

VOLTAMMETRIC BEHAVIOUR OF BENZOPHENONE ON GLASSY CARBON ELECTRODE IN AQUEOUS MEDIUM: A QUANTITATIVE EVALUATION OF pH DEPENDENT ADSORPTION EFFECTS

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ABSTRACT

Voltammetric behaviour of benzophenone reduction on glassy carbon (GC) electrode was evaluated and the results were compared with the behaviour on mercury electrode reported in the literature. In strong alkaline conditions (water containing 50% ethanol and 0.1 M NBu_4OH medium), although the same product is formed on mercury as well under similar conditions, the reaction mechanism is quite different on both electrodes. GC stabilises the product and shifts the reduction potential by as much as 200 mV. E_p is also found to be independent of pH on GC electrodes. In addition to this, a time-dependent adsorption pre-wave is noticed in the lower pH (6.0). The adsorption charge reaches maximum value corresponding to about 30% coverage of GC electrode surface. The adsorption effects depend on the nature of the GC surface as well as the anion of the supporting electrolyte medium.

Key Words: Voltammetry, glassy carbon electrode, benzophenone

INTRODUCTION

The voltammetric behaviour of carbonyl compounds like benzophenone has been characterised by polarography and other related techniques in aqueous [1-6] as well as non-aqueous solvents such as DMF [6-8] pyridine [9] and acetonitrile [10]. It is generally known that benzophenone gives a two electron wave corresponding to the reduction of keto group into alcoholic group in most aqueous media [1-5] whose reduction potential depends very much on pH [1,4]. In aprotic media two single electron reduction to anion radical and dianions are noted [7-10]. However, all these studies have been carried out on mercury (Hg) alone. A voltammetric study on gold minigrad electrode [11] considers the spectroelectrochemical aspects of benzophenone reduction.

Recently the voltammetric response has been considered on glassy carbon (GC) and Hg electrodes for inorganic [12-14] and organic [15] reactions and substantial changes were noticed in charge-transfer kinetics [12-15] as well as in the stability and kinetics of chemical reactions following charge transfer [15]. Here this approach has been extended to the study of carbonyl compounds. Benzophenone exhibits some interesting, time-dependent adsorption effects which depend on pH.

EXPERIMENTAL

5mm diameter GC discs fixed into a glass tube using epoxy was used as the working electrode. The GC electrode was polished using gradually finer grade emeries up to 4/0, washed with triple distilled water and electrochemically activated by sweeping to sufficiently anodic (1.2V) and to cathodic (-0.8V) at slow sweep rates for at least 15 minutes according to the procedure evolved earlier [16]. The reproducibility and the activity of electrode was tested by measuring the cyclic voltammetric response for ferriyanide/ferrocyanide system in 0.1 M KCl medium [16].

A H-type cell with provisions for gas inlets and luggin in the working electrode compartment was used. Platinum foil counter electrodes and saturated calomel electrode (SCE) as reference were used. N_2 purified

through pyrogallol, H_2SO_4 and water was used for deaeration. All the experiments were carried out at $30 \pm 0.5^\circ\text{C}$. A potentiostat and scan generator were used for generating the voltage response. The current was recorded using a X-Y-t recorder. A.R. chemicals and triple distilled water were used throughout. Alcoholic (50% ethanol in water) tetra alkyl ammonium salts were used throughout to minimise adsorption effects as in the studies on Hg electrodes [5].

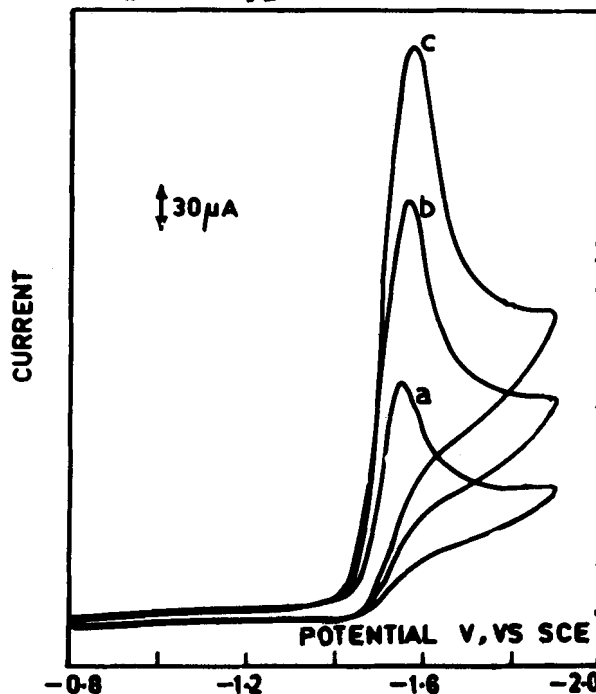


Fig.1 : Cyclic voltammograms for the reduction of benzophenone in different concentrations in 0.1M NBu_4OH / 50% Et OH. Sweep rate 100 mV s^{-1} . Concentrations (a) 2.173 mM (b) 4.255 mM (c) 6.25 mM

RESULTS

Typical cyclic voltammograms of benzophenone (BP) in 50% alcoholic solutions containing 0.1 M tetra n-butyl ammonium hydroxide (TBAH) at various concentrations are presented in figure 1. A single well defined cathodic peak which increases linearly with concentration of BP (C_{BP}) in the range of 1- 12mM and the square root of sweep rate ($V^{1/2}$) in the range of 10 mV/sec to 200 mV/sec was noticed. The peak potential also is found to shift cathodically at higher sweep rates. The $dE_p/d\log V$ value was found to be close to zero at slow sweep rates (<100 mV/sec) and reaches a value of 30 mV at higher sweep rates. The peak potential also shifts cathodically with concentration of BP. In the reverse sweep of the Cycle Voltammetric (CV) curves no anodic current was noticed even at substantially higher sweep rates.

Some interesting features, however, were noticed when the CV experiments were carried out in 50% alcoholic solutions of 0.5 M tetraethyl ammonium p-toluene sulphonate (TEAP) whose pH was found to be around 6. Typical cyclic voltammograms for BP at various sweep rates in this medium are presented in figure 2. The main peak is found at approximately

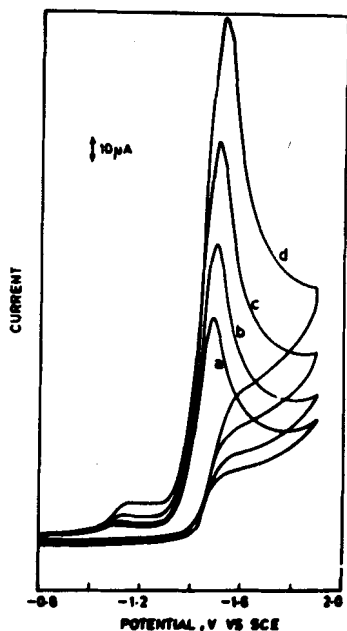


Fig.2 : Cyclic voltammograms for the reduction of benzophenone in 0.5M TEAPS/50% Et OH.

Concentration : 3.345 mM (a) 10 mV s⁻¹ (b) 20 mV s⁻¹ (c) 40 mV s⁻¹ (d) 80 mV s⁻¹

the same potential ($\approx 1,500$ vs SCE) where the peak appeared in TBAH. In addition to this peak, an additional prepeak is noticed in this medium. When the multisweep CV curves were recorded continuously, the prepeak disappeared completely in the second sweep itself even when very slow sweep rates were employed (figure 3). This indicates that the prepeak is due to a slow time-dependent process. To evaluate the time effect, the CV curves in the prepeak region alone were run at the same sweep rate after various time intervals between the earlier sweeps. Such CV curves at higher sensitivities are presented in figure 4, which shows that the prepeak attains a maximum value in about 3 minutes time. If the whole CV curves are now recorded with this time interval between each experiment, the CV curves in both the prepeak and main peak regions are completely reproducible. The CV curves for further analysis were thus recorded in this method.

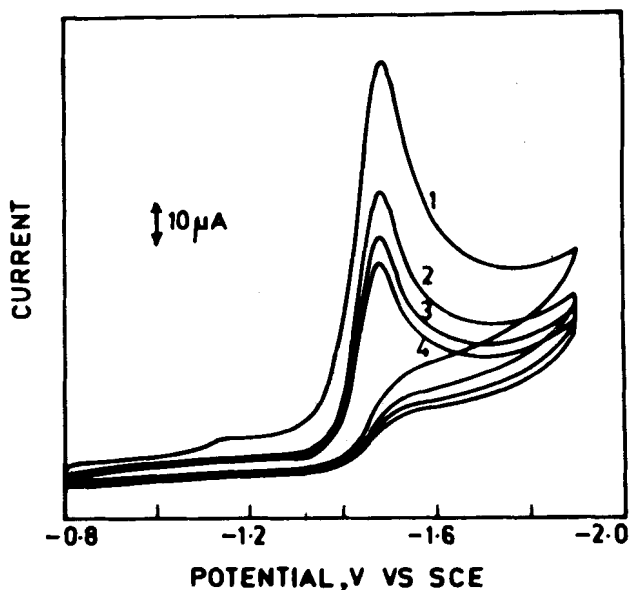


Fig.3 : Cyclic voltammetric behaviour of benzophenone in 0.5M TEAPS/50% EtOH, Concentration 1.691 mM in multisweep. Sweep rate 40 mV s⁻¹. (Numbers indicate the sweeps)

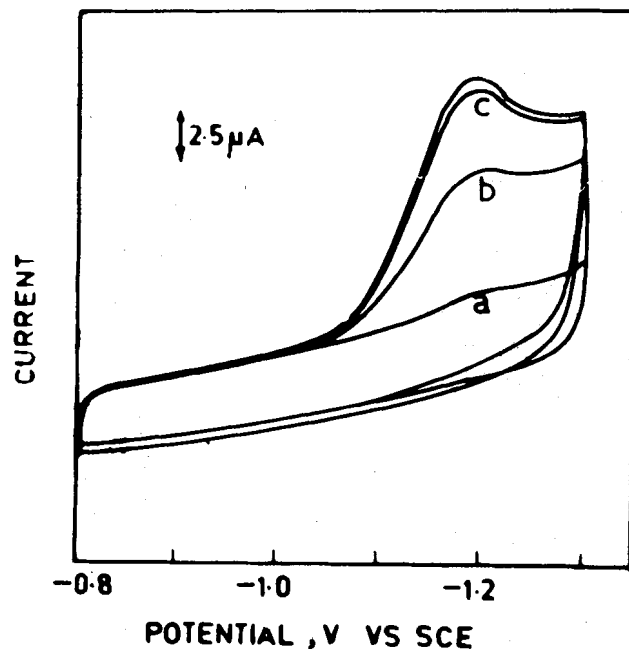


Fig.4 : Time effect on cyclic voltammetric adsorption pre-wave for benzophenone. Concentration, 1.691 mM (a) 30 secs (b) 120 secs (c) 180 secs

Under these conditions the main peak was found to be linearly proportional to C_{BP} and $V^{1/2}$. The $dE_p/d\log V$ values were found to be 33 mV at slow sweep rates and much higher at higher sweep rates (fig 5). The peak

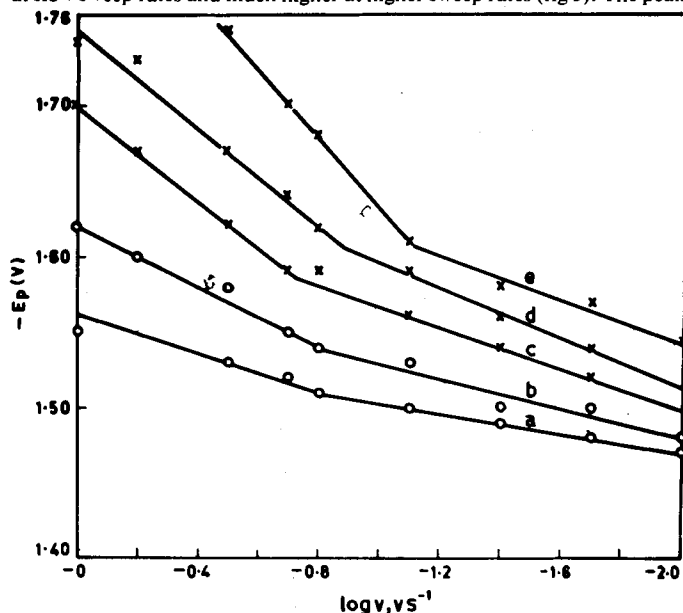


Fig. 5 : $E_p - \log V$ diagrams for benzophenone in 0.5 M TEAPS/50% EtOH (a) 1.691 mM (b) 3.345 mM (c) 6.547 mM (d) 9.616 mM (e) 15.385 mM

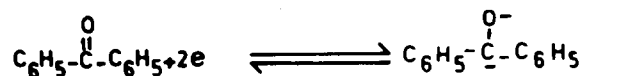
potential is also found to shift cathodically with concentration (figs 2 and 5). Accurate measurements at higher sensitivities in the prepeak region also indicate that the height of the prepeak increases linearly with V rather than $V^{1/2}$. The prepeak height is insensitive to the bulk concentration of B P. The $E^{1/2}$ value of this prewave also is independent of sweep rate and concentration.

DISCUSSION

Electroreduction of benzophenone in solution — The main peak

The fact that i_p of the main peak is proportional to C_{BP} as well as $V^{1/2}$ suggests that the peak should correspond to the diffusion-controlled reduction of benzophenone in solution. The peak current constant values ($i_p/ACV^{1/2}$ where A is the area of working electrode) at slow sweep rates are equal for both high (TBAH) and low pH (TEAP) values. The fact that the peak current is independent of pH suggests that the wave corresponds to a two-electron reduction wave on GC electrode in both the pH conditions. On Hg electrode also, a single two-electron reduction wave is noted in a narrower pH region.

However, two differences are noted between the voltammetric behaviour on GC and Hg. The peak potential is shifted by almost 200 mV in the positive direction on GC electrode under otherwise identical conditions. Secondly the E_p is found to be independent of pH. The fact that the reduction potential is independent of pH can only be explained by assuming that both



Scheme.1

the electron transfer steps precede the protonation step and that the solvent itself functions as the protonating species for the dianion formed (Scheme 1).

SCHEME 1

In this scheme SH denotes the solvent molecule (probably H_2O rather than ethanol which is a poorer proton donor). Since the protonation is a fast step with solvent as proton donor, the E_p is independent of pH.

This reaction mechanism differs from the second order disproportionation mechanism that operates on Hg electrode where the first protonation step precedes the second electron transfer [5] since in this case E_p was found to shift cathodically with pH. It seems, therefore, that GC electrode stabilizes the products of charge transfer such that both the electron-transfers take place simultaneously. This product stabilization (possibly through intermediate adsorption) is also probably responsible for the 200 mV positive shift in the reduction potential.

The reaction scheme may be considered as an overall EC mechanism involving reversible charge transfer (eq. 1) followed by irreversible chemical reaction [17,18]. Since the overall wave looks like an irreversible charge transfer wave, the data may be analysed using equations corresponding to irreversible charge transfer [17] as has been done in some recent simulation works [19,20]. The $dE_p/d\log V$ value of 30 mV and $E_p - E_p/2$ value of 50 mV in TBAH medium correspond to an αn value 1.0 [21]. Substituting this value and $n=2$ in an irreversible charge transfer equation (eq. 3)

$$i_p = 2.98 \times 10^5 n (\alpha n_a)^{1/2} ACV^{1/2} D^{1/2}$$

we get $D = 3.53 \times 10^{-6} \text{ cm}^2/\text{sec}$. Although no D value for benzophenone in this medium is available, this value is logically consistent with a higher D value of $7.0 \times 10^{-6} \text{ cm}^2/\text{sec}$. for acetophenone in aprotic media [6].

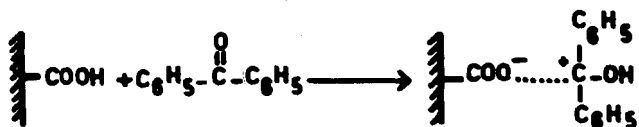
At higher concentrations the main reduction peak is affected by some adsorption effects. The cathodic shift of E_p with concentrations (Figs. 1 and 5) and a second larger slope for $dE_p/d\log V$ values at higher sweep rates noticed in these voltammograms are caused by such adsorption effects.

Electroreduction of adsorbed benzophenone—the prepeak

Whenever the CV curves are recorded at 3 minute intervals between each recording, the prepeak current is found to increase linearly with sweep rate. This type of behaviour should certainly correspond to a surface process [22, 23]. However, in usual voltammetric studies the prewave would correspond to product adsorption and the postwave would correspond to reactant adsorption [22, 23]. In the present case, however, the prepeak cannot correspond to the product adsorption since this wave completely disappears in the second sweep during multisweep experiments (Fig 3). Since the prepeak wave height increases with time interval between successive sweeps at the starting potential (where no product formation can be assumed) as shown in figure 4, this wave should correspond to a slow reactant adsorption step alone.

The numerical simulation work corresponding to slow adsorption step in CV response is also available [24]. However, in general, direct adsorption of organic molecules cannot be such a slow step to exhibit time effects in the range of minutes [23]. Capacitance measurements of organic adsorption on Hg electrodes, for example do not show time effects of such order.

It appears, therefore, that the slow step involved in the surface coverage process on GC electrodes is an adsorption process initiated by surface protonation. It has already been established that the GC surface contains functional groups such as -OH, -COOH and -CHO groups [25, 26]. In the low pH involved in reduction of BP in TFAP, BP is adsorbed by a slow chemical process of the type.



Scheme 2

Such a chemical step can be really slow and may take a few minutes for completion. Since the protonated BP species formed in this process must be more easily reducible than BP itself, it is noticed as a prewave.

Some slow time effects are not uncommon. In one of the earlier studies [14], some time effect in the Ti^{4+}/Ti^{3+} redox process has been noticed in citric acid although no proper explanation could be offered then. The present study certainly indicates the rich information that may be obtained by a careful analysis of such time effects.

The linear sweep voltammogram may itself be considered as an $i-t$ transient since the potential axis is directly related to time. The charge accumulated for each time can be obtained by direct integration with appropriate background correction. The charge obtained by such integration

Table I: Charge corresponding to the adsorption of benzophenone as a function of time

No	Time (sec)	q ads ($\mu C/cm^2$)
1	30	11.69
2	60	31.13
3	120	76.35
4	180	107.48

is presented in Table 1. The charge accumulated approximately varies linearly with time before reaching a limiting value in about 3 minutes time. (Since each measurement takes 6 sec and the background corrections are also involved, such estimates are certainly approximate in nature). If we further assume that the adsorbed BP species also undergoes a two electron reduction, the maximum surface charge for a monolayer coverage would be around $350 \mu C/cm^2$ [23]. Hence in the present case of maximum coverage of about $110 \mu C/cm^2$ (Table I), the maximum surface coverage would be about 30% if the surface roughness factor is unity. Practically, even a mirror finish GC used here should possess a microscopic roughness and hence the maximum surface coverage would be even less. This shows that the adsorption process is not determined by the total surface area but rather to the availability of surface functions, another factor supporting the model proposed in eq. 4.

CONCLUSIONS

The present voltammetric studies of benzophenone on glassy carbon indicates that the compound undergoes a two-electron reduction to the corresponding hydroxy compound in the pH range investigated. Although the same product is formed on Hg as well under similar conditions, the reaction mechanism is quite different on both electrodes. GC surface stabilises the product and shifts the reduction potential by as much as 200 mV. There is slow time-dependent adsorption effect as well which involves the surface functional groups present on GC electrode.

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