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Electrochemical Investigations on Hydrazono Compounds

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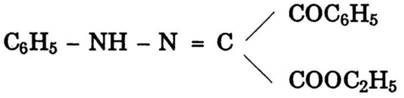
Electrochemical reduction of ethyl-2-arylhydrazono-3-phenyl-propanoate-1,3-dione and 1,5-diphenyl-3-benzoylformazan was studied at d.m.e. and G.C. electrodes. Ethyl-2-arylhydrazono-3-phenylpropanoate-1,3-dione gave one, four electron, diffusion-controlled, irreversible wave, whereas 1,5-diphenyl-3-benzoylformazan gave two reduction waves corresponding to the reduction of azo and hydrazono groups. Products of controlled potential electrolysis were successfully identified and a mechanism postulated. The effect of ionic-strength and solvent composition for the reduction of hydrazono group is also reported.

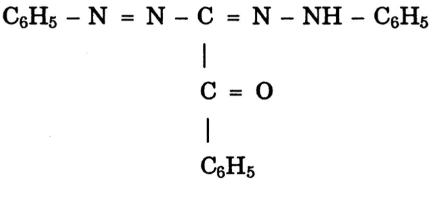
INTRODUCTION

Arylhydrazone have found wide applications in synthetic organic chemistry in the synthesis of medicinally important compounds.[1-4] In analytical chemistry, hydrazones have been used for the detection and identification of a number of metal cations.[5] Keeping in view the variegated use of hydrazones, it was considered worthwhile to investigate the electrochemical behaviour of ethyl-2-arylhydrazono-3-phenyl-propanoate-1,3-dione (*I*), 1,5-diphenyl-3-benzoylformazan (*II*) and have been reported in this communication.



$$C_6H_5-NH-N=C\left\langle\begin{matrix}COC_6H_5\\COOC_2H_5\end{matrix}\right.$$

I



$$C_6H_5-N=N-\underset{\substack{|\\C=O\\|\\C_6H_5}}{C}=N-NH-C_6H_5$$

II

EXPERIMENTAL

Compounds *I* and *II* were synthesized by the method developed in this laboratory and purified.[6] Polarographic curves were recorded on a pen recording Elico-DC CL25 polarograph. 1.0 x 10^{-3} M stock solutions of the hydrazones were prepared in dimethylformamide (Anal R). To study the effect of pH on $E_{1/2}$, Britton Robinson buffer was used. Saturated calomel electrode was used as a reference electrode. Potentiometric studies were carried using an expanded scale pH meter with glass electrode, which was previously standardized with buffers[7] of known pH.

Cyclic voltammetric studies were carried out on a BAS CV-27 cyclic voltammograph connected to a digital electronic 2000 omnograph x–y/t recorder. A three electrode cell was used for this purpose. The solution was deoxygenated by bubbling with purified[8] nitrogen gas for about 15 minutes and then a blanket of nitrogen gas was maintained throughout the solution. The reference electrode used was Ag/AgCl electrode, and the auxiliary electrode was a platinum wire. In this study a glassy carbon (GC) electrode was used as the working electrode. The reproducibility and the activity of the electrode was tested by measuring the cyclic voltammetric response for ferricyanide/ferrocyanide system in 0.1 M KCl.[9]

In a typical polarographic experiment, *e.g.* when studying the influence of pH on the polarographic behaviour of 5.0 x 10^{-5} M solution of these compounds, containing 0.5 ml compound in 30% dimethylformamide (DMF) (which was used to prevent precipitation) and appropriate B.R. buffer with tetraethylammonium bromide as supporting electrolyte, the reaction solution was deoxygenated by a stream of nitrogen gas for about 15 minutes and then the $i - E$ curves were recorded. The characteristics of d.m.e. were as follows: 5.2 mg/s^{-1} and t = 5.9/s in 1.0 M KCl (0.0 V *vs.* SCE). Unless otherwise stated, polarographic curves were recorded at h = 69 cm at 25 °C. The number of electrons involved in the reduction was determined by comparing the waves with the waves of cadmium sulphate in B.R. buffer at different pH by the method of Devries and Kroon[10] using a mercury pool cathode. The value of 'n' was also determined by controlled potential electrolysis.[11]

A modified Lingane H-type cell[12] was used for the controlled potential electrolysis. A large pool of mercury at the bottom of the large compartment was used as the cathode and a similar pool of mercury at the bottom of the smaller compartment served as the anode. The cathode compartment was filled with 10.0 ml of compound solution, 20 ml DMF, 5 ml tetraethylammonium bromide (1.0 M), and 20 ml B.R. buffer solution of pH 6.5. A potential of –1.2 V and atmosphere of nitrogen gas were maintained throughout electrolysis. Progress of the electrolysis was monitored by recording the polarographic reduction wave and cyclic voltammograms at different intervals of time, until the reduction wave completely disappeared. The catholyte so obtained was worked up for product.

The temperature coefficient of the electrode process was evaluated by Nejedly's[13] method as modified by Meites.[14]

RESULTS AND DISCUSSION

Electrochemical Behaviour of Ethyl-2-arylhydrazono-3-phenylpropanoate-1,3-dione

D.C. Polarography

A single four electron polarographic wave was observed in the B.R. buffers of pH range 2.0–12.0. The diffusion controlled nature of the limiting current was established on the basis of the plots of i_d *vs.* h and i_d *vs.* concentration. A comparison of the limiting current at various pH indicates that depolarizer is reduced consuming the same number of electrons in the entire pH range studied (Table I). The low value of the temperature coefficient (below 1.60% per degree) further supported the diffusion-controlled nature of the electrode process. The half-wave potentials were dependent on pH

TABLE I

Polarographic characteristics of ethyl-2-arylhydrazono-3-phenyl propanoate-1,3-dione, conc. 0.5 x 10^{-4} *M*

S. No.	pH	$(-)E_{1/2}$ / V	s.d.	i_d / μA	s.d.	αn_a	I	$D_o^{1/2}$	$K_{f,h}^o$ / cm x s^{-1}
1.	2.5	0.58	±0.015	0.20	±0.020	0.86	0.15	1.24 x 10^{-4}	3.83 x 10^{-6}
2.	3.8	0.60	±0.020	0.25	±0.018	0.86	0.22	1.56 x 10^{-4}	1.12 x 10^{-8}
3.	4.5	0.64	±0.015	0.25	±0.018	1.29	0.22	1.56 x 10^{-4}	1.05 x 10^{-8}
4.	6.5	0.68	±0.012	0.25	±0.015	1.29	0.22	1.56 x 10^{-4}	1.59 x 10^{-9}
5.	8.5	0.78	±0.018	0.35	±0.020	0.86	0.26	2.18 x 10^{-4}	3.70 x 10^{-9}
6.	10.5	0.84	±0.015	0.25	±0.015	1.29	0.22	1.87 x 10^{-4}	7.10 x 10^{-9}
7.	12.0	0.84	±0.012	0.25	±0.015	0.86	0.22	1.56 x 10^{-4}	5.16 x 10^{-9}

and shifted towards more negative potentials with an increase in pH (Table I and Figures 1 and 2). The plot of $-E_{1/2}$ *vs.* pH (Figure 3) was linear. Linear representation of $E_{1/2}$ – pH dependence can be described by the following linear equation:

$$E_{1/2} = 0.5 + 0.03 \ \text{pH}$$

The values of αn (product of transfer coefficient and number of electrons transferred in the rate determining step) and P (number of protons) involved in the rate determining step of the reaction were determined by using the expressions:[15]

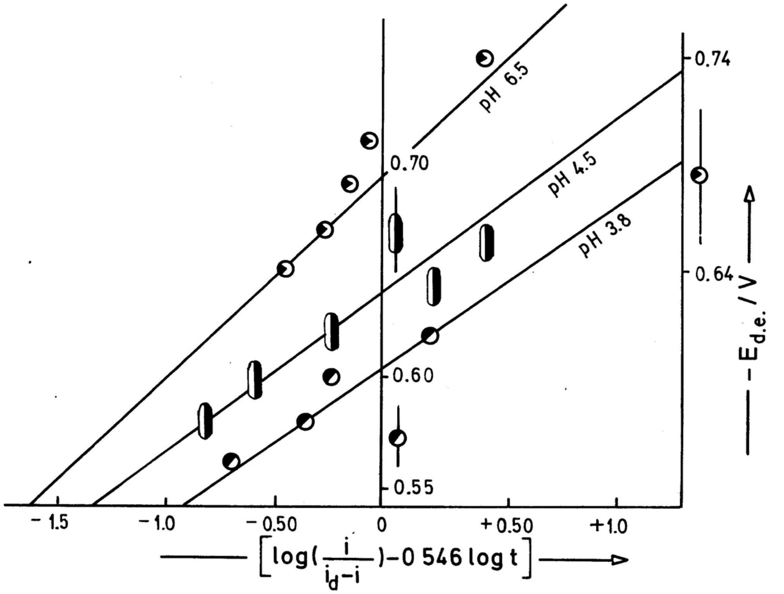


Figure 1. Plots of $-E_{de}$ *vs.* [log $(\frac{i}{i_d - i})$ -0.546 log t] for ethyl-2-arylhydrazono-3-phenylpropanoate-1,3-dione.

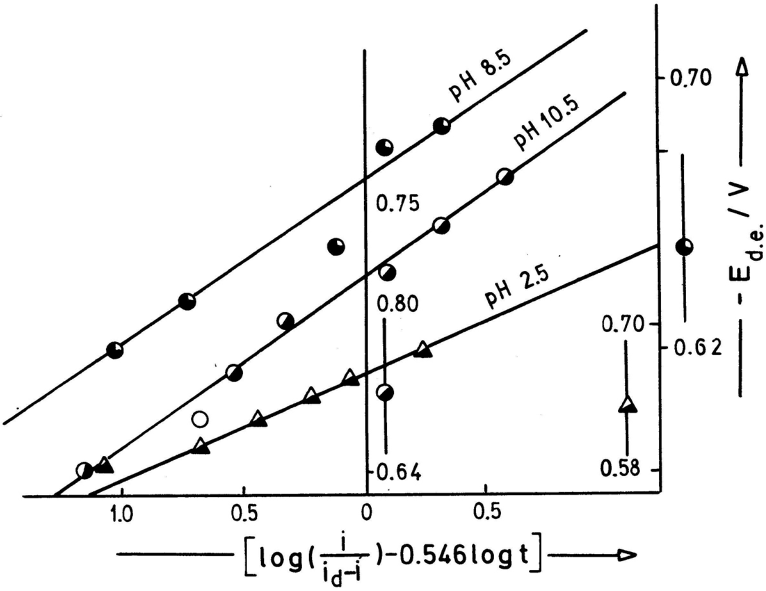


Figure 2. Plots of $-E_{de}$ *vs.* $[\log(\frac{i}{i_d-i})\ -0.546\ \log\ t]$ for ethyl-2-arylhydrazono-3-phenylpropanoate-1,3-dione.

$$E_{3/4} - E_{1/4} = -\frac{0.0517}{\alpha n_a}$$

$$\frac{dE_{1/2}}{dpH} = -\frac{0.05915}{\alpha n_a}\ P\ .$$

Linear Sweep and Cyclic Voltammetry

Typical cyclic voltammograms of ethyl-2-arylhydrazono-3-phenylpropanoate-1,3-dione in 50% dimethylformamide containing 0.1 M tetraethylammonium bromide at various scan rates are presented in Figure 4. A single well defined cathodic peak which increases linearly with the concentration of the compound in the range 0.5 x 10^{-4} M to 2.0 x 10^{-4} M and the square root of sweep rate ($\nu^{1/2}$) in the range of 10 mV/s to 200 mV/s was noticed. The peak potential was found to shift (Figure 4) cathodically with the scanrate. Limiting curves of the ill defined first reduction wave were read directly from the digital display. The peak potential also shifted cathodically with the concentration of the compound. This behaviour clearly indicates the diffusion-controlled nature of the electrode process in acidic as well as in alkaline media.

The peak potential shifted towards a more negative potential with an increase in pH. In the reverse sweep, a small hump was also observed at positive potentials. The voltammetric characteristics are presented in Table II. To ascertain whether the oxidation peak (*IIa*) is related to the reduction peak (I_c), cyclic voltammograms were also recorded by initiating the sweep in positive direction. It was noticed that the oxidation peak (*II*a) appeared at the same potential. A comparison of peak potentials for both peaks by initiating the sweep in both directions is presented in Table III. Thus, it was concluded that the processes of peaks I_c and *II*a are independent reactions. The ab-

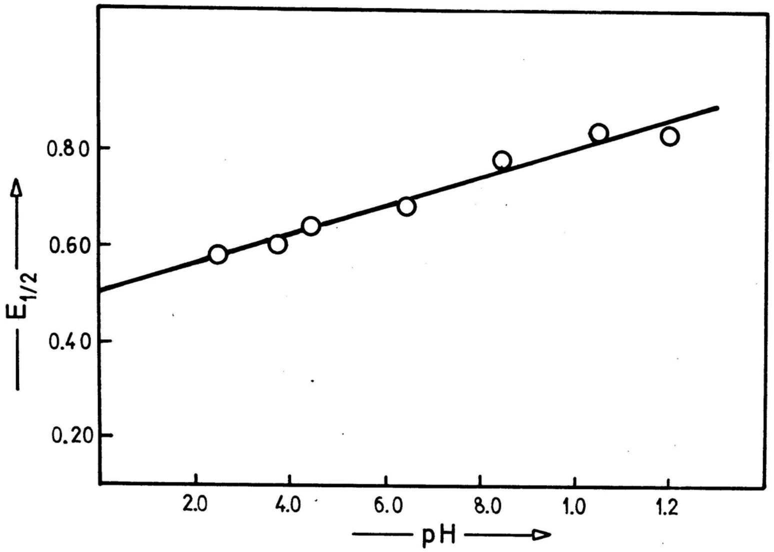


Figure 3. Plot of $E_{1/2}$ *vs.* pH for ethyl-2-arylhydrazono-3-phenylpropanoate-1.3-dione.

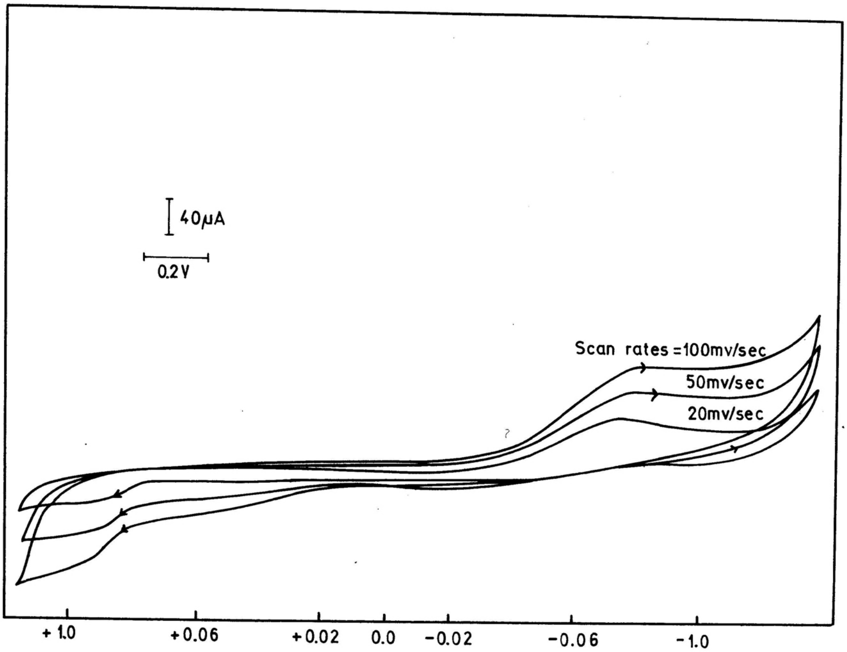


Figure 4. Cyclic voltammograms of ethyl-2-arylhydrazono-3-phenylpropanoate-1,3-dione at different scan rates at pH 6.5 at glassy carbon electrode *vs.* Ag/AgCl electrode.

TABLE II

Values of peak potentials at various scan rates for ethyl-2-arylhydrazono-3-phenylpropanoate-1,3-dione at conc. 1.0 x 10^{-4} M, pH 12.0

S. No.	Scan rate	$-(E_p)I_C$ V	s.d.	$+(E_p)II_a$ V	s.d.
1.	20	0.54	±0.021	0.84	±0.023
2.	50	0.58	±0.018	0.92	±0.021
3.	100	0.62	±0.015	0.94	±0.023
4.	150	0.64	±0.020	0.96	±0.018
5.	200	0.68	±0.023	0.98	±0.020

TABLE III

Effect of sweep directions on the peak of ethyl-2-arylhydrazono-3-phenylpropanoate-1,3-dione at different pH, scan rates mV/s, conc. 1.0 x 10^{-4} M

Scan							
Positive				Negative			
$-(E_p)I_c$ V	s.d.	$+(E_p)II_a$ V	s.d.	$-(E_p)I_c$ V	s.d.	$+(E_p)II_a$ V	s.d.
0.58	±0.018	0.86	±0.020	0.57	±0.023	0.87	±0.021
0.84	±0.020	0.82	±0.023	0.84	±0.021	0.80	±0.018
1.10	±0.021	0.80	±0.021	1.10	±0.018	0.80	±0.023

sence of the corresponding anodic peak in the reverse scan indicates that the electrode process is irreversible. This is further confirmed by the negative shift of the cathodic peak potentials with increasing the sweep rate (Table II). The cyclic voltammetric experiments also gave strong evidence for weak absorption[17,18] of the depolarizer at the electrode surface, as observed from the deviation in the E_{pc} towards higher values at higher sweep rates and also from the abnormal decrease in the current values during repeated scans.

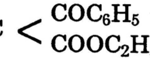
Coulometry and Production Identification

Controlled potential electrolysis of these compounds was carried out at mercury pool cathode and at GC and the plateau potential of the wave or peak was applied to determine the number of electrons in the reduction. The value of n was found to be 4.0±0.20 at all values, as confirmed by practically equal limiting currents (Table I). Similar values of n at both the electrodes indicate that the electrode process for reduction at d.m.e. and G.C. proceeds by the same mechanism.

The progress of the electrolysis was monitored also by recording UV-VIS spectra at different intervals of time. λ_{max} at 365 nm due to –NH–N=C– grouping showed a systematic decrease in the absorption maxima after each interval of time and finally it disappeared. This observation shows that no intermediate with sufficient half-life is generated during electroreduction of these compounds. After controlled potential electrolysis (~10 hours), the catholyte was subjected to product analysis. The electrolyzed solution, on separation by TLC using hexane:methanol (80:40 *v/v*) system, gave two products. One of the product was identified as aniline, on the basis of identical R_f

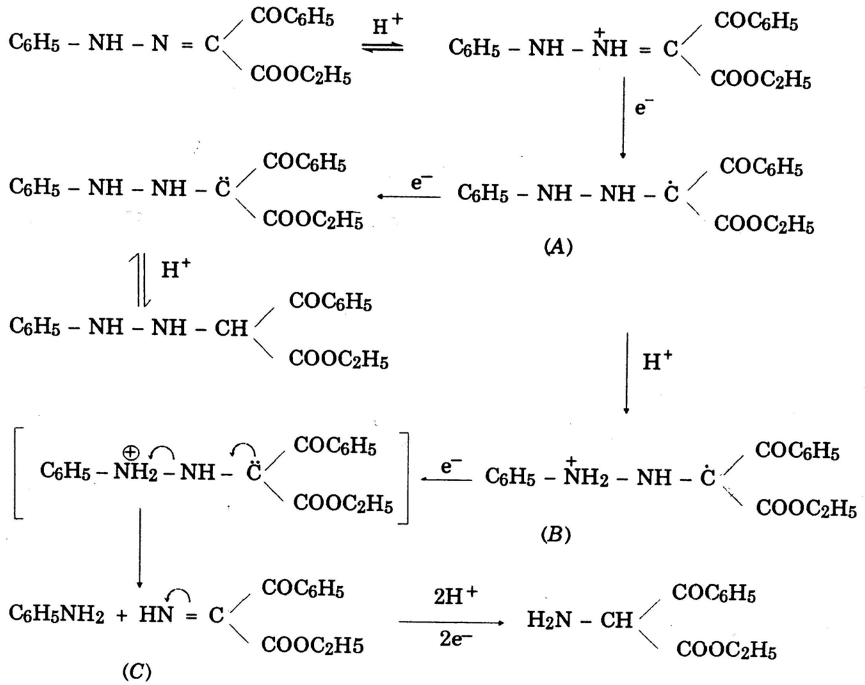
values by comparison with the authentic sample. Furthermore, the dye test also confirmed formation of aromatic amine.

The IR spectrum of the second product gave the primary amine stretching band at 3120 cm^{-1}, C–H linkage at 2680 cm^{-1} and a peak for >CO group at 1630 cm^{-1}. All these bands point toward the structure $H_2N{-}C \left\langle \begin{matrix} COC_6H_5 \\ COOC_2H_5 \end{matrix} \right.$. This is a new compound and no reference was available for comparison. This aliphatic amine is quite an interesting intermediate and this method may be used for its synthesis.



Redox Mechanism

Since the half-wave potentials are pH dependent and the limiting current is pH independent, it was concluded that both acidic and basic forms of the compounds reached the electrode surface and are electroactive.[19,20] Thus, the proton transfer reaction preceded the electrode process. In such cases, out of the two general sequences[20-22] for the proton and electron addition *viz.*, H$^+$, e$^-$, H$^+$, e$^-$ and H$^+$, e$^-$, e$^-$ H$^+$, the former sequence is more probable for these compounds in the light of their structural genesis. On the basis of H$^+$, e$^-$, H$^+$, e$^-$ sequence of addition following the general mechanism can be put forward for the reduction of –NH–N=C< group.



As it is clear from the mechanism, after addition of one proton and one electron, the radical *A* would accept the proton to form a protonated radical *B* which, after taking one electron, gets cleaved at nitrogen bond with the formation of aniline. The imine *C* formed gets further protonated and reduced. Alternatively, the radical *A* could combine with one electron instead of proton but this possibility is discarded on the basis that such a reduction would involve only two electrons whereas electrochemical data clearly indicate a four electron transfer reduction. Furthermore, the above mechanism finds support from the increase of $E_{1/2}$ and E_p with pH as the protons are cosumed in the reduction. These results are also in agreement with the mechanism proposed by other workers[22-26] for the electrochemical reduction of hydrazono group. However, the difference of about 100–300 mV/pH at d.m.e. and GC electrodes may be due to the radius of the electrodes. Furthermore, the solid electrodes are usually not free from adsorption complications and do not permit a free orientation of the species undergoing reduction and, hence, the reduction potentials are expected more negative at GC in comparison to d.m.e.

Effect of Ionic-Strength

The effect of the double layer structure on the $E_{1/2}$ of a process preceded by the protonation is given by equation.[27]

$$\Delta E_{1/2} \approx \Delta\psi_1 \left[\frac{\alpha n_a - Z}{\alpha n_a} - \frac{dE_{1/2}F}{dpH\, 2.30\, RT}\right].$$

Where ψ_1 is the variation in the double layer potential, α is the transfer coefficient, n_a the number of electrons transferred in the rate determining step and Z is the charge of the particle being discharged. The effect of varying the ionic-strength on $E_{1/2}$ should be expected when the depolarizer is in the ionic form and no such effect should be observed when it is in non-ionic form *i.e.*, when $Z = 0$. Since the second form in the brackets of this equation is nearly equal to 1 and $Z = 0$, $E_{1/2}$ will be almost independent of ψ_1 or of ionic-strength. This was studied by carrying out the experiments with varying concentrations of KCl (0.01 M to 2.0 M). The $E_{1/2}$ and i_d remained unaffected by the change in concentration of the supporting electrolyte.

Effect of Solvent Composition

First, the polarograms of these compounds were recorded in the minimum amount of dimethylformamide (30%) necessary for dissolving the compound. The DMF percentage was then systematically increased from 30% to 70% to observe the effect of solvent composition on the electrode process. It was observed that $E_{1/2}$ shifted towards the negative potential with increasing concentration of DMF in the solvent mixture. The i_d values, however, goes on decreasing and at a very high percentage of DMF in the solvent mixture, well defined waves could not be realized.

In electrode processes preceded by protonation, the shift in $E_{1/2}$ towards the negative potential can be due to a rise in pH of the solution and an increase in the dissociation constant at the protonated species.[28] Both of these factors decrease the rate of protonation, resulting in a shift of $E_{1/2}$ towards a more negative potential. From the data it appeared that these two factors are not only the factors responsible for the observed shift in $E_{1/2}$. This additional shift in $E_{1/2}$, greater than expected, may be due to the decrease in adsorbility and, hence, surface concentration of the depolarizer with an increasing percentage of DMF in aqueous-organic mixture.[28] Obviously, decreased surface concentration would retard the electrode process resulting in a decrease of i_d and shifting of $E_{1/2}$ towards a more negative potential.

Electrochemical Studies of 1,5-Diphenyl-3-benzoyl Formazan

The formazan selected for the present study is a very important compound from the electrochemical point of view since it contains hydrazono group along with azo group. This compound exhibits two polarographic waves and, similarly, two peaks in the cyclic voltammograms in acidic as well as in alkaline media. Typical cyclic voltammograms are shown in Figure 5. Polarographic characteristics are shown in Table IV. The limiting current of both waves varied linearly with the concentration of the compound and with the square root of the mercury column height. These facts indicate that both waves were diffusion-controlled. Logarithmic analysis of the waves further confirmed that the waves are irreversible in nature. The half-wave potential shifted toward more negative values with an increase in pH for both waves, suggesting that protons are involved in the rate determining step.

The cyclic voltammograms of the compound showed two cathodic peaks throughout the pH range studied in the forward scan (Figure 5). In reverse scan, except for a small hump at the positive potential, no peak was observed. This suggests the irreversible nature of the electrode process. This is also confirmed by the negative shift in

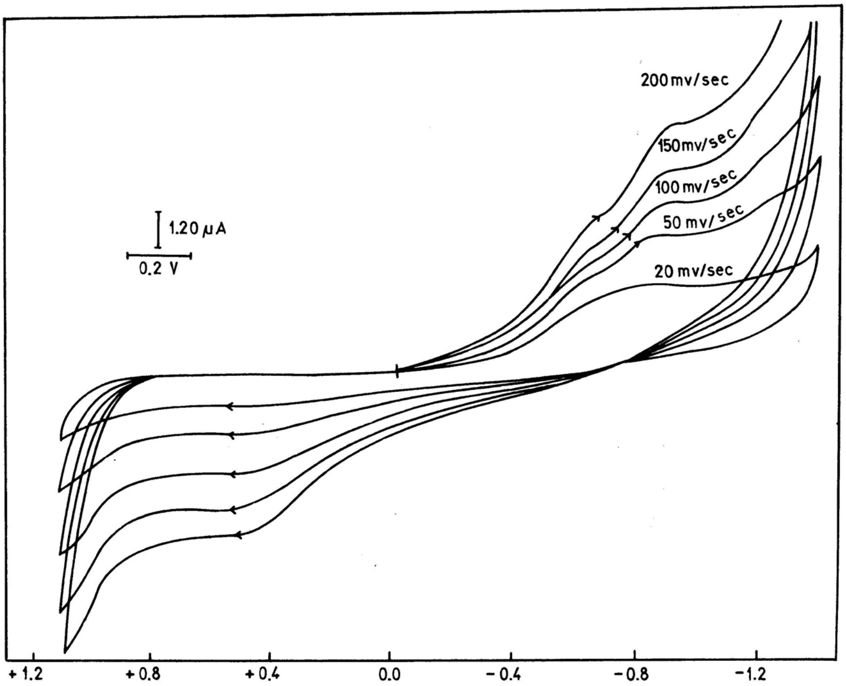


Figure 5. Cyclic voltammograms of 1,5-diphenyl-3-bezoylformazan at different scan rates at pH 2.5 at glassy carbon electrode *vs.* Ag/AgCl electrode.

TABLE IV

Polarographic characteristics of 1,5-diphenyl-3-benzoyl formazan at conc. = *0.5 x* 10^{-4} *M*

pH	$-E_{1/2}$/V				i_d/μA			
	First wave	s.d.	Second wave	s.d.	First wave	s.d.	Second wave	s.d.
2.5	0.30	±0.014	0.60	±0.011	0.10	±0.008	0.20	±0.003
3.8	0.35	±0.006	0.62	±0.015	0.12	±0.009	0.20	±0.006
4.5	0.42	±0.009	0.67	±0.006	0.15	±0.006	0.25	±0.009
5.6	0.51	±0.012	0.68	±0.008	0.12	±0.009	0.20	±0.005
6.5	0.58	±0.014	0.80	±0.012	0.15	±0.010	0.25	±0.011
8.5	0.62	±0.012	0.84	±0.011	0.10	±0.008	0.20	±0.008
10.5	0.66	±0.015	0.87	±0.015	0.15	±0.005	0.20	±0.009
12.0	0.67	±0.006	0.88	±0.011	0.10	±0.006	0.25	±0.005

the peak potential with increasing sweep rates. The total number of electrons involved in the polarographic and CV reduction process was found to be two and four, respectively, for the first and second waves. The first wave was assigned to the reduction of –N=N– group involving two electrons. The second wave is ascribed to the reductive cleavage of the hydrazono group at a more negative potential, on the basis of the number of electrons involved in the electrode process and difficult reduction in comparison to azo group. On the basis of the difference in reduction potential, the electrochemical method can be used for a simultaneous estimation of azo an hydrazono groups in the concentration range 10^{-3} M to 10^{-5} M.

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SAŽETAK

Elektrokemijsko istraživanje hidrazonijevih spojeva

R. Jain, R. R. Agarwal i R. K. Shrivastava

Istražena je elektrokemijska redukcija etil-2-arilhidrazono-3-fenilpropanoat-1,3-diona i 1,5-difenil-3-benzilformazana na kapajućoj živinoj elektrodi i elektrodi od staklastog ugljika. Etil-2--arilhidrazono-3-fenilpropanoat-1,3-dion pokazuje jedan 4-elektronski difuzijom kontroliran ireverzibilni redukcijski val, dok 1,5-difenil-3-benzilformazan daje dva redukcijska vala, od kojih jedan odgovara redukciji azo- a drugi hidrazono-skupine. Identificirani su produkti elektrolizze pri kontroliranom potencijalu i predloženi su mehanizmi reakcija, a i tražen je i utjecaj ionske jakosti i sastava otapala na redukciju hidrazono-skupine.