pH range 4.0–8.2 as evidenced by the linear plots of $i_p$ vs. $v^{1/2}$ passing through the origin (Fig. 2). Slight adsorption complications are observed in basic media. The cleavage of carbon-chlorine bond is not noticed in the present study. This can be attributed to the possible formation of a stable free radical anion and its immediate solvation in the solution. In the case of the electrochemical reduction of $m$-chlorobenzophenone[7], it was shown that the free radical anion formed by uptake of one electron was more stable even in non-aqueous media such as liquid ammonia.

The number of electrons involved in the reduction process of keto group is calculated to be one in the pH range 4.0 to 8.2 and two in the above pH range
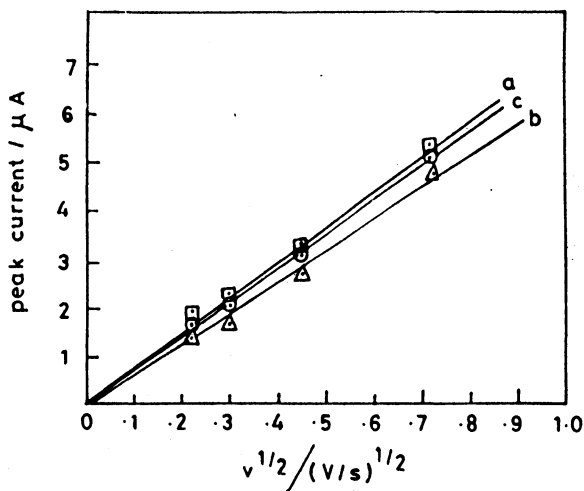
Fig. 2  $i_p$ vs $v^{1/2}$ plots of 4'-chloro-2-hydroxy-4-methoxybenzophenone in 40% ethanol in (a) acetate buffer of pH 4.0, (b) acetate buffer of pH 5.5 and (c) ammonia buffer of pH 8.2.

studied. It is also supported by the values obtained from the differential pulse polarogram using the equation[8].

$$\Delta W_{1/2} = \frac{3.52\, RT}{nF}\, mV \qquad (1)$$

where $\Delta W_{1/2}$ is half peak width in millivolts and n the number of electrons involved in the reduction process and R, T and F have their usual significance.

The peak current values vary in a bell-shaped form with increase in pH. This can be attributed to the formation of *geminal*-diol anion[9]. In acidic solutions, the rate constant becomes significant leading to the formation of more and more *geminal*-diol anion which in turn increases the free carbonyl form.

The kinetic parameters like diffusion coefficients (D) and heterogeneous forward rate constants ($k^o_{f, h}$) have been evaluated utilizing the following equations[10, 11],

$$i_p = 3.01 \times 10^5\, n\, (\alpha n_a)^{1/2} AD^{1/2} Cv^{1/2} \qquad (2)$$

$$-E_p = -1.14\, \frac{RT}{\alpha n_a F} + \frac{RT}{\alpha n_a F}\, \ln\left(\frac{k^o_{f, h}}{D^{1/2}}\right) - \frac{RT}{2\alpha n_a F}\, \ln\,(\alpha n_a v) \qquad (3)$$

where $i_p$ is peak current in $\mu A$, $\alpha$ the transfer coefficient, A the area of the HMDE in $cm^2$, C the concentration of the electroactive species k in mM.
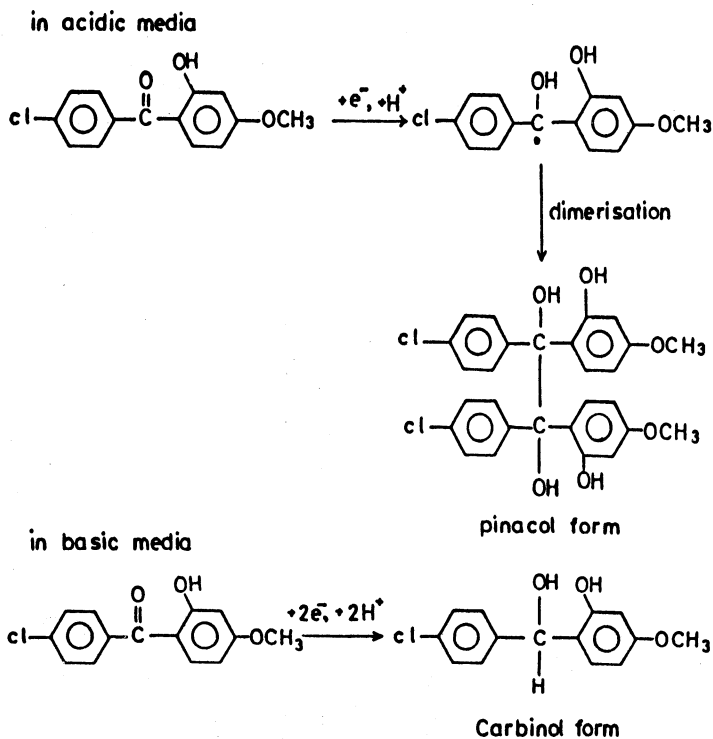
Typical kinetic data is presented in Table-1. The diffusion coefficient values are smaller in magnitude in solutions of pH range 10.2 to 11.8 as compared to those in other supporting electrolytes. This may be accounted for by the fact that

the diffusion coefficient values obtained from the peak current values corresponding to 40–50% of the two electron diffusions peak and hence observed decrease in the diffusion coefficient values in the above supporting electrolytes of pH range 10.3 to 11.8. The $k_{f,h}^0$ values are found to increase considerably as expected with the increase of pH in both the media. The rate constant values obtained in DMF-water mixture are found to be less than those calculated in ethanol-water mixture as expected since the former is aprotic. As the solvent composition increases, the $E_p$ value shifts to more negative side due to the adsorption of solvent molecules on the electrode surface.

TABLE-1
TYPICAL CYCLIC VOLTAMMETRIC DATA OF 4'-CHLORO-2-HYDROXY-
4-METHOXYBENZOPHENONE

| Concn. | 0.3 mM | | | | (a) 40% Ethanol |
| Scan rate | 50 mV s$^{-1}$ | | | | (b) 40% DMF |

| Supporting electrolyte | $-E_p$ (V) | $i_p$ ($\mu A$) | $D \times 10^5$ (cm$^2$ s$^{-1}$) | $k_{f,h}$ (cm s$^{-1}$) |
|---|---|---|---|---|
| Acetate buffer of pH 4.0 | (a) 1.38 | 1.55 | 2.00 | $1.26 \times 10^{-21}$ |
| Acetate buffer of pH 5.5 | (a) 1.41 | 1.45 | 1.75 | $4.60 \times 10^{-22}$ |
| | (b) 1.45 | 1.00 | 0.69 | $1.09 \times 10^{-26}$ |
| Ammonia buffer of pH 8.2 | (a) 1.46 | 1.75 | 2.46 | $2.13 \times 10^{-23}$ |
| | (b) 1.52 | 0.95 | 0.75 | $9.76 \times 10^{-24}$ |
| Carbonate buffer of pH 10.3 | (a) 1.62 | 0.60 | 1.21 | $5.57 \times 10^{-25}$ |
| | (b) 1.65 | 0.60 | 0.70 | $1.43 \times 10^{-36}$ |
| Britton-Robinson buffer of pH 11.8 | (a) 1.68 | 0.75 | 1.56 | $3.02 \times 10^{-30}$ |
| | (b) 1.70 | 0.40 | 0.34 | $9.20 \times 10^{-38}$ |

Based on the results obtained, it can be concluded that the title compound undergoes irreversible one-electron addition leading to the formation of the corresponding pinacol in the supporting electrolytes of pH 4.0 to 8.2 and two electron addition forming the corresponding carbinol in the orther supporting electrolytes as shown in Scheme. The proton involvement in the rate-determining step is evidenced from linear plots of $E_p$ vs pH. Due to the inductive effect offered by the methoxy and hydroxy groups, the cabonyl group is reduced at more cathodic potential when compared to that of unsubstituted benzophenone in similar conditions[3].

in acidic media



dimerisation

pinacol form

in basic media



Carbinol form

## ACKNOWLEDGEMENT

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