

## Electrochemical Reduction of *p*-Hydroxyphenacyl Bromide

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The electrochemical reduction of carbon-bromine bond in *p*-hydroxyphenacyl bromide has been studied employing Differential pulse polarographic and cyclic voltammetric techniques in 40% (v/v) ethanol-water mixture in a suitable pH range from 5.5 to 10.0. The effect of solvent and the nuclear substitution on the reduction rate constant values are evaluated and reported. The possible electrochemical reduction mechanism is proposed.

### INTRODUCTION

Electrochemical reduction of carbon-halogen bond has been studied polarographically by several workers<sup>1-3</sup>. The anomalous behaviour of carbon-bromine bond cleavage in phenacyl bromides, where additional waves due to hydrolysis products are observed, is studied by Elving and others<sup>3</sup>. The ease of reduction of C-Br bond in  $\alpha$ -haloketones is facile when compared to the analogous normal halides. The presence of keto group adjacent to the C-Br bond facilitates C-Br cleavage in  $\alpha$ -haloketones. Jayarama Reddy *et al.*<sup>4-6</sup> have extensively studied these systems employing cyclic voltammetric, chronopotentiometric and chronoamperometric techniques. An attempt is made in the present investigation to study the electrochemical reduction of *p*-hydroxyphenacyl bromide at dropping mercury electrode (DME) and having mercury drop electrode (HMDE).

### EXPERIMENTAL

*p*-Hydroxyphenacyl bromide was prepared by the bromination<sup>7</sup> of *p*-hydroxyacetophenone. The product was recrystallised from benzene and the melting point was found to be 129°C (lit. 130°C)<sup>7</sup>. The test solutions were prepared by dissolving the required quantity of the substance in the solvent and made up with the supporting electrolyte to get the desired concentration. AnalaR grade chemicals were used for the preparation of the supporting electrolytes in doubly distilled water. The test solution was purged with pure nitrogen and then voltammograms were obtained. All experiments were carried out at  $301 \pm 1$  K.

Voltammograms were taken by Polarographic Analyser Model 264 A and

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SMDE 303 (PARC) coupled with an X-Y Recorder Model RE0150 (Allen Datagraph). The electrode of area  $0.0096 \text{ cm}^2$  is used as working electrode and  $\text{Ag}/\text{AgCl}(\text{s}), \text{Cl}^-$  as reference electrode in both the techniques. Elico Digital pH meter was used for pH measurements.

## RESULTS AND DISCUSSION

### Differential pulse polarographic results

Two waves were observed for the reduction of *p*-hydroxyphenacyl bromide over a pH range from 5.5 to 9.0. In more acidic and more basic media, well-defined waves were not obtained. A typical differential pulse polarogram obtained in ammonia buffer of pH 9.0 is shown in Fig. 1, where the two waves appeared at  $-0.28 \text{ V}$  and  $-1.62 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}(\text{s}), \text{Cl}^-$  electrode. The first wave is attributed to the reduction of C-Br bond since the  $E_p$  of second wave is found to coincide with that of the keto group in the corresponding acetophenone. Variation of  $E_p$  with increase in concentration of the depolarizer indicates the irreversible nature of the electron transfer in the C-Br bond cleavage. Typical kinetic parameters like transfer coefficient ( $\alpha_a$ ), diffusion coefficient ( $D$ ) and forward rate constants ( $k_{\text{f}}^0$ ) have been evaluated and reported (Table 1).

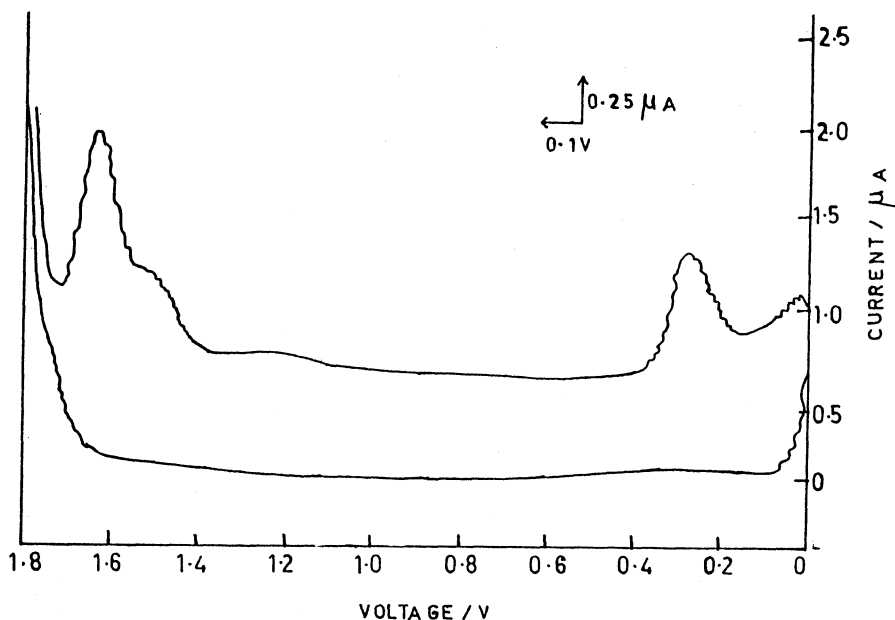


Fig. 1 Typical differential pulse polarogram of *p*-hydroxyphenacyl bromide.  
 Supporting electrolyte: Ammonia buffer of pH 9.0  
 Drop time : 1 Sec.  
 Concentration : 0.2 mM  
 Solvent : 40% Ethanol

TABLE 1  
TYPICAL DIFFERENTIAL PULSE POLAROGRAPHIC DATA OF  
*p*-HYDROXY PHENACYL BROMIDE (C-Br bond reduction)

Sl. No.	Supporting electrolyte	$-E_p/V$	$i_m/\mu A$	$\alpha n_a$	$D \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	$k_{f,h}^0 \text{ cm s}^{-1}$
1.	Acetate buffer of pH 5.5	0.14	0.43	0.93	0.845	$4.395 \times 10^{-10}$
2.	Acetate buffer of pH 6.5	0.18	0.67	1.18	2.054	$2.963 \times 10^{-12}$
3.	Ammonia buffer of pH 8.2	0.24	0.60	1.18	1.647	$1.186 \times 10^{-13}$
4.	Ammonia buffer of pH 9.0	0.28	0.47	0.92	1.011	$2.954 \times 10^{-12}$
5.	Carbonate buffer of pH 10.0			Ill-defined peaks		

Conc.: 0.1 mM; Drop time: 1 sec.; Solvent: 40% ethanol

### Cyclic voltammetric results

Two cathodic peaks were obtained for the reduction of the title compound out of which the first may be due to the reduction of C-Br bond and the second one may be due to the reduction of keto group. The second peak was found to merge with buffer discharge in acidic media. A typical cyclic voltammogram in ammonia buffer of pH 8.2 is shown in Fig. 2. The reduction peak of C-Br bond is found to be diffusion-controlled and adsorption-free in all the media studied as seen

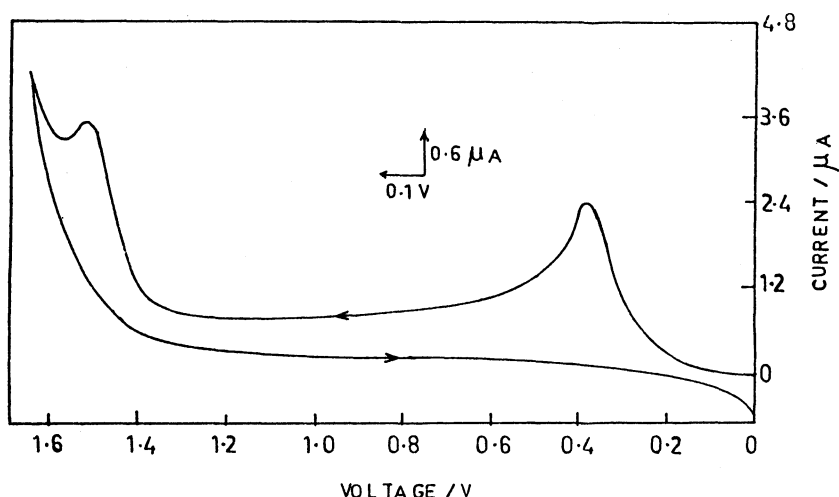


Fig. 2 Typical cyclic voltammogram of *p*-hydroxyphenacyl bromide.  
Supporting electrolyte: Ammonia buffer of pH 8.2  
Concentration : 1.0 mM  
Scan Rate :  $50 \text{ mVs}^{-1}$   
Solvent : 40% Ethanol

from the  $i_p$  vs.  $v^{1/2}$  plots. The electron transfer in the C-Br cleavage is found to be irreversible as seen from the shift of peak potential towards negative side and the absence of anodic peak in the reverse scan. Typical kinetic data are reported in Table 2.

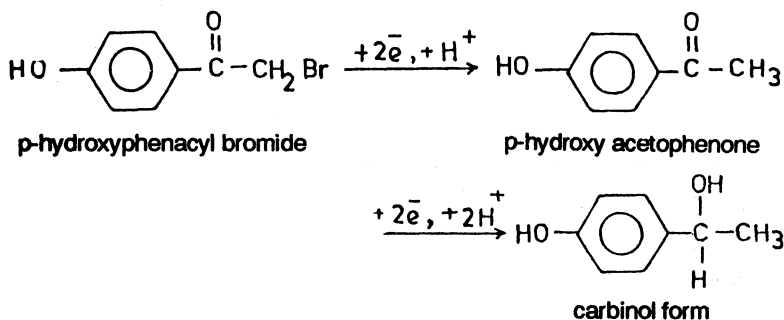
TABLE 2  
TYPICAL CYCLIC VOLTAMMETRIC DATA OF  
*p*-HYDROXYPHENACYL BROMIDE (C-Br bond reduction)

Sl. No.	Supporting electrolyte	$-E_p/V$	$i_m/\mu A$	$\alpha n_a$	$D \times 10^{-6}$ $cm^2 s^{-1}$	$k_{f,h}^0$ $cm s^{-1}$
1.	Acetate buffer of pH 5.5	0.34	4.20	1.20	3.352	$6.111 \times 10^{-3}$
2.	Acetate buffer of pH 6.5	0.36	2.22	0.43	2.575	$7.701 \times 10^{-6}$
3.	Ammonia buffer of pH 8.0	0.37	2.88	0.56	3.350	$2.272 \times 10^{-6}$
4.	Ammonia buffer of pH 9.0	0.37	1.45	1.20	3.995	$1.716 \times 10^{-10}$
5.	Carbonate buffer of pH 10.0	0.48	2.82	0.53	3.400	$1.418 \times 10^{-10}$

Conc.: 1.0 mM; Solvent: 40% Ethanol; Sweep rate: 50 mVs<sup>-1</sup>

From the result, thus obtained, it is seen that the cleavage of C-Br bond involves in an irreversible two-electron addition. Hydroxyl substituent is found to have no noticeable effect on the reduction of C-Br bond since the substituent is two carbon atoms away from the C-Br bond. The forward rate constant values are found to decrease slightly with increase of pH as expected. With the increase in solvent composition in the solution, the  $E_p$  values are found to shift towards negative side indicating the reduction process to be difficult which may be due to the possible adsorption of solvent molecules on the electrode surface<sup>8</sup>.

From controlled potential electrolysis results, the product at the potential of the first wave was found to be *p*-hydroxyacetophenone. It is also found that the number of electrons involved in the reduction of keto group is two from millicoulometric results. Hence, the reduction mechanism for *p*-hydroxyphenacyl bromide may be proposed as follows:



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## REFERENCES

1. I. Rubinstein and E. Kariv, *Tetrahedron*, **33**, 1487 (1976).
2. F. Barba, M.P. Velasco and A. Guirado, *Electrochim. Acta*, **28**, 259 (1983).
3. J. Philip, Elving and T. Joseph, Leone, *J. Am. Chem. Soc.*, **82**, 5076 (1960).
4. A.S. Reddy and S.J. Reddy, *J. Indian Chem. Soc.*, **63**, 752 (1986).
5. K.M. Rao and S.J. Reddy, *J. Indian Chem. Soc.*, **65**, 411 (1988).
6. \_\_\_\_\_, *Asian J. Chem.*, **1**, 47 (1989).
7. Buu Hoi, Xuong and Lavit, *J. Chem. Soc.*, 1034 (1954).
8. K. Ganapathi and M. Ramanujam, *Indian J. Chem.*, **21A**, 1031 (1982).

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