
GLASSY CARBON SURFACE EFFECTS ON THE ELECTROREDUCTION OF AROMATIC CARBONYL COMPOUNDS. II* BENZOPHENONE

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Results of the voltammetric study of benzophenone reduction in dimethylformamide and aqueous media on GCE are presented together with the comparative discussion of the data for mercury and other electrodes available in the literature. The formation and stability of anion radicals and dianions and their reactivity with protonating agents on GCE are similar to those on mercury electrodes. A new surface prewave noticed in aprotic and neutral aqueous solutions on GCE has not so far been reported on any other electrode. All experimental evidences support the view that this prewave is due to the surface protonation by the acidic functional groups on GCE. The surface protonation is found to be a slow time-dependent process requiring 3–4 minutes for completion. The surface concentration evaluated from the faradaic response of the surface process is found to be around 30% or even less if the surface roughness factor is considered. The importance of this finding to the general concept of surface acidity effects on electrocatalysis is also emphasised.

The catalytic influence of acidic or basic groups present on the electrode surface has received serious attention in recent time.^{1,2} The protonating effect of sulphonic acid groups present in a Nafion coated glassy carbon electrode (GCE) for example has been reported quite recently.³ Since GC surface itself contains some acidic functional groups⁴, a systematic investigation of their influence on the electroreduction of aromatic carbonyl compounds of different basicity was undertaken.⁵ The electroreduction of benzaldehyde on GCE shows some catalytic effects which depend very much on the nature of surface pre-treatment.⁶ Compared to benzaldehyde, benzophenone (BP) is a stronger base. In this part, it is indeed shown that the surface effect on GCE for this compound is much stronger, reproducible and well defined. Some efforts to quantify the surface functional groups on the basis of their faradaic interaction with the benzophenone are also made in this work.

The electrochemistry of benzophenone in both aqueous and non-aqueous media on mercury and other electrodes is well known.^{7–18} Two brief investigations on carbon electrodes namely glassy carbon¹⁹ and carbon paste electrode²⁰ reported

* Part I see ref.⁶.

in the literature do not indicate any substantial difference when compared to mercury electrode. This is in contrast to the substantial differences noticed and discussed in the present work. A brief note on GCE surface effects in aqueous media for benzophenone reduction has also been published.^{5,21}

EXPERIMENTAL

The glassy carbon electrode (5 mm dia, Tokai GCA) was fabricated, polished, cleaned and activated through electrochemical cycling procedures as described elsewhere.²² The electrode activity in aqueous solution was evaluated using the cyclic voltammetric response of ferricyanide–ferrocyanide redox couple in 0.1M-KCl media.²² In non-aqueous solvents the voltammetric response depended very much on the level of polishing and pre-treatment. From a number of experiments it was found that a “perfectly polished” GCE surface for non-aqueous studies was obtained by polishing GCE from 1/0 to 4/0 emery paper for ten minutes each, washing with water, trichloroethylene and the solvent supporting electrolyte (SSE) solution and introducing it into the cell in a wet condition and electrochemically activating it by cycling in the potential region of interest at 10 mV s^{-1} for 15 minutes without adding the compound. The electrode already activated according to this procedure, produces the voltammetric response of anthracene (An) reported in the literature for mercury²³ and platinum²⁴ electrodes in the same potential region.

A H-type cell with platinum counter electrode was used for voltammetric studies. The saturated calomel electrode (SCE) was connected to the working electrode compartment through a KCl-Agar Luggin capillary. For cyclic voltammetry in DMF, the Luggin capillary was equilibrated for 1 h in solvent supporting electrolyte mixture just before use. The solvent supporting electrolyte itself was kept in suspended alumina for 24 h and filtered just before use. The working electrode compartment was deaerated with purified nitrogen until dissolved oxygen was completely removed (as indicated by the absence of reduction peak around -0.8 V). All experiments were carried out at $25^\circ \pm 1^\circ \text{C}$. 50% ethanolic solutions were used in aqueous studies. All chemicals were of AR grade.

RESULTS

BP in low concentration (say 0.1 mmol l^{-1}) gives a small wave (a prewave) around -1.4 V (Fig. 1, curve a). This wave gradually increases as the concentration of BP increases and above a critical concentration (say $> 1 \text{ mmol l}^{-1}$), two main waves in addition to the prewave are noticed (Fig. 1, curves c–e). On the reverse sweep, one anodic peak corresponding to the first main peak is noticed even at very low sweep rates. The peak heights increase with the increase in sweep rates as well as concentration. The prewave current also increases with the increase in sweep rate. However, the prewave is insensitive to change in concentration of BP (Fig. 1) beyond 0.1 mmol l^{-1} . The prewave completely disappears in the second and the subsequent sweeps (Fig. 2).

Among the protonating agents investigated, addition of water in millimolar concentration does not have any effect on the voltammetric response of BP in DMF.

However, a more powerful protonating agent *o*-cresol increases the cathodic peak current of the first wave (Fig. 3). The peak potential also shifts positively with increase in *o*-cresol concentration. The anodic peak of the first main cathodic peak as well as the second cathodic peak disappear at higher concentration of *o*-cresol (about 7 mmol l^{-1}). The prewave, however, is not affected by *o*-cresol addition. In the case of benzoic acid addition, the wave height in the prewave region gradually increases at the expense of the first main peak with the increase in concentration of benzoic acid (Fig. 4). At its higher concentration (say 1 mmol l^{-1}) a single cathodic wave is noticed around -1.6 V (in the prewave region, Fig. 4) whose height is almost double the wave height of BP in its absence. The anodic peak corresponding to the first cathodic peak completely disappears. The effect of ion-pair forming Li^+ ion on the voltammetric response of BP indicates that the prewave is almost insensitive to the addition of Li^+ ion (Fig. 5). The first main cathodic peak current increases with the increase of Li^+ ion concentration. The anodic peak gradually decreases and finally disappears with the increase in Li^+ ion concentration.

In aqueous acidic media, only one reduction peak for BP around -0.75 V is noticed. The peak current increases with its concentration as well as with higher sweep rates. The peak potential shifts cathodically with increase in sweep rate and concentration of BP. In neutral pH solution, a prewave around -1.1 V and a main peak around -1.5 V with no anodic peak are noticed (Fig. 6A). The main peak current increases with increasing sweep rate as well as BP concentration. It should be noted that under identical conditions, the main wave alone is noticed on a mercury

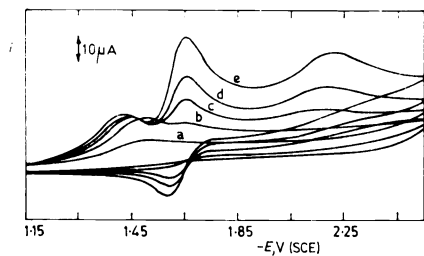


FIG. 1

Cyclic voltammograms for the reduction of benzophenone on GCE in 0.1M TBAI/DMF at various concentrations (mmol l^{-1}): a 0.1; b 0.3; c 0.5; d 0.7; e 1.0; v 40 mV s^{-1}

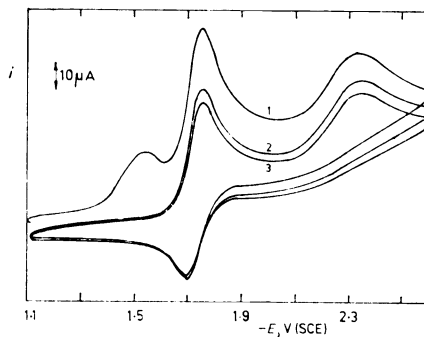


FIG. 2

Cyclic voltammograms for the reduction of benzophenone on GCE in 0.1M TBAI/DMF. 1.0 mM BP , v 100 mV s^{-1} ; numerals indicate number of sweeps

plated Pt electrode (Fig. 6B). The prewave obtained in this neutral pH region (Fig. 6A) resembles the prewave noticed in DMF media (Fig. 1). In both the media, the prewave cannot be removed by any amount of polishing and pre-treatment of GCE. This prewave is also observed in tetrabutyl ammonium iodide (TBAI) and bromide (TBAB) aqueous solution. The prewave is neither observed in acid and alkaline media (see later). The prewave current also increases with sweep rate and is almost insensitive to concentration of BP.

In multisweep cyclic voltammetry experiments, the prewave is completely absent in the second and the subsequent sweeps similar to Fig. 2 obtained in DMF. To evaluate the time effect, the cyclic voltammogram in the prewave region alone was

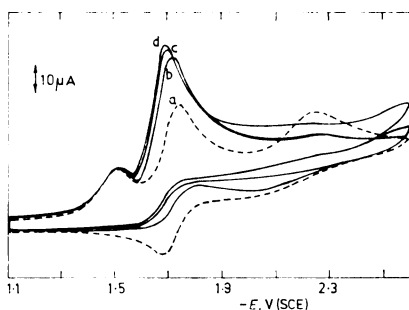


FIG. 3

Effect of *o*-cresol as proton donor on the reduction of 1 mM benzophenone on GCE in 0.1M TBAI/DMF at 40 mV s^{-1} . Conc. of *o*-cresol (mmol l^{-1}): a 0; b 1.0; c 5.0; d 7.0

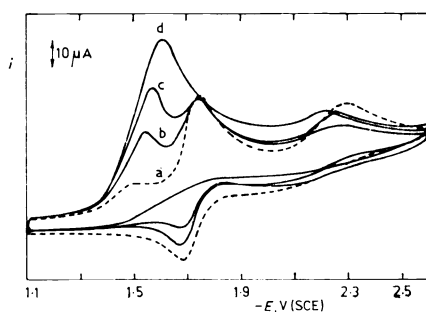


FIG. 4

Effect of benzoic acid as proton donor on the reduction of 1 mM benzophenone on GCE in 0.1M TBAI/DMF at 40 mV s^{-1} . Conc. of benzoic acid (mmol l^{-1}): a 0; b 0.5; c 1.0; d 1.4

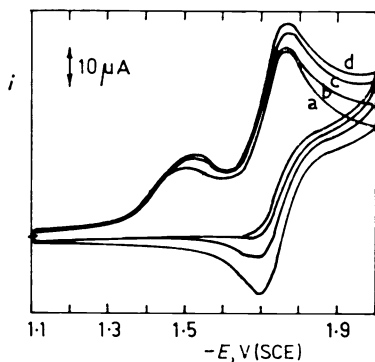


FIG. 5

Effect of Li^+ ion on the reduction of 1 mM benzophenone on GCE in 0.1M TBAI/DMF at 40 mV s^{-1} . Conc. of LiClO_4 (mmol l^{-1}): a 0; b 1.0; c 3.0; d 5.0

recorded. Its limiting current attains its maximum if about 3 min time interval is given between the recording of two consecutive voltammograms. Below this time limit, the limiting current increases with time (Fig. 7).

In aqueous tetrabutyl ammonium hydroxide (TBAH) medium also, one wave around -1.5 V is observed without any prewave. The peak current increases with sweep rate as well as concentration, the peak potential also shifts cathodically with increasing sweep rate and concentration. No anodic peak is noticed even at higher sweep rates. Quantitatively the voltammetric results on GCE are given in Table I

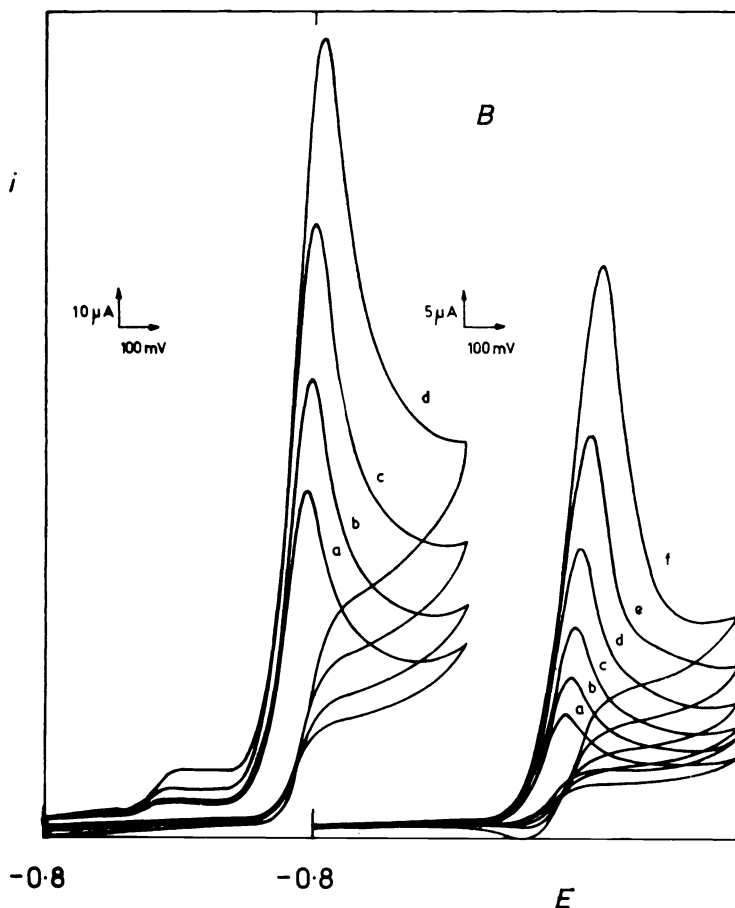


FIG. 6

Cyclic voltammograms for the reduction of benzophenone (3.4 mM BP) on GC (A) on mercury plated Pt, (B) in $0.1 \text{ M TEATS}/50\% \text{ EtOH}$ at various sweep rates (mV s^{-1}): A: a 10; b 20; c 40; and d 80; B: a 10; b 20; c 40; d 80; e 160; f 320

TABLE I

Voltammetric behaviour of benzophenone in aprotic and protic media. 1 mM Benzophenone, sweep rate 40 mV s⁻¹

Medium	GCE		Hg	Other solid electrodes
	$-E_{p/2}$, V	i_p , μA	$-E_{1/2}$, V	$-E_{1/2}$, V
I. 0.1M TBAI/DMF	1.690	36	1.71 ^a	1.72 ^b (Pt)
	2.170	21	2.28	2.49
	1.420	13	—	—
	(prewave)			
<i>Additives</i>				
7.0 mM <i>o</i> -cresol	1.630	56	—	—
1.4 mM Benzoic acid	1.500	62	—	—
4.9 mM Lithium perchlorate	1.690	46	—	—
II. 0.1M-H ₂ SO ₄ /50% EtOH	0.715	36	0.87 ^c	—
III. 0.1M TEATS/50% EtOH	1.420	50	1.38 ^c	1.445 ^f (Pt/Hg)
	1.190	2.0	—	—
IV. 0.1M TBAH/50% EtOH	1.490	56	1.497 ^d	1.55 ^e (Au/Hg)
	—	—	—	2.00

^a Ref.⁸; ^b DMF/TMAB ref.¹²; ^c pH 1.3, pH 8.5, 48% EtOH, ref.¹⁵; ^d 0.1M-NaOH, ref.¹⁴; ^e 0.05M-NaOH/40% EtOH, ref.¹⁸; ^f present work.

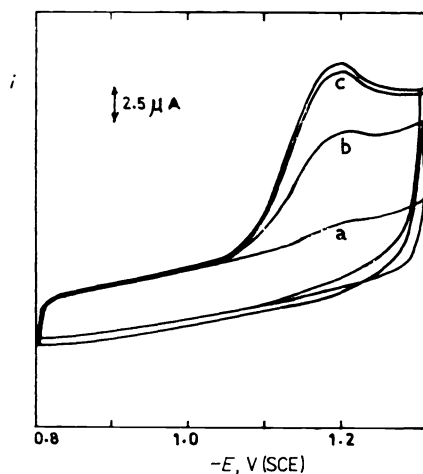


FIG. 7
Time effect on cyclic voltammetric adsorption prewave for benzophenone reduction (1.7 mM BP) on GCE in 0.1M TEATS/50% EtOH at 80 mV s⁻¹. *t*(s): a 30; b 120; c 180

along with comparable results on mercury electrode collected from the literature for comparison.

When GC plate electrode was employed for constant potential electrolysis, the cell current drops substantially within very short time and reaches very low values. Hence no detectable quantities of reduction product could be obtained under these conditions, probably due to the filming effect on the GC electrode. Similar film forming effect is also observed on mercury⁹ electrode in protic media and Au or Ag electrode¹¹ in aprotic media for benzophenone reduction.

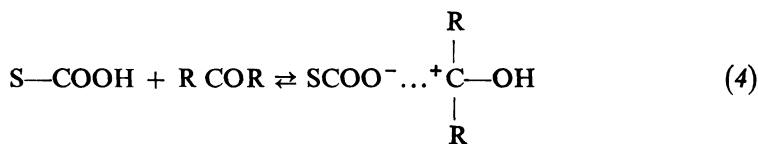
DISCUSSION

Electroreduction of Benzophenone in DMF

The two main waves noticed in the voltammograms of BP reduction (Fig. 1) are quite similar to those observed on mercury and other solid electrodes (Table I). The anion radical obtained in the first main peak region is quite stable and gives the anodic peak in the reverse sweep. However, the dianion undergoes some irreversible chemical reaction as is evidenced by the absence of anodic peak for the second main cathodic peak. Hence the following scheme may be proposed (where R = C₆H₅)



The most significant difference in the voltammetric behaviour of BP on GCE is the appearance of the prewave. As mentioned earlier, this prewave has not been reported in the earlier studies on mercury and other solid electrodes. Even on GCE and carbon paste electrode, this prewave was not noticed.^{19,20} That the prewave is not due to any experimental artifact was confirmed by careful experimental procedure, recording the background level in each experiment and by repeated checking with anthracene/anthracene anion radical system. The prewave is always noticed on a clean GCE surface. The prewave alone is noticed at very low concentrations of BP. It reaches a maximum current limit beyond which only the main reduction peaks show concentration dependence. These facts indicate that the prewave is due to a BP interaction with the surface functional groups on GCE. Since the prewave appears only in aprotic media (Fig. 1) and neutral solution of aqueous media (Fig. 6), it may be assumed that the acidic functional groups present on GCE may be responsible for the prewave.



In this equation S denotes the GCE surface. Since this surface protonated species can get reduced more easily as compared to the unprotonated species, the prewave is noticed. In acidic media, BP can undergo bulk protonation. In alkaline media, the surface functional groups would be in the basic form and hence cannot offer protons. Hence the prewaves are not noticed in acid and alkaline media.

The relative acidity of the GC surface and basicity of the carbonyl compound would control the extent of surface interaction of this type. For a relatively weaker base like benzaldehyde, the prewave is absent on a perfectly polished GCE⁶. The relatively low concentration of surface functional groups present on such a clean surface is, however, enough for the formation of a prewave with BP which is substantially more basic than benzaldehyde.

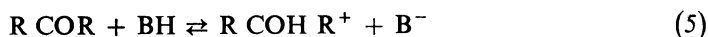
The surface protonation process responsible for prewave formation seems to be time dependent as seen from multisweep experiments (Fig. 2). This aspect will be quantitatively treated later.

Many features such as decreasing peak current constant value with concentration, cathodic shift of E_p with concentration and abnormal $E_p - E_{p/2}$ and $dE_p/d \log v$ values are associated with blocking effects, which are common to solid electrodes.^{25,26} The increase in peak separation $\Delta E_p = (E_a - E_c)$ for BP/BP⁻ at constant sweep rate with increasing concentration is also due to the inhibition of charge transfer by the adsorbed molecules themselves. However, if we assume that the blocking effects would be marginal at least at quite low BP concentration, Nicholson's method²⁷ which relates the ΔE_p values with the dimensionless charge transfer rate constant parameter ψ can still be employed to estimate approximately the apparent charge transfer rate constant, k_h^0 knowing that the diffusion coefficient²⁸ for BP is $0.79 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Average rate constant is found to be $13.65 \cdot 10^{-3} \text{ cm} \cdot \text{s}^{-1}$ for this process (Table II).

The anion radical formation process is not affected by the addition of small amount of water (say mmol l^{-1}). Even on mercury electrode, much larger concentration of water (in terms of moles) are required to effect small changes in voltammetric responses.⁸ In the presence of *o*-cresol, however, the peak potential of the first main peak is shifted in the positive direction and the current is increased at the expense of the second peak until finally the second peak disappears (Fig. 3). The anodic peak due to BP⁻ oxidation also disappeared with the increase in concentration of *o*-cresol. All these evidences suggest that the benzophenone reduction proceeds through ECE mechanism leading to the formation of carbinol in the presence of *o*-cresol. On

mercury the same behaviour is noticed.⁷ However, it is interesting to note that *o*-cresol has no influence on the prewave which is due to the reduction of surface protonated species mentioned earlier.

Benzoic acid, a more powerful protonating agent, actually protonates the reactant molecules itself through direct protonation.



Since the prewave noticed in the absence of protonating agents is also due to surface protonated BP species, the reduction potential of bulk protonated BP species (due to benzoic acid) is likely to be very close to the potential region of the first wave. This is indeed found to be the case. Merging of the main reduction wave of BP in presence of benzoic acid with the prewave (Fig. 4) thus lends support to the assumption that the prewave is due to the reduction of surface protonated species.

The prewave is insensitive to Li^+ ions as would be expected if the prewave is due to protonated species (Fig. 5). The first main peak current however increases with Li^+ ion concentration suggesting disproportionation of anion radicals due to ion-pair formation as observed on mercury electrode.¹³ The main peak potential however is insensitive to Li^+ ion concentration (Fig. 5). This should also be associated with the general blocking effects on solid electrodes.^{25,26}

Electroreduction of Benzophenone in Aqueous Media

In aqueous acidic medium, only one diffusion controlled wave is noticed for BP reduction. The peak current constant value slightly decreases with concentration and sweep rate due to adsorption and blocking effects mentioned above. However,

TABLE II

Heterogeneous rate constants (k_h^0) for benzophenone reduction on glassy carbon electrode, 2.0 mM BP, 0.1M TBAI/DMF; v sweep rate

$v^{1/2}, \text{V}^{1/2} \text{ s}^{-1/2}$	$\Delta E_p, \text{mV}$	$k_h^0 \cdot 10^3, \text{cm s}^{-1}$
0.1730	70	2.5
0.2000	75	1.75
0.2236	75	1.75
0.2450	70	2.5
0.4000	80	1.33
0.5657	100	0.575
<i>Average</i>		13.65

if the blocking and adsorption effects are assumed to be absent at least at low concentration, n can be calculated from peak current constant value using the diffusion coefficient value of $0.79 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ reported for BP in closely related experimental conditions.²⁸ The n value calculated by using irreversible charge transfer equation was found to be 1.2 or approximately 1. This fact and the presence of a small anodic wave at higher sweep rates suggests that BP in aqueous acidic media gets protonated and then reduced to a product leading to the formation of dimer.

The main reduction peak in neutral medium and the only reduction peak in the alkaline medium appears in the same potential region (Table I). The peak current constant value at low concentration of BP are also quite close. The n value calculated using the method employed above leads to 1.7 or approximately 2 in these media. These facts suggest that BP undergoes a direct 2e reduction, quite similar to the behaviour on mercury electrode as far as the main wave is concerned. All the features corresponding to the blocking effects indicated above are noticed at higher concentrations for direct BP reduction in neutral and alkaline media as well.

As mentioned earlier, the appearance of the prewave in aprotic media and aqueous neutral media alone indicated that this is due to surface protonation. Since many features of the prewave in both these media were very similar, more quantitative analysis was carried out in neutral aqueous media due to convenience.

The first indication for surface protonation became evident when it was found that at least 3 to 4 min time interval was required between each successive cyclic voltammetric experiment to obtain reproducibility in the response. The formation of product adsorption prewave commonly encountered in polarography²⁹ is quite a fast process requiring much shorter times for adsorption-desorption. The value of i_p/v for the prewave is not constant as would be expected for an adsorption prewave. Rather $i_p/v^{1/2}$ is found to be constant which is similar to the mass-transfer controlled response. The slow response of the surface protonation is also consistent with the view that the acidic groups on carbon surfaces would be quite weak (say carboxylic acids). The independence of the prewave on the nature of the supporting electrolyte cation (TEA^+ or TBA^+) or anion (PTS^- , Br^- , I^-) again confirms the view that surface acidity rather than adsorptivity is the determining factor.

TABLE III

Charge corresponding to the adsorption of benzophenone as a function of time. 1.7 mM BP, sweep rate 80 mV s^{-1}

Time, s	30	60	120	180
$q_{\text{ads}}, \mu\text{C cm}^{-2}$	11.69	31.13	76.35	107.48

Some quantitative evaluation of the surface prewave was also made. The linear sweep voltammogram may be considered as an $i-t$ transient since the potential axis is directly related to time. The charge accumulated for each time interval can be obtained by direct integration with an appropriate background correction. The charge obtained by such integration is presented in Table III. The charge accumulated varies approximately linearly with time before reaching a limiting value in about 3 min time. If we further assume that the adsorbed BP species also undergoes a 2e reduction, the maximum surface coverage for a monolayer coverage would be around $350 \mu\text{C cm}^{-2}$ (ref.³⁰). Hence in the present case of maximum coverage of about $110 \mu\text{C cm}^{-2}$ (Table III), the maximum surface coverage would be about 30% if the surface factor is assumed to be unity. Even a mirror finished GC used here obviously possesses 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 by the availability of surface functions, another factor supporting the surface protonation scheme.

CONCLUSIONS

The significance of the present finding lies in the fact that one can indeed catalyse an electrochemical reaction by modifying the acidity of the electrode surface by oxidising the carbon electrodes or even by attaching acidic films like Nafion films³. This approach to the acid-base properties of modified surfaces² to understand their electrocatalytic behaviour may lead to very rich dividends.

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