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ELECTROCHEMICAL BEHAVIOUR OF DIMETHYL HYDRAZONES – PART - 1 CYCLOHEXANONE DIMETHYL HYDRAZONE

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ABSTRACT

The polarographic behaviour of cyclohexanone dimethyl hydrazone at dropping mercury electrode in aqueous alcoholic medium has been investigated in presence of 0.1 M KCl as supporting electrolyte. The effect of depolariser concentration, pH, and drop time on the wave characteristics and the reaction mechanism occurring at the surface of the mercury drop electrode have been studied. Well defined irreversible diffusion controlled two cathodic waves were obtained in this medium between the pH range 6 and 8.2 and a single wave of irreversible and diffusion controlled nature was obtained between the pH 2 to 6 and 8.2 to 10.4. α, n_a and 'n' values and electrochemical reaction order of the system were calculated. The linearity of the diffusion current with concentration of the depolariser provides a rapid and precise method for the estimation of this dimethyl hydrazone in the concentration down to 10^{-4} M in aqueous alcoholic medium.

Key words: Cyclohexanone dimethyl hydrazone, polarography

INTRODUCTION

It is well known that both aliphatic and aromatic aldehydes and ketones react with simple and substituted hydrazines to give their corresponding hydrazones and dimethyl hydrazones respectively [1]. Dimethyl hydrazones have a wide variety of applications in dyeing polymide fibres and cotton with reactive dyes [2,3]. It is also extensively used as a stabilizer in the halogenated hydrocarbons particularly aliphatic chlorinated hydrocarbons [4] and chlorofluoro alkanes [5]. The polarographic behaviour of benzaldehyde-dimethyl hydrazone and mono substituted benzaldehyde dimethyl hydrazones in aqueous and alcoholic medium has been the subject of considerable investigation. The reaction products of benzaldehyde with simple hydrazine and alkyl hydrazines have been utilized [6] for polarographic determination of hydrazines. Well defined diffusion controlled irreversible wave was obtained in ethanolic solution containing quarternary ammonium salts as supporting electrolyte. Half wave potentials and diffusion current constants were obtained in Britton and Robinsons buffer over a pH range 3-12. The electrochemical behaviour of mono substituted benzaldehyde dimethyl hydrazones using DME have been reported [7,8] both in aqueous alcoholic and non-aqueous medium. The reaction has been found to be irreversible with a 'n' value of 4. However, no attempt has been made to study the electrochemical behaviour of dimethyl hydrazones of aliphatic aldehydes and ketones and that of disubstituted benzaldehydes.

EXPERIMENTAL

Chemicals and reagents

Cyclohexanone dimethyl hydrazone (CHDH) (b.pt. 177-180°C) was prepared from the freshly distilled cyclohexanone and unsymmetrical dimethyl hydrazine [9]. All other chemicals used in the preparation of the supporting electrolyte were of AR grade. The entire work was done with solutions containing 40% (v/v) ethanol because the solubility of CHDH in water is very low. Just before each experiment, a solution of the compound was prepared in absolute alcohol and an aliquot of this was added to the measured volume of the supporting electrolyte. The cell solution was deaerated with electrochemically generated hydrogen gas which was first washed free from other impurities by passing through gas washing bottles containing alkaline pyrogallol solution, dilute sulphuric acid, and distilled water separately. Finally, before passing into the polarographic cell it was allowed to bubble through a solution of identical composition of the supporting electrolyte, to avoid alcohol loss of the supporting electrolyte due to the carry over by the hydrogen gas. All experiments were carried out at 30 ± 1°C.

Apparatus

The current voltage curves were recorded using X-Y recorder attached to a potentiostat and a function generator. An externally connected calomel electrode connected to the cell by means of agar-agar bridge (3.0% agar + 4 % KCl) served as the reference electrode. Mercury pool electrode served as the counter electrode. The capillary characteristics measured in 0.1 M KCl (40 % alcohol + 60 % water) at potential – 0.8 V (SCE) were m = 3.45 mg; t = 4.2 sec. and $h_{(corrected)}$ = 50 cm. Necessary corrections were made for residual current in determining the limiting current data. The polarographic current values in this report were measured with no R.C. damping. The currents were measured at the end of the drop life as recommended [10] in the case of organic compounds.

RESULTS AND DISCUSSION

a) General behaviour

Typical polarograms of CHDH are shown in figure 1. Between the pH 6 and 8.2 two well defined, diffusion controlled, irreversible waves appear. In other pH ranges i.e. 2.5 to 5.6 and 8.2 to 10.4 only one wave appears and the half wave potential of this single wave coincides with that of the first of the two waves which appear in neutral to slightly alkaline pH range. The half wave potential of first wave is independent of pH in the entire pH range in which the investigation is made. It indicates that the electron transfer takes place first and then protonation. No hydrogen ion is involved in the rate determining step of the reduction process of the compound in the first wave. It was observed [11] that the electrochemical reduction of azomethene compounds on metals with high hydrogen overvoltage took place via an electronic mechanism i.e. electron transfer preceding protonation. In the

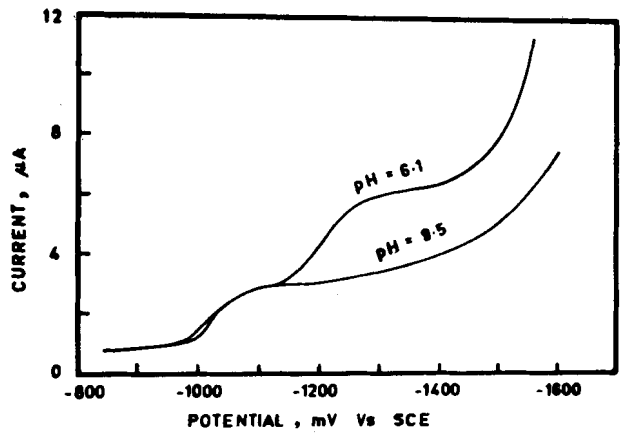


Fig. 1 : Polarograms of 1.07×10^{-4} M CHDH

case of second wave, the half wave potential is pH dependent and shifts to more negative potentials with rise of pH indicating that hydrogen ions are involved in the rate determining step and protonation precedes electron transfer. The $E_{1/2}$ / pH relation of the second wave is a straight line with a slope of 0.052 V/pH in the pH range 6 to 8.2 (Fig. 2). This indicates that one H^+ ion is involved in the rate determining step during the second wave because of linear relationship of $E_{1/2}$ – pH plot [12].

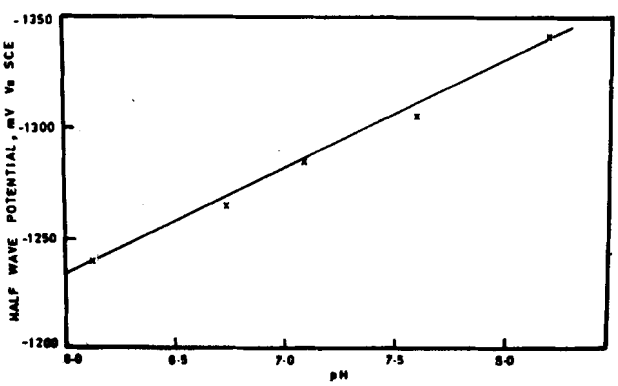


Fig. 2 : Dependence of $E_{1/2}$ on pH for 1.07×10^{-3} M CHDH (Second wave)

While going to the acidic pH range the second wave rapidly disappears. This may be due to the fact that the half wave potential of the second wave of the depolariser coincides with the hydrogen evolution potential in acidic media. When the pH is made alkaline then also the second wave disappears slowly and it may be due to the non-availability of protonated species because of lower proton concentration. The plots of the limiting currents vs concentration of CHDH prove the validity of the Ilkovic equation. Satisfactory linear lines passing through the origin are obtained at all pH values (Fig. 3). The applicability of this method for the analysis of this compound is also supported by the constancy of i_d/c values. The effect of mercury height i.e. $h_{(corrected)}$ on the limiting currents of both the waves exhibits diffusion controlled process at different pH.

b) Reaction order and Tafel slope

The electrochemical reaction order can be determined from the concentration dependence of the current density at a constant potential, however, the employed potential must be located in the validity range of the Tafel line. Then the reaction order is obtained from the measured cathodic current density as a function of the concentration [13].

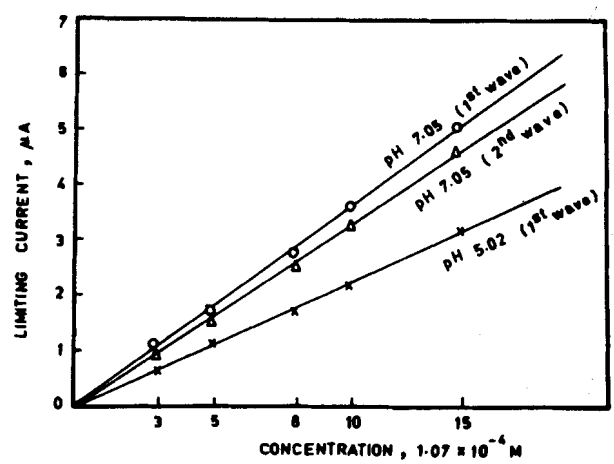


Fig. 3 : Effect of concentration of CHDH vs i_d

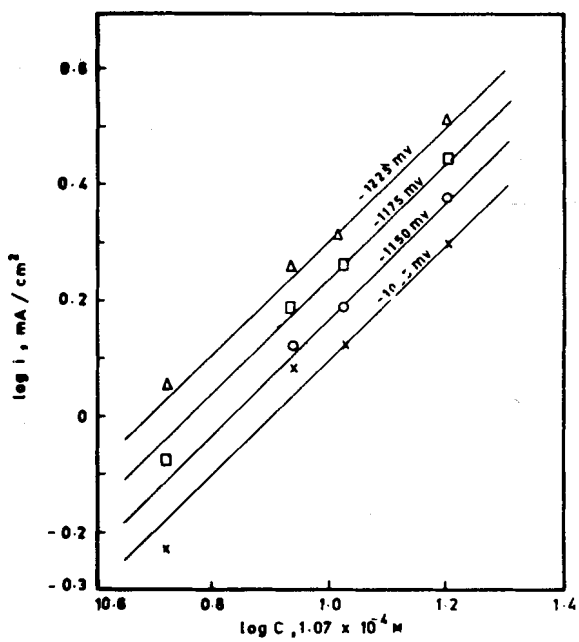


Fig. 4 : Reaction order with respect to the concentration of CHDH

Figure 4 shows the reaction order plots for both the waves. In both the cases, the reaction orders are independent of the potentials at which they are calculated, provided that these are within the range of potentials corresponding to the foot of the wave. The value of the reaction order is one for both waves and is independent of pH.

Figure 5 gives the log c.d. vs potential data corresponding to the electroreduction of CHDH at varying pH values for both the waves. The slopes of the straight lines obtained at the potentials corresponding to the foot of the waves are independent of the pH with an average value of 224 mV per decade and 87.3 mV per decade for first and second wave respectively. The transfer coefficients have also been calculated from the Tafel slopes for both the waves independently and the values are 0.274 for first wave and 0.704 for the second wave indicating the irreversible nature of the waves.

c) Determination of number of electrons

In order to throw light on the mode of the electrode process it was deemed

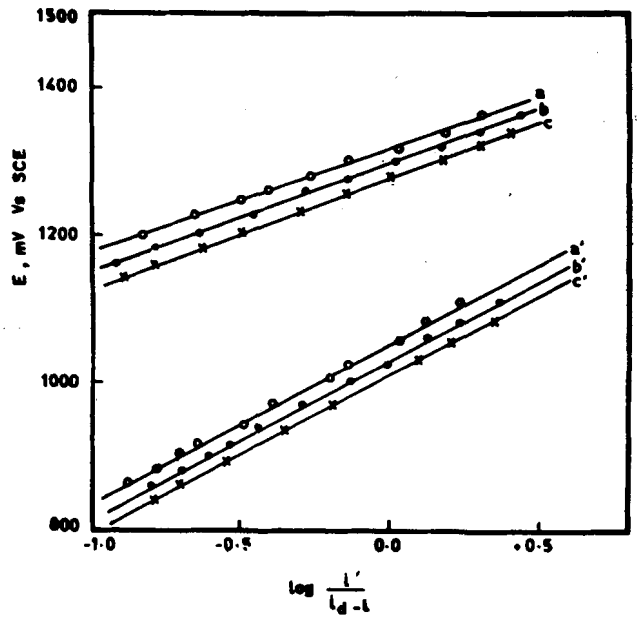


Fig. 5: Tafel plots at different pH's

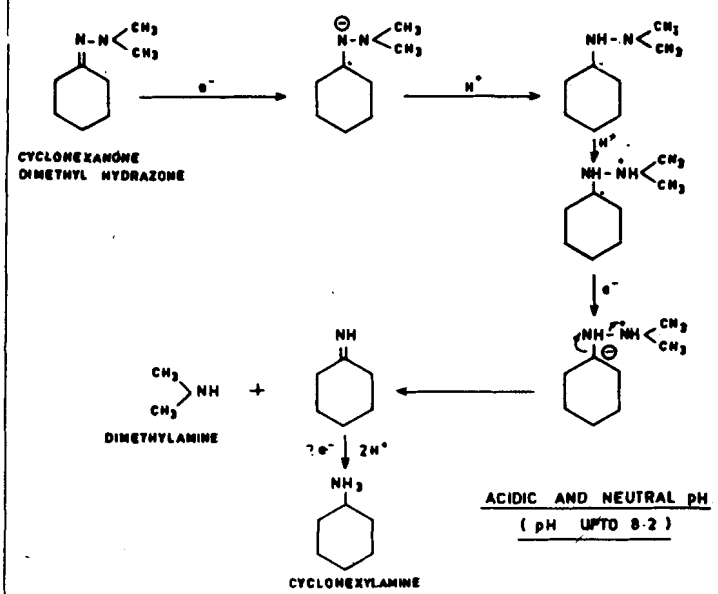
a) 8.2 b) 7.0 c) 6.2 (First wave)

a') 8.2 b') 7.8 c') 7.0 (Second wave)

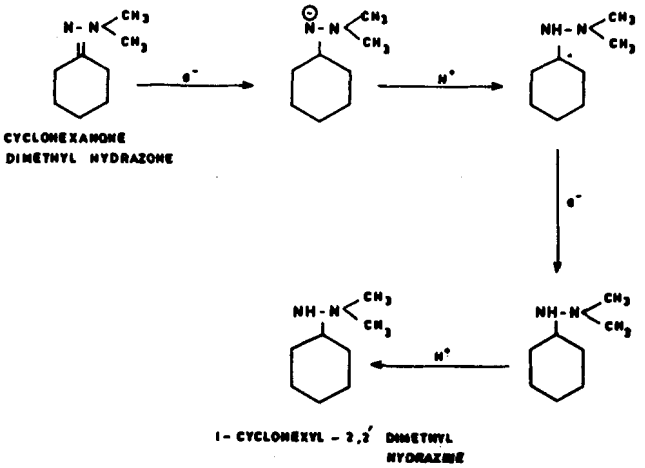
necessary to calculate 'n' value. Being an irreversible reaction it is not possible to calculate the 'n' value by logarithmic analysis and hence it was calculated by substituting the different terms of the Ilkovic equation [14]. It was found that the reduction proceeds with the uptake of two electrons in each step amounting to a total of four electron uptake.

REACTION MECHANISM

Based on the experimental facts the following overall reaction mechanism has been proposed.



Reaction Scheme 1.



Reaction Scheme 2.

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