

Electrochemical reduction of some benzophenones in molten acetamide at 85°C[‡]

R SARASWATHI and R NARAYAN*

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Abstract. Benzophenones undergo a one-step two-electron reduction in molten acetamide containing sodium acetate, both at the mercury and the glassy carbon electrodes. The reduction process is irreversible. The $E_{1/2}$ potentials of some of the benzophenones can be fitted into a Hammett plot. The αn_a and $k_{f,h}^0$ are evaluated and discussed.

Keywords. Benzophenone; molten acetamide; half-wave potentials; Hammett plot.

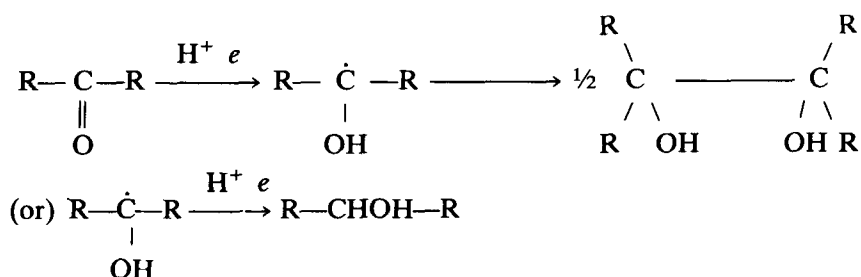
1. Introduction

There are a large number of papers in the literature dealing with the electrochemical reduction of aromatic carbonyl compounds at the mercury electrode (Day *et al* 1952; Perrin 1965; Zuman *et al* 1968a). In particular, studies on the electrochemical reduction of benzophenone in the aqueous-alcoholic media have been numerous (Elving and Leone 1958; Pfister and Bonastre 1965; Sivakumar *et al* 1983), using polarography, controlled-potential electrolysis, cyclic voltammetry and chronoamperometry. The kinetics and mechanism of the reduction process in acidic, neutral and alkaline (Suzuki and Elving 1961; Zuman 1968; Nadjo and Saveant 1971) solutions have been investigated and the conditions for the formation of free radicals and radical ions have been discussed. In acidic and in neutral media benzophenone gives two equal and well-defined d.c. polarographic waves, each wave corresponding to a one-electron reduction process. In the pH range of 6-8, the two waves merge to give only one wave. At still higher pH, a third wave appears at more negative potentials.

The first one-electron wave represents the reduction of benzophenone to the free radical $(C_6H_5)_2\dot{C}OH$ which is supposed to dimerize to pinacol. The second one-electron wave is due to the reduction of the free radical to carbinol. The two-electron combined wave involves the reduction of benzophenone to carbinol through a free radical state. The third wave at a more negative potential is attributed to the more difficult reduction of the free radical ion $[(C_6H_5)_2\dot{C}O]^-$ which is formed along with the neutral free radical. The schematic representation of the mechanism suggested is given here:

[‡] Dedicated to Prof. K S G Doss on his eightieth birthday.

* To whom all correspondence should be addressed



Zuman *et al* (1968) used polarography in their study of a series of substituted benzophenones in buffered aqueous-ethanolic media and the half-wave potentials were correlated with Hammett substituent constants (σ). Sivakumar *et al* (1984) have extended the study to aqueous-organic mixtures i.e. in 50% dioxane-water, 50% DMF-water and 50% isopropanol-water but have not made any correlations. Diffusion coefficients and rate constants were reported by the authors from the cyclic voltammetry results. Blazquez *et al* (1985) in their recent paper on the 'electrodimerisation of benzophenone on mercury electrode' have reported the results of a reinvestigation of the mechanism of the first reduction step of benzophenone in buffered ethanol-water solutions below a pH of 6. Current-time curves and differential capacitance-potential curves were used to establish the reversible nature of the first electron transfer.

The electrochemical reduction behaviour of benzophenone has also been investigated in non-aqueous solvents – namely formamide (Harry Letan and Gropp 1953), dimethyl formamide (Given and Peover 1960; Wawzonek and Gundersen 1960), acetonitrile (Lunnazi *et al* 1971), pyridine (Michelli and Elving 1968) and dimethyl sulphoxide (Tallant and Evans 1969). Two successive one-electron steps are observed, the first is attributed to the formation of a free radical anion and second to the benzhydrol dianion. The first reduction step is found to be more reversible than the second one. The effect of proton donors on the reduction behaviour has also been studied.

Saveant and Nadjo (1971) and Saveant and Thiebault (1978) have studied the reduction behaviour of halo-derivatives of benzophenone in DMF, DMSO, acetonitrile and liquid ammonia. The reduction of these compounds in aqueous media is found to follow the same reaction path as the unsubstituted compound (Zuman *et al* 1968b) whereas in aprotic solvents a reductive cleavage of the carbon-halogen bond is observed at potentials positive to the carbonyl group reduction. The possible reduction mechanisms are also discussed.

In our laboratory, considerable amount of work has been done in molten acetamide at 85°C on the electrochemical reduction of oxygen, metal ions and a few quinones (Phani 1984). The study indicated that molten acetamide behaves like water. The present study was undertaken to follow the electrochemical reduction of benzophenones in molten acetamide. The diffusion coefficients and the kinetic parameters are evaluated and the results are discussed.

2. Experimental

Pure samples of acetamide (E Merck) (m.p. 81.5°C, density 0.997 g/ml at 85°C) are dried over fused calcium chloride under vacuum. The solid is then transferred to

the electrolytic cell with minimum exposure to the atmosphere and melted in a dry hydrogen atmosphere. The cell is a double-walled vessel with provision for circulation of water. The temperature of the melt is maintained at 85°C with the help of HAAKE R20 thermostat. 1.0 M CH₃COONa is generally used as the supporting electrolyte which renders the medium slightly basic.

Commercial samples of benzophenone, 2,4-dihydroxy, 2-hydroxy-5-chloro, 4-hydroxy (Bio-organics) and 4-bromo benzophenones (Fluka) were used after testing for the purity of the compounds. The other compounds were prepared as prescribed in the literature.

The dropping mercury working electrode has the characteristics of $m = 2.47 \text{ mgs}^{-1}$ and an open circuit drop time of 3 sec at a height of 57 cm of the mercury column in 1.0 M CH₃COONa in molten acetamide. The hanging mercury drop electrode (HMDE) is of a Metrohm make with an area of 0.022 cm² for a four-division drop. The area is calculated from the average weight of several drops assuming spherical shape for the drops. Two glassy carbon electrodes are used in our experiments with geometrical areas of 0.06 cm² and 0.075 cm². The true surface areas of the electrodes were determined from the standard experiment of Cd⁺² ion reduction in molten acetamide. Cd⁺² undergoes a reversible reduction at the mercury and at the glassy carbon electrodes. The diffusion coefficient of Cd⁺² ion in molten acetamide (Phani 1984) and the area of the HMDE are known. For the same concentration and sweep rates, the i_p values at these two electrodes are compared and the area of the glassy carbon electrode is calculated. The areas of the electrodes are 0.07 cm² and 0.1 cm², respectively. The glassy carbon electrodes were mounted into a Teflon cylinder with the surface flush with the edge of the cylinder. This is then made to fit snugly into a suitable glass tube using 'Araldite'. The electrical contact is by a copper wire inserted into mercury placed on top of the carbon electrode. The glassy carbon electrodes were hand-polished with various grades of fine emery papers, degreased with acetone, washed thoroughly with water and dried before use.

The reference electrode is Ag, AgCl/Cl⁻ (saturated). It is made of a thin-walled glass bulb containing molten acetamide saturated with AgCl and KCl. Contact with the melt is made by a wetted asbestos wick passing through a small hole in the glass bulb. A large platinum foil is used as the counter electrode.

The potential range of investigation with a mercury electrode is from -0.1 V to -1.6 V and with a glassy carbon electrode (GCE) is from +0.7 V to -1.9 V versus the Ag, AgCl/Cl⁻ (saturated) electrode. Platinum electrodes could not be used as a large reduction peak is observed at -1.0 V. This reduction process probably occurs at highly negative potentials with mercury and glassy carbon electrodes.

A potentiostat interfaced with a scan generator constructed from operational amplifiers in this laboratory is used for our experiments. The polarograms and the cyclic voltammograms are recorded with an X-Y recorder (Digigraphic series 2000).

At least four different concentrations of the depolarisers in the range of $2 \times 10^{-4} \text{ M}$ to $3 \times 10^{-3} \text{ M}$ were used in our study.

3. Results

Figure 1 shows the polarogram for the reduction of benzophenone in molten acetamide at different concentrations. A well-defined single wave is obtained. The reduction process is diffusion-controlled and the i_d values are proportional to the concentrations studied. A maximum is observed when the concentration exceeds about 1.5×10^{-3} M for all the benzophenones studied except 2-hydroxy-5-chloro benzophenone. For this compound, no maximum is observed upto a concentration of 2.0×10^{-3} M.

Table 1 gives the polarographic results for the reduction of benzophenones in molten acetamide. The $E_{1/2}$ values are found to change depending on the nature of the substituent. A maximum positive shift is observed with 4-bromobenzophenone and a maximum negative shift with 4-hydroxy benzophenone. The transfer coefficients (αn_d) are evaluated from the $\log [(i_d - i)/i]$ versus E plots and the diffusion coefficients are calculated using the Ilkovic equation.

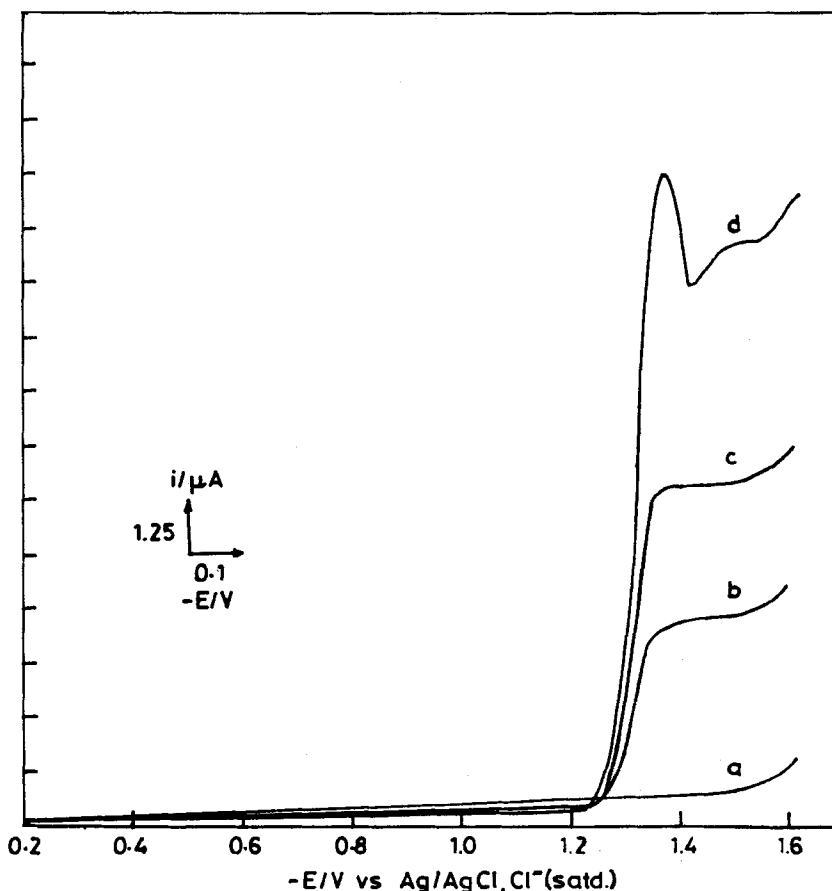


Figure 1. Polarograms for the reduction of benzophenone from molten acetamide at 85°C. Supporting electrolyte: 1.0 M CH_3COONa . Concentration of benzophenone: (a) 0.00 M (b) 0.7×10^{-3} M (c) 1.22×10^{-3} M (d) 2.01×10^{-3} M.

Table 1. Polarographic data for the reduction of benzophenones in molten acetamide at 85°C $m = 2.47 \text{ mg sec}^{-1}$; $t = 3 \text{ sec}$; $h = 57 \text{ cm}$. Supporting electrolyte 1.0 M CH_3COONa . Concentration of benzophenones $1.0 \times 10^{-3} \text{ M}$. I -diffusion current constant.

Substituent	$E_{1/2} \text{ (V)}$	I	$D \times 10^6$ ($\text{cm}^2 \text{ sec}^{-1}$)	αn_a
H	1.315	3.12	4.83	1.78
2-Hydroxy	1.36	2.65	3.49	1.78
4-Hydroxy	1.49	2.60	3.366	0.845
2,4-Dihydroxy	1.48	2.32	2.6	1.52
2-Hydroxy-5-methyl	1.35	2.84	4.0	1.66
2-Hydroxy-5-chloro	1.29	2.87	4.1	1.29
2-Amino	1.43	2.92	4.2	1.18
4-Bromo	1.275	3.24	5.2	1.62
3-Nitro-4-hydroxy	0.72*	5.78*	4.21*	1.03
	1.03			
	1.51			

* For the first reduction step only.

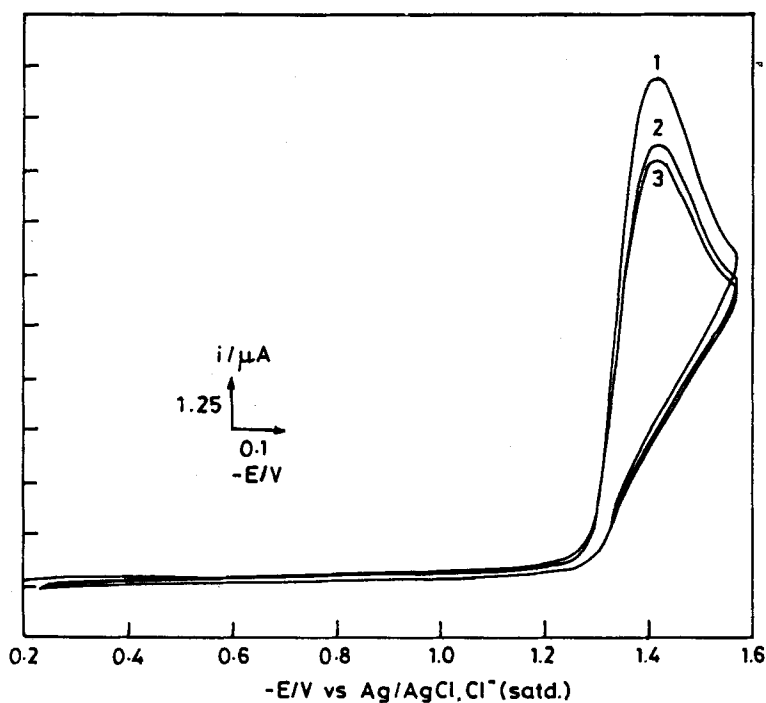


Figure 2. Cyclic voltammogram for the reduction of benzophenone from molten acetamide at 85°C. Supporting electrolyte: 1.0 M CH_3COONa at HMDE ($A = 0.022 \text{ cm}^2$). Sweep rate: 150 mVsec^{-1} , 1,2,3 correspond to the cycles. Concentration of benzophenone: $1.18 \times 10^{-3} \text{ M}$.

Figures 2 and 3 show the cyclic voltammogram of benzophenone at the HMDE and at the GCE, respectively. The i_p values are found to be proportional to $\nu^{1/2}$

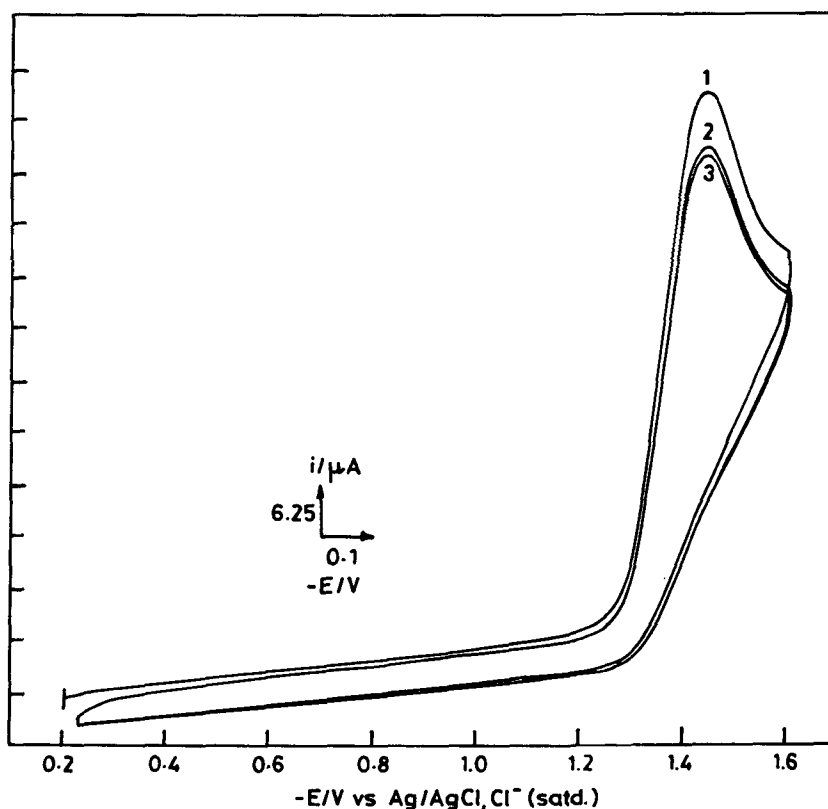


Figure 3. Cyclic voltammogram for the reduction of benzophenone from molten acetamide at 85°C. Supporting electrolyte: 1.0 M CH₃COONa at glassy carbon electrode ($A = 0.1 \text{ cm}^2$). Sweep rate: 150 mV sec^{-1} , 1, 2, 3 correspond to the cycles. Concentration of benzophenone: $1.5 \times 10^{-3} \text{ M}$.

(figure 4) and also to the concentrations studied. The irreversible nature of the reduction is clearly seen from the absence of an anodic peak in the reverse scan and also from the variation of E_p values with the sweep rates. E_p values for any one concentration shift with the nature of the substituent and show the same trend as $E_{1/2}$ potentials.

Tables 2 and 3 give the data for the reduction of benzophenones in molten acetamide from the above study. The E_p values are reported at a sweep rate of 20 mVsec^{-1} . The diffusion coefficients are evaluated using the equation

$$i_p = 3.01 \times 10^5 n (an_a)^{1/2} C_0^b \nu^{1/2}, \quad (1)$$

where i_p is the peak current in micro amperes. The transfer coefficients (an_a) are evaluated from the $E_p - \log \nu$ (figure 5) and $E_p - \log i_p$ (figure 6) graphical plots. Since the standard potentials of benzophenones are not known in literature, the standard rate constants k_s could not be evaluated. The rate constants $k_{f,h}^0$ reported here are at $E = 0 \text{ V}$.

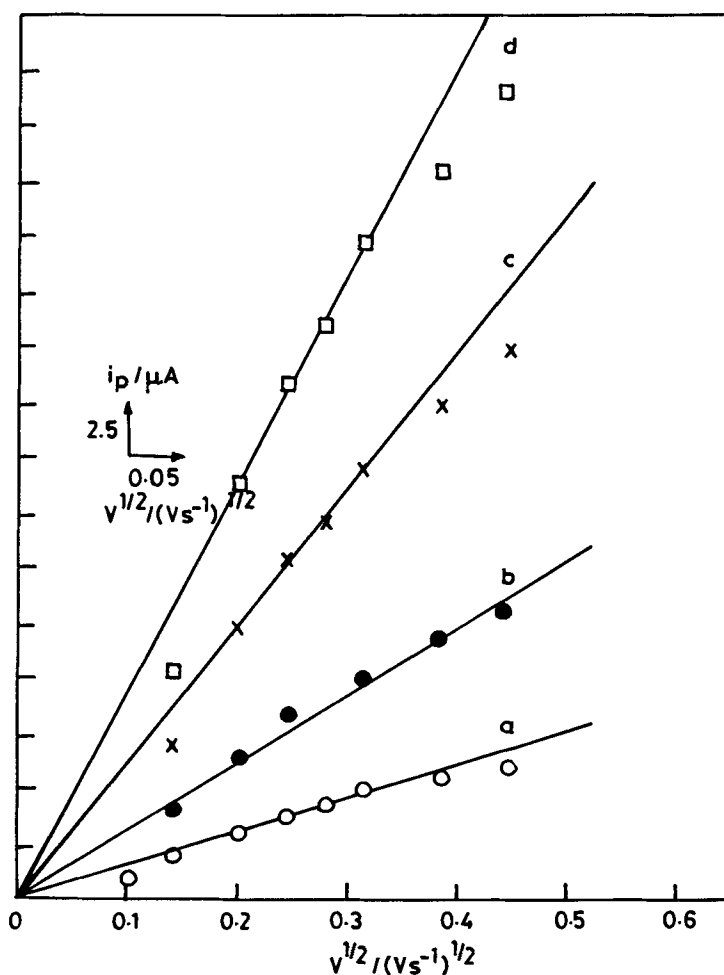


Figure 4. Plot of i_p versus $v^{1/2}$ for benzophenone reduction in molten acetamide at HMDE ($A = 0.022 \text{ cm}^2$). Supporting electrolyte $1.0 \text{ M CH}_3\text{COONa}$. Concentration of benzophenone (a) $0.57 \times 10^{-3} \text{ M}$ (b) $1.18 \times 10^{-3} \text{ M}$ (c) $2.01 \times 10^{-3} \text{ M}$ (d) $2.7 \times 10^{-3} \text{ M}$.

4. Discussion

In molten acetamide one well-defined polarographic wave is obtained for the reduction of these benzophenones at all concentrations, in the potential range of -0.1 V to -1.6 V . Molten acetamide at 85°C is known to have ionic product of $10^{-14.6}$ (Guiot and Tremillon 1968) which is comparable with that of water. Previous studies (Phani 1984) on the electrochemical reduction of O_2 , quinones and metal ions in molten acetamide show that the reduction behaviour of these compounds is similar to that in water. In aqueous-organic solvents, in the range of pH 6 and 8, benzophenone undergoes a two-electron reduction in one step (Zuman 1968). Sodium acetate is known to render the melt slightly basic and sodium perchlorate slightly acidic (Phani 1984). Benzophenone gives only one reduction

Table 2. Cyclic voltammetric data for the reduction of benzophenones at HMDE in molten acetamide at 85°C. Supporting electrolyte: 1.0 M CH₃COONa. Concentration of benzophenones ~1 × 10⁻³M.

Substituent	E_p (V) at 20 mVsec ⁻¹	$D \times 10^6$ (cm ² sec ⁻¹)	αn_a ($E_p - \log i_p$)	αn_a ($E_p - \log \nu$)	$k_{f,h}^0$ at $E = 0$ V
H	1.35	5.3	0.68	0.8	1.6 × 10 ⁻¹⁷
2-Hydroxy	1.39	3.9	0.68	0.66	8.26 × 10 ⁻¹⁷
4-Hydroxy	1.54	3.4	0.68	0.66	2.02 × 10 ⁻¹⁹
2,4-Dihydroxy	1.49	3.5	0.79	0.87	7.86 × 10 ⁻²¹
2-Hydroxy-5-methyl	1.38	2.3	1.27	1.14	1.31 × 10 ⁻²⁷
2-Hydroxy-5-chloro	1.31	1.8	1.27	1.02	3.35 × 10 ⁻²⁸
2-Amino	1.47	5.0	0.56	0.71	2.65 × 10 ⁻¹⁵
4-Bromo	1.31	4.5	0.9	1.00	2.0 × 10 ⁻²³
3-Nitro-4-hydroxy	0.78	3.67*	0.78*	0.71*	-
	1.56				

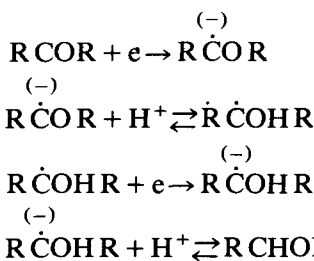
* For the first reduction step.

Table 3. Cyclic voltammetric data for the reduction of benzophenones at GCE in molten acetamide at 85°C. Supporting electrolyte: 1.0 M CH₃COONa. Concentration of benzophenones ~1 × 10⁻³M.

Substituent	E_p (V) at 20 mVsec ⁻¹	$D \times 10^6$ (cm ² sec ⁻¹)	αn_a ($E_p - \log i_p$)	αn_a ($E_p - \log \nu$)	$k_{f,h}^0$ at $E = 0$ V
H	1.33	2.0	0.6	0.48	1.12 × 10 ⁻¹⁷
2-Hydroxy	1.38	3.6	0.69	0.35	1.45 × 10 ⁻¹⁸
4-Hydroxy	1.60	2.3	0.55	0.50	1.24 × 10 ⁻¹⁷
2,4-Dihydroxy	1.48	2.02	0.66	0.60	6.0 × 10 ⁻²⁰
2-Hydroxy-5-methyl	1.34	2.5	0.81	0.60	9.8 × 10 ⁻²²
2-Hydroxy-5-chloro	1.30	1.9	0.70	0.50	1.79 × 10 ⁻¹⁸
2-Amino	1.44	3.16	0.67	0.7	1.73 × 10 ⁻²⁰
4-Bromo	1.26	2.3	0.79	0.83	5.6 × 10 ⁻²⁰
3-Nitro-4-hydroxy	1.1	3.35*	0.40*	0.4*	
	1.65				

* For the first reduction step.

wave with either supporting electrolyte. Hence it is inferred that benzophenone undergoes a one-step two-electron reduction in molten acetamide. The mechanism suggested in aqueous medium at this pH is (Zuman 1968):



with proton transfers as fast processes.

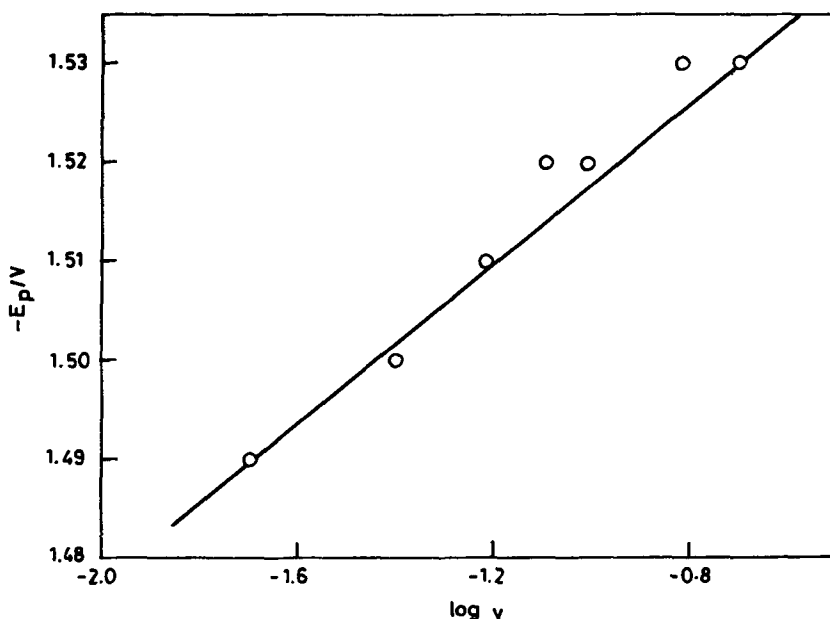


Figure 5. Plot of peak potential (CVM) versus log (sweep rate) for the reduction of 2, 4-dihydroxy benzophenone in molten acetamide at 85°C. Concentration: 0.45×10^{-3} M Supporting electrolyte: 1.0 M CH_3COONa .

The $\log [(i_d - i)/i]$ versus E plots are linear but the slope of approximately 50 mV indicates irreversibility of the reduction process. The αn_a values do not vary much with the substituents. The change in the $E_{1/2}$ values with various substituents on the benzophenone is found to follow the same trend as in an aqueous medium.

The addition of an electron at the carbon atom of the carbonyl group is facilitated by a low electron density at the carbonyl group and the half-wave potentials are shifted to more positive values. Hence the presence of electron withdrawing substituents makes the reduction easier. Accordingly the *p*-bromo benzophenone shows a positive $E_{1/2}$ shift of 40 mV while the *p*-hydroxy benzophenone a negative shift of 175 mV with respect to the unsubstituted compound. In the case of 2-hydroxy-5-chloro benzophenone, the presence of a hydroxyl group ortho to the carbonyl group may additionally hinder the electron addition due to the hydrogen bonding and steric effects. However, the presence of a chloro group meta to the carbonyl group gives a net positive shift of 25 mV in the $E_{1/2}$ value. The expected negative shifts in $E_{1/2}$ values are observed for the other compounds.

The half-wave potentials in buffered aqueous-ethanolic (Zuman *et al* 1968b) solvent have been correlated to the nature of the substituents through a Hammett plot. The Hammett plot ($E_{1/2}$ versus σ) for a number of para and meta substituted benzophenones gave a value of +0.25 for the reaction constant ρ at a pH of 9.3. In the present study linearity is observed between the $E_{1/2}$ values and the substituent constants (σ) for the following compounds: 4-bromo ($\sigma = +0.26$); 4-hydroxy (-0.7); 2-hydroxy-5-chloro ($+0.373$) and 2-hydroxy-5-methyl (-0.069). The value of σ taken for -OH group is for O^- (Jaffe 1953). The σ value of the last two

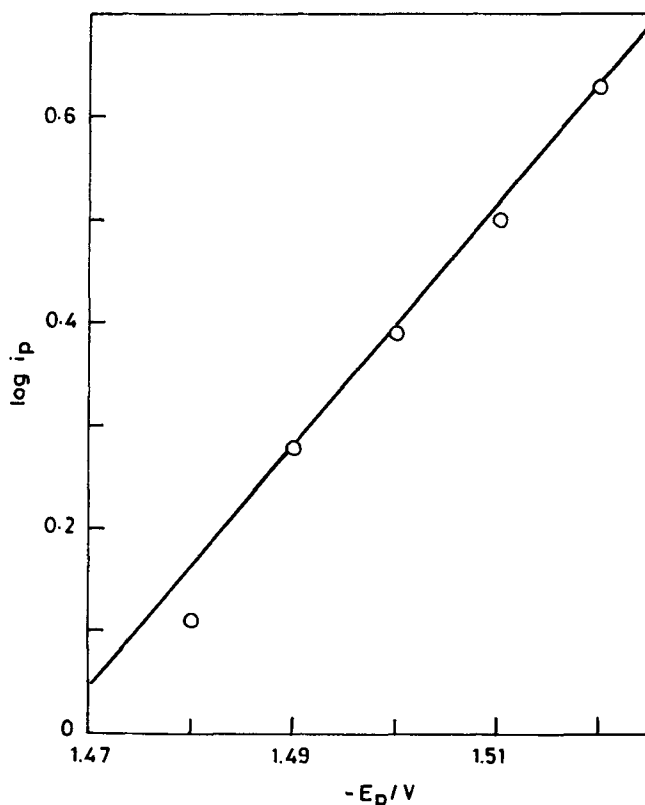


Figure 6. Plot of \log (peak current) versus peak potential for the reduction of 2, 4-dihydroxy benzophenone in molten acetamide. Concentration: 0.45×10^{-3} M. Supporting electrolyte: 1.0 M CH_3COONa .

compounds are taken for the corresponding meta substituents. The reaction constant ρ works out to be +0.218. Further experiments are to be carried out to confirm these observations.

4.1 Diffusion coefficients

The diffusion coefficients are evaluated from the polarographic and cyclic voltammetric results using the appropriate equations. Generally it is observed that the diffusion coefficients of the substituted compounds are smaller than the unsubstituted compound. No unusual results are observed: The reported value of the diffusion coefficient of benzophenone in aqueous medium at 25°C at a pH of 6.8 is $6.7 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ (Sivakumar and Jayaram Reddy 1984). The D values are found to be smaller in molten acetamide than in water. The same observation was made in earlier studies with quinones and metal ions in molten acetamide (Phani and Narayan 1985). The decrease in D value is perhaps associated with the higher value of the viscosity of molten acetamide ($\eta_{85^\circ\text{C}}$ acetamide – 2.01 cP; $\eta_{25^\circ\text{C}}$ water – 0.892 cP).

The polarographic reduction of 3-nitro-4-hydroxy benzophenone gives three waves with the $E_{1/2}$ values of -0.72 V, -1.03 V and -1.51 V. The diffusion

current of the first wave only is found to be proportional to the concentrations. The nitro group is known to undergo reduction at more positive potentials than that of the reduction of the carbonyl group (Lund 1973). The first reduction step of the nitro group is a four-electron step. The D values reported in the tables are calculated from the diffusion current values of the first wave.

The wave at -1.51 V is inferred to be the reduction of the carbonyl group since there is no reduction process observed at this potential range for nitrobenzene in acetamide ($E_{1/2}$ potentials are -0.79 V and -1.03 V, respectively). It may be mentioned however that the $E_{1/2}$ of the reduction of the nitro group is shifted to more positive values in the presence of hydroxyl groups in the ortho position and benzoyl group meta to the nitro group. It is known from the reduction of *o*-nitro phenol in aqueous medium (Aistle and McConnel 1943) that the presence of the hydroxyl group in the ortho position facilitates the reduction of the nitro group. Whether the presence of the benzoyl group has any additional effect is to be investigated. It is seen from table 1 that the presence of the nitro group has no additional effect to that of the *p*-hydroxyl group on the reduction of the carbonyl group. This is possible due to the prior reduction of the nitro group to $-NHOH$. Analysis of the reduction of the nitro compounds will be dealt in a subsequent communication.

The cyclic voltammograms at the HMDE and at the GCE also show a single reduction step in the range of potentials studied. The E_p values at both the electrodes are found to be nearly the same and are slightly more negative than the $E_{1/2}$ values. The diffusion controlled nature of the reduction is inferred from the $i_p - v^{1/2}$ plots passing through the origin and the i_p values are proportional to the concentrations of the benzophenones. The reduction mechanisms at both the HMDE and the GCE thus seem to be the same. The ratios of the i_p values at the HMDE and the GCE are found to be in proportion to the ratios of their areas, with due corrections for the slightly different αn_a values. The D values are obtained from the $i_p/v^{1/2}$ versus C plots using the corresponding αn_a values (tables 2 & 3). The values are found to be a little lower than the polarographic values but the same trend is followed.

4.2 Electrochemical kinetic parameters

The standard rate constant for a totally irreversible process can be obtained from the analysis of the polarographic wave following the procedure suggested by Koutecky. Suzuki and Elving (1961) reported a formal rate constant of 10^{-19} at $E = 0$ V with respect to SCE for the reduction of benzophenone. It is easier to obtain the rate constants from linear sweep voltammetry. Sivakumar *et al* (1983) have reported $k_{f,h}^0$ values from the cyclic voltammetric results in a number of publications for various substituted benzophenones. The $k_{f,h}^0$ values vary from 10^{-16} to 10^{-35} . The relevance of these values was not discussed and no correlations were made.

The standard rate constant k_s for a totally irreversible process can be obtained from the following equation (Galus 1976):

$$E_p = E^0 - \frac{RT}{\alpha n_a F} \left(0.78 - \ln k_s + \ln \left(\frac{\alpha n_a F D v}{RT} \right)^{1/2} \right), \quad (2)$$

if E° is known. Alternatively,

$$E_p = 1.14 \frac{RT}{\alpha n_a F} + \frac{RT}{\alpha n_a F} \ln \frac{k_{f,h}^0}{D^{1/2}} - \frac{RT}{2\alpha n_a F} \ln \alpha n_a \nu, \quad (3)$$

where $k_{f,h}^0$ is the rate constant at $E = 0$ V. The peak current i_p of a totally irreversible process is also related to the standard rate constant as follows (Nicholson and Shain 1964),

$$i_p = 0.227 nFA C_0^b k_s \exp \left(\frac{-\alpha n_a F}{RT} (E_p - E_0) \right). \quad (4)$$

Accordingly, a plot of $\log i_p$ versus E_p will be linear with a slope of $(\alpha n_a F / 2.303 RT)$ and hence if the standard potential E_0 is known, k_s can be calculated from the intercept. Since the standard potentials of benzophenones are not known in acetamide, the formal rate constants $k_{f,h}^0$ are evaluated at $E = 0$ V and are tabulated (tables 2 & 3). It may not be strictly correct to compare these $k_{f,h}^0$ values since the standard potentials are reported to vary by 100–200 mV depending on the substituents (Flaig *et al* 1968). However, since these are the first values to be reported in molten acetamide, we wish to draw attention to some important observations.

- (1) Even when $\Delta E_{1/2}$ is positive, the $k_{f,h}^0$ value is much lower for the reduction of *p*-bromo benzophenone than that of benzophenone.
- (2) The $\Delta E_{1/2}$ is negative for 2-hydroxy benzophenone but the rate constant is nearly the same as for benzophenone.
- (3) The $E_{1/2}$ shift for 2-amino benzophenone is negative but the $k_{f,h}^0$ is higher than that of the benzophenone. It has been reported that even for *p*-amino derivative the $E_{1/2}$ does not fall in the Hammett plot (Zuman 1960).
- (4) The $k_{f,h}^0$ values indicate that the reduction is faster at the glassy carbon electrode than at the HMDE.

4.3 αn_a -values

The αn_a values are generally reported from the difference in the peak potential and the half-peak potential values by the equation,

$$E_p - E_{p/2} = (1.857 RT / \alpha n_a F). \quad (5)$$

It is found that a 10% error in the αn_a value results from an error of 5 mV in the peak potential values. Hence the αn_a values are evaluated from the $(\log i_p - E_p)$ and $(E_p - \log \nu)$ plots and used in our calculations. The αn_a values are close to 0.6 ± 0.1 for the reduction at the mercury electrode except for 4-bromo, 2-hydroxy-5-methyl and 2-hydroxy-5-chloro derivatives. In the work of Zuman *et al* (1968) the αn_a from the polarographic analysis is close to one for most of the compounds, though for a few compounds for which the $E_{1/2}$ shift is in the positive direction, the αn_a values are smaller (~ 0.8). The authors have indicated that the αn_a values cannot be used for structural correlations because of the relatively large error involved in their calculations. In the present studies also, the variations in the polarographic αn_a values are small (table 1), but the values from the cyclic

voltammetric data show a definite trend. It is possible that a change in the mechanism of reduction at the HMDE may be the cause for the higher αn_a values. Since only a single reduction step is observed and if the mechanism followed is an EHEH one, then the $\alpha = 1$ is associated with the proton transfer as the rate determining step and $\alpha = 0.5$ with the electron transfer as the rate determining step. It is more probable that $n_a = 2$ and $\alpha = 0.5$ in the reduction of the three compounds. The proton transfer is generally accepted as the fast step (Zuman *et al* 1968). It is not clear at present as to why the substituents bring about this variation.

This investigation is being continued with a further series of substituted benzophenones, as well in N-methyl acetamide and dimethyl acetamide.

5. Conclusions

- (1) Molten acetamide essentially functions like water.
- (2) Substituent effects on the reduction of the carbonyl group follow the same trend as in aqueous and in aqueous-organic mixtures.
- (3) The electrochemical reduction of the carbonyl group is faster on a glassy carbon surface.

Acknowledgement

The authors thank Dr K K Balasubramanian for helpful discussions.

References

- Astle M J and McConnel W 1943 *J. Am. Chem. Soc.* **65** 35
Blazquez M, Rodriquez-Mellado J M and Ruiz J J 1985 *Electrochim. Acta* **30** 1527
Day R A, Milliken S R and Shults W D 1952 *J. Am. Chem. Soc.* **74** 2741
Elving P J and Leone J T 1958 *J. Am. Chem. Soc.* **80** 1021
Flaig W, Beutal Spacher H, Riemer H and Kalke E 1968 *Ann. Chem.* **719** 96
Galus Z 1976 *Fundamentals of electrochemical analysis* (Chichester: Ellis Harwood) p. 236
Given P H and Peover M E 1960 *J. Chem. Soc.* 385
Guiot S and Tremillon B 1968 *J. Electroanal. Chem.* **18** 261
Harry Letan Jr and Gropp A H 1953 *J. Phys. Chem.* **57** 965
Jaffe H H 1953 *Chem. Rev.* **53** 191
Lund H 1973 in *Organic electrochemistry* (ed.) M M Baizer (New York: Marcel Dekker) chapt. 7
Lunnazi L, Maccagnani G, Mazzanti C and Placucci G 1971 *J. Chem. Soc.* **B71** 162
Michielli R F and Elving P J 1968 *J. Am. Chem. Soc.* **90** 1989
Nadjo L and Saveant J M 1971 *J. Electroanal. Chem.* **33** 419
Nicholson R S and Shain I 1964 *Anal. Chem.* **36** 706
Perrin C L 1965 *Progress in physical organic chemistry* (eds) S G Cohen, A Streitwieser and R W Taft (New York: Interscience) Vol. 3, p. 221
Pfister G and Bonastre J 1965 *Bull. Soc. Chim. Fr.* 1993
Phani K L N 1984 *Electrochemical studies in molten acetamide* Ph.D. thesis, Indian Inst. Technol., Madras
Phani K L N and Narayan R 1985 *J. Electroanal. Chem.* **187** 187
Saveant J M and Nadjo L 1971 *J. Electroanal. Chem.* **30** 41
Saveant J M, Halla F M and Pinson J 1978 *J. Electroanal. Chem.* **89** 347
Saveant J M and Thiebault 1978 *J. Electroanal. Chem.* **89** 335
Sivakumar A and Jayarama Reddy S 1984 *Trans. Soc. Adv. Electrochem. Sci. Technol.* **19** 295

- Sivakumar A, Jayarama Reddy S and Krishnan V R 1983a *Indian J. Chem.* **A22** 800
Sivakumar A, Jayarama Reddy S and Krishnan V R 1983b *J. Electrochem. Soc. India* **32** 129
Sivakumar A, Jayarama Reddy S and Krishnan V R 1984 *J. Electrochem. Soc. India* **33** 177
Suzuki M and Elving P J 1961 *J. Phys. Chem.* **65** 391
Tallant D R and Evans D H 1969 *Anal. Chem.* **41** 835
Wawzonek S and Gundersen A 1960 *J. Electrochem. Soc.* **107** 537
Zuman P 1960 *Collect. Czech. Chem. Commun.* **25** 3225
Zuman P 1968 *Collect. Czech. Chem. Commun.* **33** 2548
Zuman P, Barnes D and Ryvolova-Kejharova A 1968a *Discuss. Faraday. Soc.* **45** 202
Zuman P, Exner O, Rekker R F and Nauta T H 1968b *Collect. Czech. Chem. Commun.* **33** 3213