

**VOLTAMMETRIC REDUCTION OF ACETOPHENONE ON METAL AND GLASSY CARBON ELECTRODES**

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Voltammetric behaviour of acetophenone reduction on glassy carbon (GC) and lead electrodes were investigated in acid, neutral and alkaline media and the results were also compared with the literature data on Hg electrode. In alkaline media, the electroreduction on GC electrode takes place at a much more negative potential as compared to metal electrodes. In acidic medium the electroreduction takes place at closer potential ranges on all the three electrodes. Theoretically on the basis of lower density of states of electron on carbon electrodes, a much slower charge transfer rate on GC electrode should be expected under all the conditions. The experimental observations of the present work is explained by assuming that the acidic surface functional groups present on GC surface catalyses the electroreduction of acetophenone in acid medium.

**Key words:** Voltammetry, acetophenone, glassy carbon electrode

**INTRODUCTION**

Acetophenone is one of the comprehensively investigated carbonyl compounds in polarography. The redox behaviour in a wide range of aqueous [1-5], aqueous ethanolic [6-7] and non-aqueous [8-10] media on Hg electrode has been reported. Effects of complexing inorganic species on the redox behaviour are also known [11]. However the voltammetric behaviour on other electrodes has not received much attention except for the electrochemical synthesis of diphenyl carbinol from acetophenone on solid electrodes [12-14]. Since the preparative work is thus carried out on solid electrodes, voltammetric investigations on these electrodes were initiated. In this work, the voltammetric responses of acetophenone reduction on glassy carbon (GC) and lead electrodes are reported and the results are also compared with the polarographic responses on Hg electrode reported in the literature [3].

**EXPERIMENTAL**

5mm dia. glassy carbon (GC - A type, Tokai Mfg. Co. Tokyo) and high purity lead (99.99%) tight-fitted into teflon holder (area 0.2 cm<sup>2</sup>) were used as working electrodes. Connections were taken from the inner side of the teflon holder using copper rod with screw at one end. Platinum foil was used as counter electrode and saturated calomel electrode (SCE) served as the reference electrode. A typical H type cell with provision for deaeration was used. The temperature was kept at 298 ± 1K.

GC electrode was electrochemically activated by potential cycling and the activity was established using ferricyanide/ferrocyanide redox system as described earlier [15].

Lead electrode was also washed, cleaned and inserted into the electrochemical cell by the usual procedure. Care was taken not to polarise the electrode to the anodic side of the rest potential and the electrode was not kept under open-circuit conditions for longer periods, in order to avoid formation of PbSO<sub>4</sub> and thereby affecting reproducibility. Details on electrode pretreatment have been earlier reported [16].

All the solutions were prepared using triple distilled water and all the chemicals used were of analar grade.

**RESULTS**

Typical cyclic voltammograms of 20mM acetophenone in 0.1M 50% alcoholic H<sub>2</sub>SO<sub>4</sub> at various sweep rates on GC electrode are presented in Fig.1. A single well defined cathodic peak is noticed.

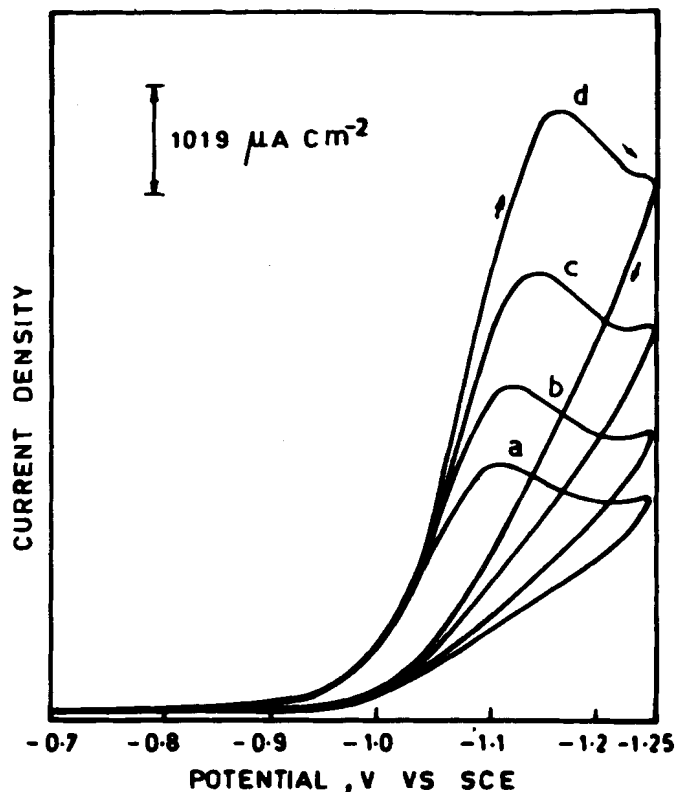


Fig.1: Cyclic voltammogram of acetophenone (20 mM) in 0.17 M H<sub>2</sub>SO<sub>4</sub>/0% (v/v) ethanol on GC electrode at sweep rates (mV.s<sup>-1</sup>): (a) 20 (b) 40 (c) 80 (d) 160

No anodic peak is observed in the anodic sweep. The peak current ( $i_p$ ) of the cathodic process is found to be proportional to acetophenone concentration ( $C_A$ ) at constant sweep rates. The  $i_p$  is also directly proportional to  $\nu^{1/2}$  at constant  $C_A$  where  $\nu$  denotes the sweep rate. The peak current constant value ( $I_p$ ) =  $i_p / AC_A \nu^{1/2}$  (where A is area of electrode) is found to be a constant at low concentrations of acetophenone and low sweep rates. Slight decrease in the  $I_p$  is noticed at higher sweep rates ( $>100 \text{ mV} \cdot \text{s}^{-1}$ ) and higher concentration ( $> 20 \text{ mM}$ ).

Similar voltammetric behaviour was noticed in 50% alcoholic  $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$  mixtures, McIlvaine buffer,  $\text{Na}_2\text{SO}_4$ , NaOH and tetra n-butyl ammonium hydroxide media as well. Typical cyclic voltammograms in alcoholic NaOH and n-butyl ammonium hydroxide solutions on GC electrodes are presented in Figs.2 and 3 respectively. The peak potential ( $E_p$ ) and  $I_p$  of the

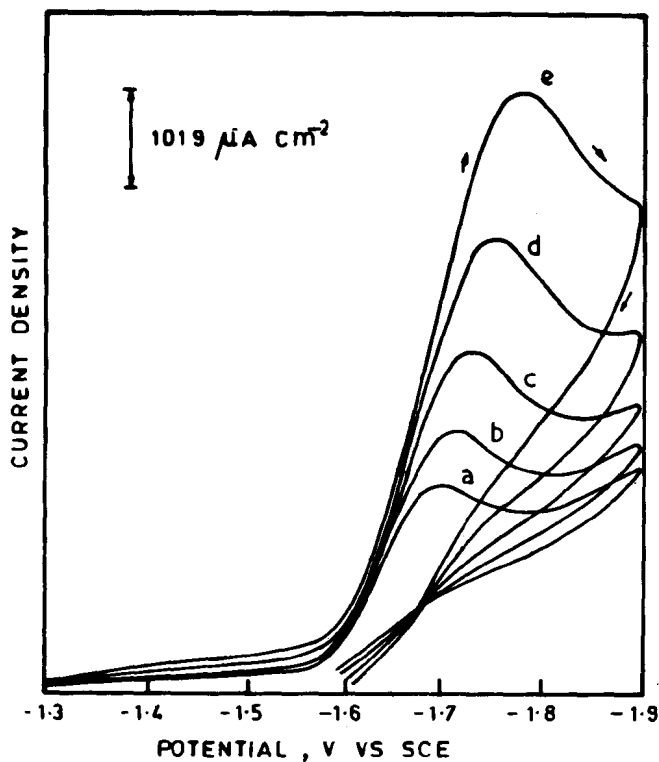


Fig.2: Cyclic voltammogram of acetophenone (20 mM) in 0.1M NaOH/50% (v/v) ethanol on GC electrode at sweep rates ( $\text{mV} \cdot \text{S}^{-1}$ ): (a) 10 (b) 20 (c) 40 (d) 80 (e) 160

voltammograms however showed some variation. These values are presented in Table I. The  $I_p$  was otherwise found to be proportional to  $C_A$  as well as  $\nu^{1/2}$  and showed the irreversible response as in the case of acetophenone reduction in  $\text{H}_2\text{SO}_4$  medium discussed above. The  $E_p - E_{p1/2}$  value in all these cases was found to be around 60mV at slower sweep rates ( $< 100 \text{ mV} \cdot \text{s}^{-1}$ ).

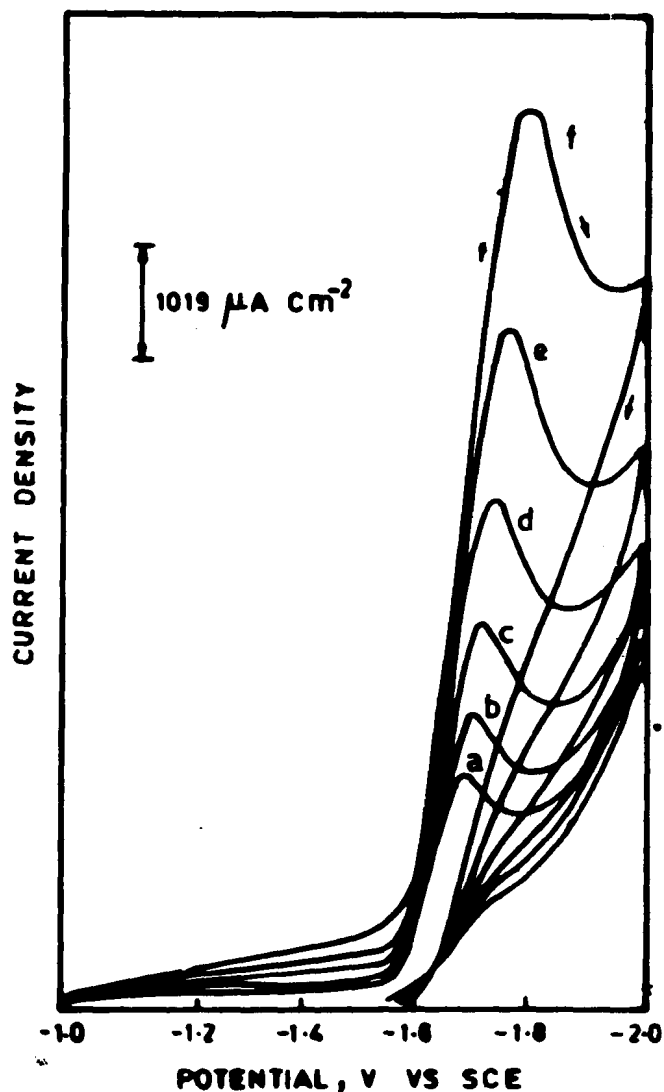


Fig.3: Cyclic voltammogram of acetophenone (20 mM) in 0.1M tetra n.butyl ammonium hydroxide/50% (v/v) ethanol on GC electrode at sweep rates ( $\text{mV} \cdot \text{s}^{-1}$ ): (a) 10 (b) 20 (c) 40 (d) 80 (e) 160 (f) 320

The voltammetric behaviour of acetophenone on lead electrode is also similar to that of GC electrode. A single well defined irreversible peak is noticed. Typical cyclic voltammogram of acetophenone in McIlvaine buffer is presented in Fig.4. The  $i_p$  again varies linearly with  $C_A$  and  $\nu^{1/2}$ . The  $E_p$  shifts more sharply with increasing sweep rate.

The  $E_p$  values in the voltammetric reduction over a wide pH range was found to vary substantially. The half peak potentials ( $E_{p1/2}$ ) obtained in the present work on GC and lead electrodes are tabulated along with the literature values on Hg electrode in Table II.

TABLE-I: Comparative voltammetric behaviour of acetophenone on GC electrode in aqueous media of different pH

No.	Medium	pH	$i_p/AC_A \nu^{1/2}$	$E_p^*$
1.	0.1M H <sub>2</sub> SO <sub>4</sub> /50% alcohol	1.0	90.09	-1.085
2.	0.1M H <sub>2</sub> SO <sub>4</sub> (25%) + 0.1M Na <sub>2</sub> SO <sub>4</sub> /50% alcohol	1.8	90.14	-1.14
3.	0.1M McIlvaine buffer/50% alcohol	5.0	99.11	-1.475
4.	0.1M Na <sub>2</sub> SO <sub>4</sub> /50% alcohol	6.5	85.58	-1.69
5.	0.1M NaOH/50% alcohol	13.3	112.61	-1.675
6.	0.1M tetra n-butyl ammonium hydroxide/50% alcohol	18.7	127.6	-1.68

\*  $E_p$  = peak potential values at 0.02 V.s<sup>-1</sup> scan rate and 4 mM concentration of acetophenone

TABLE-II:  $E_{p1/2}$  and  $E_{1/2}$  of acetophenone on GC and Hg electrodes respectively

	$E_{1/2}$ at DME [3] (V)	$E_{p1/2}$ at Pb (V)	$E_{p1/2}$ at GC (V)
0.1M H <sub>2</sub> SO <sub>4</sub> /50% alcohol	-	-1.045	-1.04
0.1M H <sub>2</sub> SO <sub>4</sub> (25%) + 0.1M Na <sub>2</sub> SO <sub>4</sub> (25%)/50% alcohol	-	-	-1.085
0.1M McIlvaine buffer/50% alcohol	-1.64	-1.40	-1.415
0.1M Na <sub>2</sub> SO <sub>4</sub> /50% alcohol	-	-	-1.635
0.1M NaOH/50% alcohol	-	-	-1.645
0.1M Tetra-n-butyl ammonium hydroxide/50% alcohol	-1.480	-	-1.63
DMSO and (n-Bu) <sub>4</sub> NClO <sub>4</sub>	-1.94	-	-

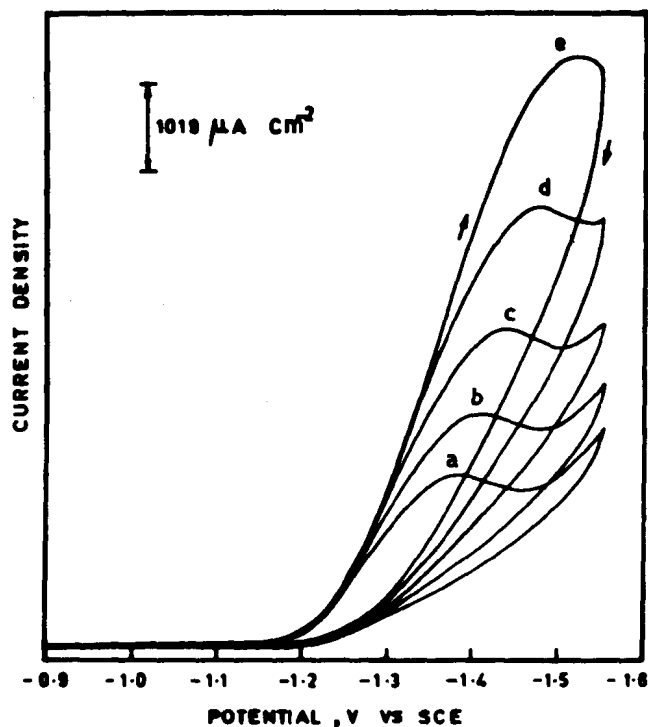


Fig.4: Cyclic voltammogram of acetophenone (4 mM) in 0.1M McIlvaine buffer/50% (v/v) ethanol on lead electrode at sweep rates (mV.s<sup>-1</sup>): (a) 20 (b) 40 (c) 80 (d) 160 (e) 320

#### DISCUSSION

Acetophenone is found to give a single well-defined cathodic peak

without any reverse anodic peak. The cathodic current is proportional to  $C_A$  and  $\nu^{1/2}$ . This type of voltammetric behaviour should either correspond to simple diffusion controlled irreversible charge transfer [17-20] or reversible charge transfer followed by an irreversible fast chemical reaction [7,19,20] coupled with mass transfer effects. However the  $E_p - E_{p1/2}$  value in all these cases was found to be around 60mV. This should correspond only to a one electron reversible charge transfer process. For an irreversible charge transfer this should be 96 mV. Hence it may be concluded that the overall electrochemical mechanism for the reduction of acetophenone is a one electron reversible charge transfer followed by an irreversible chemical reaction.

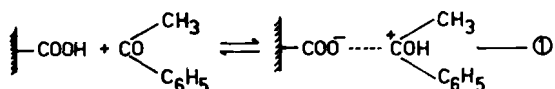
It may be assumed that the chemical reaction is a dimerisation reaction based on the following factors. In both acidic and alkaline media, it has been established [1-7] that acetophenone gives diphenylcarbinol dimer in the potential region of first one electron reduction wave. The  $E_p - E_{p1/2}$  on GC also suggests a one electron reduction wave as mentioned above. Under wide pH variation the  $I_p$  on GC electrode does not vary substantially, suggesting that in all the pH ranges the electroreduction is a one electron process. Similar arguments also hold for lead electrode suggesting that diphenyl dicarbinol is the sole product in the potential region of the first reduction wave/peak on all the three electrodes.

The  $I_p$  decreases slightly with decreasing pH in the media investigated as is evident from Table I. This may either be due to some reactant adsorption giving rise to higher currents in alkaline pH or due to blocking effect by electroinactive substances in acid pH giving rise to lower current in this medium. Similar adsorption effects may also be responsible for the lowering of  $I_p$  at high sweep rates and concentrations.

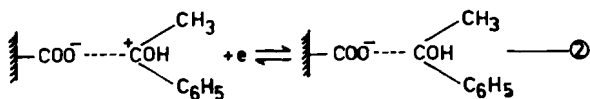
In cathodic shift of  $E_p$  (Table I) as well as  $E_{p1/2}$  (Table II) with increasing pH (Table I) is obviously due to the involvement of

protonated species in the electroreduction in acidic media and unprotonated species in alkaline media. However there is an interesting observation when the  $E_{1/2}$  values on Hg and GC are compared. In tetra n-butylammonium hydroxide, acetophenone is reduced on GC at a potential much more negative (Table II) than that on Hg [7]. This is in line with the trend of easier reduction on metals when compared to carbon because of the difference in the density of electronic states. However in acidic media, the electroreduction of acetophenone is observed at more or less the same potential on all the three electrodes. In fact in McIlvaine buffer, acetophenone is reduced at much more positive potential on GC (Table II) as compared to Hg [3].

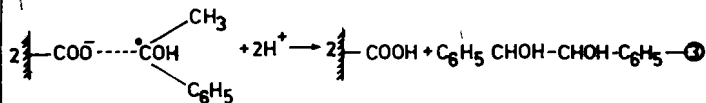
This type of catalytic activity of GC electrode in neutral and acidic pH conditions is probably associated with the acidic surface functional groups present on these electrodes. The presence of surface functional groups on GC electrodes have been well established in earlier work [21-27]. The pH dependence of these surface redox processes have also been investigated [27]. The acidic groups (say-COOH) present on GC surface can form a protonated species with acetophenone in neutral and acidic media.



This can get reduced more easily in McIlvaine buffer as compared to the unprotonated species on Hg electrode.



This type of activation is responsible for the reduction of acetophenone at more positive potentials as compared to Hg. The one electron reduction product, of course, dimerise in the irreversible chemical step to give the end product.



This type of surface acidity effects have also been noticed in the electroreduction of benzophenone in aqueous media [28] and diacetyl in aprotic media [29].

### CONCLUSION

Acetophenone undergoes a one electron reduction on GC and lead electrodes similar to one on Hg electrode. The reaction mechanism involves reversible one electron reduction followed by irreversible chemical dimerisation reaction. In alkaline media, the

electroreduction of acetophenone takes place at much more negative potential on GC as compared to the Hg electrode. However in acidic medium there is a catalytic influence on the GC electrode. The acidic surface functional groups are responsible for this catalytic effect.

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