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Electrochemical Reduction Behaviour of Benzophenones and Phenylhydrazones—A Comparative Account

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Electrochemical reduction behaviour of benzophenones and phenylhydrazones has been studied using the techniques such as cyclic voltammetry, a.c. polarography, d.c. polarography and differential pulse polarography. Similarities and differences between benzophenones and phenylhydrazones with respect to electrochemical reduction have been discussed. Kinetic parameters are also evaluated using the above techniques and discussed.

INTRODUCTION

Polarographic studies on benzophenones and substituted benzophenones are many but most of the studies concentrated on the fundamental electrode processes. Nadjo and Saveant[1], Vodzinakii and Korshunow[2], Cisak and Elving[3], Pasternak[4] and Poever and Given[5] were some of the workers who have employed the polarographic technique to study the electrochemical reduction behaviour of benzophenone[6]. Phenylhydrazones are the derivatives of carbonyl compounds. Electrochemical reduction of phenylhydrazone is very easy compared to the parent carbonyl compound. This advantage and the importance of phenylhydrazones in medicine, synthetic and analytical chemistry encouraged the scientists to study the reduction behaviour of phenylhydrazones. In the present study some disubstituted benzophenones such as 4,4′-dimethoxybenzophenone and 4,4′-dichlorobenzophene and their phenylhydrazone derivatives as well as simple benzophenone phenylhydrazone are studied employing the techniques such as differential pulse polarography, a.c. polarography, d.c. polarography and cyclic voltammetry. Controlled potential electrolysis and millicoulometric techniques are also used to identify the products and to evaluate the number of electrons involved in the electrode process respectively.

EXPERIMENTAL

Benzophenones used were supplied by Aldrich U.S.A. Their phenyl hydrazones were prepared by using the procedure given by Vogel[7]. 0.5 g of colourless phenylhydrazone hydrochloride and 0.8 g of sodium acetate were dissolved in 5 ml of water and 0.4 g of the ketone taken in a little pure ethanol was added. Contents of the mixture were shaken well until the clear solution was obtained and a little more ethanol was added to clear off the turbidity. The contents were warmed on a water bath for 15 min. and cooled The crystaliine derivative was filtered and recrys-

tallized from dilute ethanol. Purity of the compounds was tested by sharp melting points and thin layer chromatography. The melting points obtained for benzophenone phenylhydrazone-4,4′-dimethoxybenzophenone phenylhydrazone and 4,4′-dichlorobenzophenone phenylhydrazone are 136°C, 121°C and 118°C respectively. They are in agreement with the literature values[8].

All chemicals used for preparing the supporting electrolytes were of AnalaR grade, 0.1M perchloric acid, Clarks and Lubs buffer (pH 1.50), McIlvaine buffers (pH 2.50, 3.50 and 8.50), phosphate buffer (pH 6.85) and Bates and Bower buffer (pH 11.70) were employed as supporting electrolytes in methanol-water mixtures in the present study.

RESULTS AND DISCUSSION

Benzophenones are found to give two waves in acid solutions and only one wave in other solutions in d.c. polarographic technique. Both the waves are found to consume one electron each forming pinacol and carbinol respectively. Single wave in neutral and basic media is found to consume two electrons and observed to form carbinol. In the remaining techniques and in all the supporting electrolytes they are found to give only one wave. In acid solutions they are found to consume one electron and form pinacol. In neutral and alkaline media they are noticed to take two electrons and form carbinol.

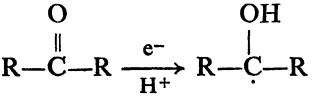
Phenylhydrazones are noticed to give two waves in more acidic solutions (pH $\leqslant$ 1.50) and one wave in acidic solutions. Precipitation of the electroactive species occurred in neutral and basic media in both solvent water mixtures. Two waves observed in more acidic media are found to be due to the reduction of phenylhydrazone into imine intermediate[9] (scission of N—N bond) with two electron addition and amine formation (saturation of C=N bond), with two more electron addition. The imine intermediate is observed to be more stable in low pH solutions and found to reduce at more negative potential. Due to this two well separated waves are observed in low pH solutions. As the pH increases the imine intermediate is found to be less stable and reduced immediately after formation and hence only one four-electron wave is observed in pH ranges.

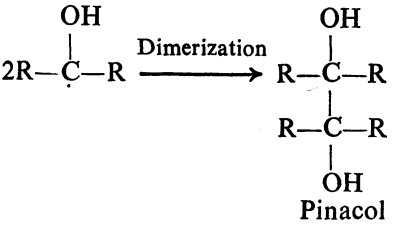
Reduction Mechanism

From the results obtained the general reduction mechanisms for benzophenones are given as follows:

In acidic media:

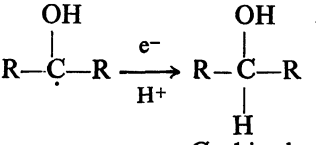
(i) First wave





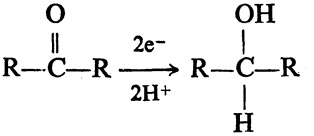
Pinacol

(ii) Second wave:



Carbinol

In neutral and basic media:

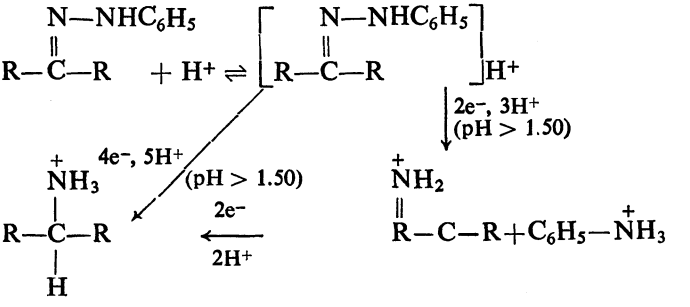


Carbinol

R : —⟨O⟩—OCH_3; 4,4′-dimethoxybenzophenone

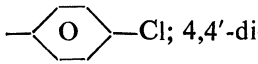
R : —⟨O⟩—Cl; 4,4′-dichlorobenzophenone

The data obtained from different techniques employed for the reduction of phenylhydrazones are found to give evidence for the following general mechanism:



R = —⟨O⟩; Benzophenone phenylhydrazone

R = —⟨O⟩—OCH_3; 4,4-Dimethoxybenzophenone phenylhydrazone



An interesting point to compare between benzophenones and phenylhydrazones is half-wave/peak potentials. The half-wave potential of benzophenone is around −0.8 V vs. SCE in low pH values. Substituted benzophenones are also found to have either more or less half-wave potentials compared to that of benzophenone depending on the nature of the substituent present in benzene ring. But when these benzophenones are converted into phenylhydrazones the latter compounds are found to be reduced at less negative potentials. Half wave/peak potential values obtained from the reduction of substituted benzophenones and their phenylhydrazones are very much useful for the comparison of substituent effects on the reduction of carbonyl and aromethine groups from these values; the order of ease of reduction of benzophenones and phenylhydrazones are seen as follows:

Benzophenone system

4,4′-Dichlorobenzophenone· > 4,4′-dimethoxybenzophenone

Phenylhydrazone system

4,4′-Dichlorobenzophenone phenylhydrazone > Benzophenone phenylhydrazone > 4,4′-Dimethoxybenzophenone phenylhydrazone.

The diffusion/peak current values in case of benzophenones are noticed to increase upto neutral medium and then decrease in basic solutions. The decrease in diffusion/peak current values in alkaline media is found to be due to the formation of germinol-diol anion. In case of phenylhydrazones diffusion/peak current values are observed to be gradually decreased with increase of pH. This is best explained on the basis of protonation of the electroactive species before reduction. In more acidic solutions phenylhydrazones are observed to be in protonated form, which is noticed to be reduced very easily giving more current values. As the pH increases, the protonated form dissociates and neutral phenylhydrazones are found to reduce at more negative potentials with difficulty giving low diffusion/peak current values. Even in these low diffusion/peak current conditions the end product is observed to be amine. I.R. spectral studies have helped in the confirmation of the product.

There is similarity in adsorption phenomena; both benzophenones and their phenylhydrazone derivatives are found to be adsorbed on the electrode surface (Fig. 1, 2). Their reduction products are not observed to be adsorbed on the electrode surface. The electrode processes are found to be irreversible in both the systems.

Kinetic parameters are evaluated and reported in Tables 1 and 2.

TABLE 1

SUMMIT POTENTIALS OF BENZOPHENONES AND PHENYLHYDRAZONES

Drop time: 3 sec, Solvent: 50% MeOH, Conc.: 0.5 mM

Supporting electrolyte	pH	4,4′-DMB $-E_s$/V	4,4′-DMBPH $-E_s$/V	B.P.H $-E_s$/V	4,4′-DCB $-E_s$/V	4′,4′-DCBPH $-E_s$/V
0.1M $HClO_4$		*	0.80	0.74	0.98	0.73
Clarks and Lubs buffer	1.50	*	0.96	0.88	1.00	0.85
McIlvaine buffer	2.50	*	1.12	1.02	1.04	0.98
McIlvaine buffer	3.50	*	1.25	1.18	1.20	1.15
Phosphate buffer	6.85	1.45	†	—	1.32	—
McIlvaine buffer	8.50	1.56	†	—	—	—
Bates and Bower buffer	11.70	1.68	†	—	—	—

4,4′-DMB = 4,4′-Dimethoxybenzophenone
4,4′-DMBDH = 4,4′-Dimethoxybenzophenone phenylhydrazone
BPH = Benzophenone phenylhydrazone
4,4′-DCB = 4,4′-Dichlorobenzophenone
4,4′-DCBPH = 4,4′-Dichlorobenzophenone phenylhydrazone.

*Peak is merging with hydrogen evolution. †EAS is getting precipitated.

TABLE 2

DIFFUSION COEFFICIENT VALUES FROM CYCLIC VOLTAMMETRIC TECHNIQUE

Conc.: 0.5 mM, 50% MeOH, Scan rate: 40 mVs^{-1}

Supporting electrolyte	pH	4,4′-DMB $D\times10^6$ $cm^2\ s^{-1}$	4,4′-DMBPH $D\times10^6$ $cm^2\ s^{-1}$	B.P.H. $D\times10^6$ $cm^2\ s^{-1}$	4.4′-DCB $D\times10^6$ $cm^2\ s^{-1}$	4,4′-DCBPH $D\times10^6$ $cm^2\ s^{-1}$
0.1M $HClO_4$		*	8.58	9.56	6.15	7.91
Clarks and Lubs buffer	1.50	*	7.01	7.47	5.93	5.96
McIlvaine buffer	2.50	*	5.02	7.40	6.54	5.19
McIlvaine buffer	3.50	*	4.19	7.29	3.79	3.95
Phosphate buffer	6.85	8.02	†	—	5.60	—
McIlvaine buffer	8.50	4.21	†	—	—	—
Bates and Bower buffer	11.70	5.35	†	—	—	—

4,4′-DMB = 4,4′-Dimethoxybenzophenone
4,4′-DMBPH = 4,4′-Dimethoxybenzophenone phenylhydrazone
BPH = Benzophenone phenylhydrazone
4,4′-DCB = 4,4′-Dichlorobenzophenone
4,4′-DCBPH = 4,4′-Dichlorobenzophenone phenylhydrazone

*Peak is merging with hydrogen evolution. †EAS is getting precipitated.

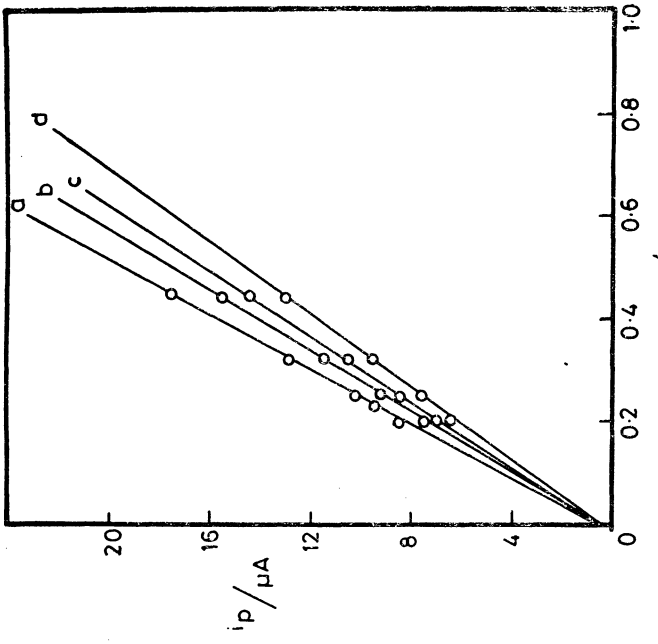


Fig. 2. i_p vs. $v^{1/2}$ plots of 4,4′-dichlorobenzophenone phenylhydrazone: (a) 0.1M $HClO_4$, (b) Clarks and Lubs buffer, (c) McIlvaine buffer, (d) McIlvaine buffer. Conc.: 0.5 mM, Solvent: 5% MeOH.

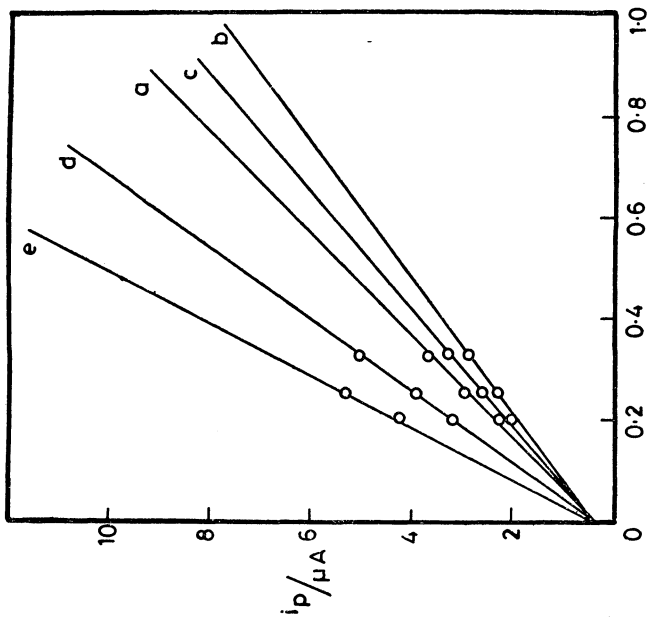


Fig. 1. i_p vs. $v^{1/2}$ plots of 4,4′-dichlorobenzophenone: (a) 0.1M $HClO_4$, (b) Clarks and Lubs buffer, (c) McIlvaine buffer, (d) McIlvaine buffer. Conc.: 0.5 mM, Solvent: 50% MeOH.

Diffusion coefficient values are in general found to be decrease with increase of pH. This generalisation is found to be true in case of phenylhydrazones, but in benzophenones it is observed to vary with diffusion current values. Diffusion coefficient values are noticed to be in good agreement in all the techniques for each compound. But diffusion coefficient values are found to vary from compound to compound. This is noticed to be due to the difference in molecular weight. Diffusion coefficient values are observed to decrease with increase of molecular weight. This is noticed in both the systems.

Rate constant values are found to decrease with increase of pH as expected. This is seen in all the compounds studied in both the systems. The observed decrease of rate constant values with increase of pH is indicative of the fact that the electrode process becomes more and more irreversible.

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