Polarographic Investigations of Certain Propiophenone Benzoic Acid Hydrazones

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Abstract

The electrochemical behavior of (a) propiophenone benzoic acid hydrazone, (b) 4'– methyl propiophenone benzoic acid hydrazone, (c) 4'– methoxy propiophenone benzoic acid hydrazone, (d) 4'– hydroxy propiophenone benzoic acid hydrazone and (e) 4'– chloro propiophenone benzoic acid hydrazone were investigated at the dropping mercury electrode by employing DC polarography. The variables that influence the electrode process were extensively studied. All compounds under investigation gave a single well defined polarographic wave. The mechanism for the electrode process was proposed in acid as well as in basic media.

Keywords: Polarographic studies; 4'– (substituted) propiophenone benzoic acid hydrazone; Kinetic parameters; Thermodynamic parameters; Mechanism of electrode reaction.

Introduction

Most of the azomethine compounds find numerous applications in analytical chemistry[1, 2]. They also find extensive applications in medicinal field[3-6]. Because of the pervasive applications in several fields, the characteristics of hydrazones are most widely studied by many workers. Among them, the electrochemical studies [7-9] involving oxidation-reductions of hydrazones are the most important because they thought to be useful for enlighting the metabolic pathway of the drug containing hydrazones. Hence the knowledge of electrochemical reduction of hydrazones is a prerequisite for understanding the mechanism of their biological or pharmacological activity[10,11]. The fundamental study on electrochemical reduction of hydrazones was reported by Laud[12]. Since then many workers have reported the electrochemical behavior of hydrazones in different solvents[13-21]. A survey literature suggests that many workers have reported[22-26] a four electron reduction of hydrazones in acid as well as in alkaline media with the formation of amino compounds. Similar observations were reported by Mathur et. Al[27] and Rajiv and his coworker[28]. A survey of literature reveals that not many propiophenone benzoic acid hydrazones were studied for their electrochemical behavior at the dropping mercury electrode.

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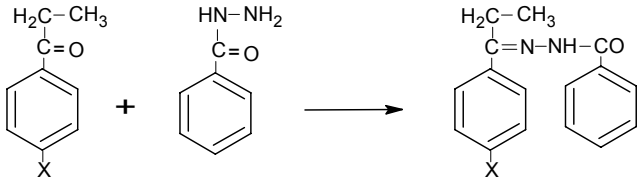
Materials and Methods

Synthesis of hydrazones of propiophenone

Equimolar solutions of benzoic acid hydrazide and the corresponding ketone in ethanol solution were refluxed for four hours and cooled. The solid derivative separated was filtered and washed with water. The crude sample thus obtained was recrystallised from ethyl alcohol to obtain crystalline substance.



X = -H (a), -CH_3 (b), -OCH_3 (c), -OH (d) and -Cl (e)

Preparation of solutions

The hydrazone solutions were prepared in dimethylformamide. The required amount of hydrazone was dissolved in 100 mL of the dimethylformamide to give a solution of concentration 0.01M.

Acetic acid (0.04 M), phosphoric acid (0.04 M), boric acid (0.04 M) and sodium hydroxide (0.2M) were used to prepare Britton-Robinson buffers in the pH range 2.1 to 10.1.

Instruments employed

An Elico D.C. polarograph CL 357 was used for polarographic studies. An Elico pH meter Model LI 613 was used for pH measurements.

General experimental procedure

12.5 mL of Britton-Robinson buffer solution of required pH, 2.5 mL of the solution of the required hydrazone were taken in a 25 mL standard flask and diluted to the mark with dimethylformamide. The contents of the flask were shaken well and transferred into the polarographic cell. Pure nitrogen gas was passed into the cell for about 15 minutes to expel the dissolved oxygen out and then the polarograms were recorded.

Results and Discussion

Effect of pH

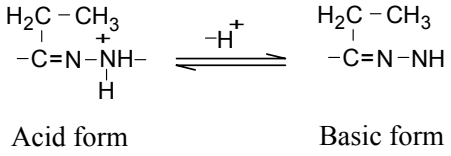
The polarographic investigations were carried out in buffer solutions ranging from pH 2.1 to 10.1.

An inspection of the structure of the compound suggests that the sites susceptible for reduction are the exocyclic >C=N–NH– and the exocyclic amide-I carbonyl group (–CO–NH–). However exocyclic >C=N–NH– is more susceptible for reduction than exocyclic amide-I carbonyl group (–CO–NH–). This was practically confirmed by the fact that benzoic acid hydrazide fails to undergo reduction under the given experimental conditions, hence the polarographic wave observed in the

reduction of 4'– (substituted) propiophenone benzoic acid hydrazone was attributed to the reduction of exocyclic >C=N–NH– group.

Limiting current-pH relation

It is evident from figure 1 that the limiting current decreases with increase in pH, the decrease in limiting current was attributed to the acid-base equilibrium occurring between the two structural forms of the depolarizer.



Acid form Basic form

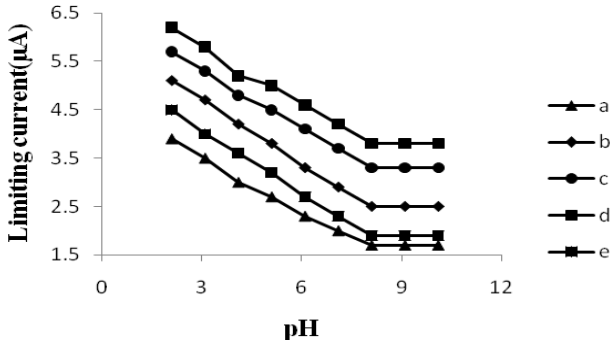


Figure 1. Effect of pH on limiting current of hydrazone
[Hydrazone] = 1×10^{-3}M; Medium = Dimethylformamide (50% by volume)

It was noticed that 4'– (substituted) propiophenone benzoic acid hydrazones were reduced in the pH range of study giving a single reduction peak whose height decreases with increase in pH since the rate of protonation decreases with the increase in pH. In alkaline solutions, the hydrazones (a to e) exist in the azomethine anionic form[29] and the later in alkaline solutions undergoes chemical change partially into corresponding carbonyl compound. There exists equilibrium between the azomethine anionic form and carbonyl compound. The decrease in limiting current with increase in pH was attributed to the chemical cleavage of the depolarizer but the acid-base equilibrium cannot be ruled out.

Half wave potential–pH relation

In the acidic medium, the half wave potential '$E_{1/2}$' shifts to more negative values with increase in pH. The corresponding plot is shown in figure 2(A) and (B). The $E_{1/2}$ – pH relationship is represented by

$-E_{1/2} = 0.62 + 0.08 \times$ pH V vs SCE for a
$-E_{1/2} = 0.87 + 0.07 \times$ pH V vs SCE for b
$-E_{1/2} = 1.00 + 0.08 \times$ pH V vs SCE for c
$-E_{1/2} = 1.14 + 0.08 \times$ pH V vs SCE for d
$-E_{1/2} = 0.34 + 0.08 \times$ pH V vs SCE for e.

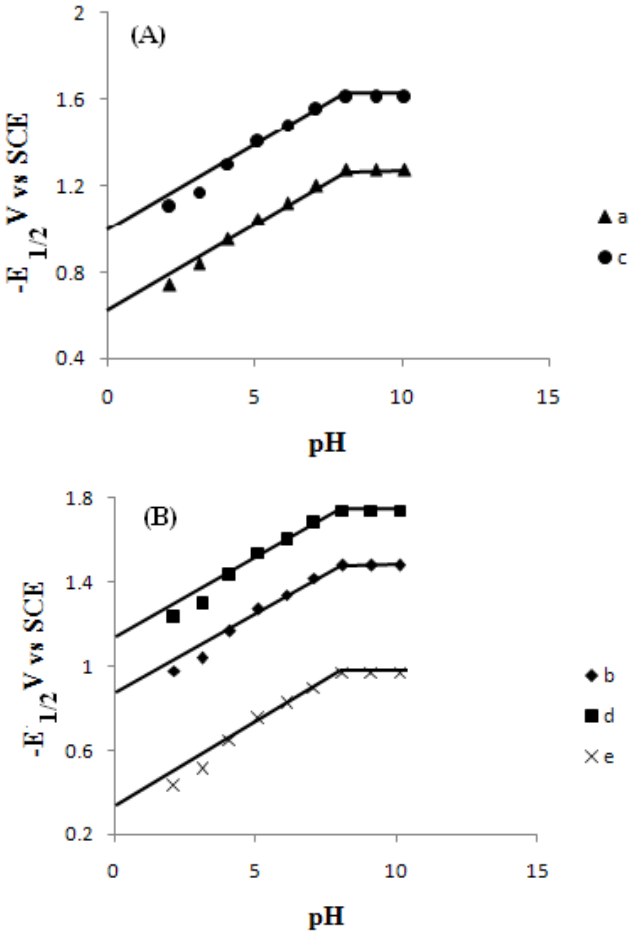


Figure 2 (A) & (B): Effect of pH on half-wave potential of hydrazone
[Hydrazone] = 1×10^{-3}M; Medium = Dimethylformamide (50% by volume)

These observations reveal that protons are involved in the reduction process [30]. The number of protons involved in the reduction process was calculated by the following equation.

$$p = \left(\frac{\Delta E_{1/2}}{\Delta p^{H}}\right)\left(\frac{\alpha n_a}{0.05915}\right)$$

Where α is the transfer coefficient and n_a is the number of electrons involved. α provides an insight into the way the transition state is influenced by the applied potential. In terms of energy barriers between the oxidized form of the species (reactant) and the reduced form (product), the free energy of the reactants can be changed by increasing or decreasing the potential applied to the electrode. The extent to which the free energy change contributes to a change in the activation energy is dependent on the magnitude of α. The value of α ranges from 0 to 1.

Effect of height of the mercury column head (h) on the limiting current (i_L)

A plot was drawn between the i_L and √h at typical pH values of 4.1 and 8.1 is shown in figures 3 and 4 respectively. The figures reveal the linear dependence of

limiting current on '$h^{1/2}$' and the plot passes through origin. The above mentioned facts suggest the diffusion controlled nature[31] of the polarographic wave.

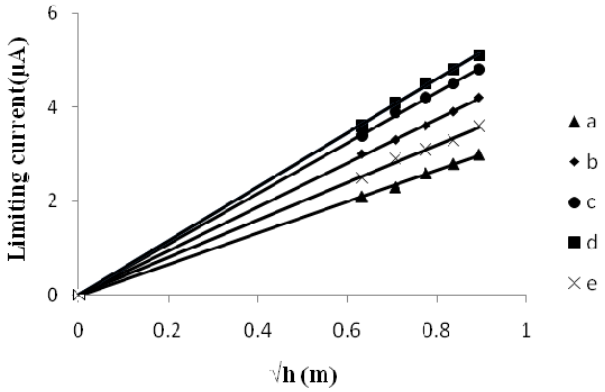


Figure 3. Effect of mercury column height (h) on limiting current of hydrazone [Hydrazone] = 1×10^{-3}M; pH = 4.1; Medium = Dimethylformamide (50% by volume)

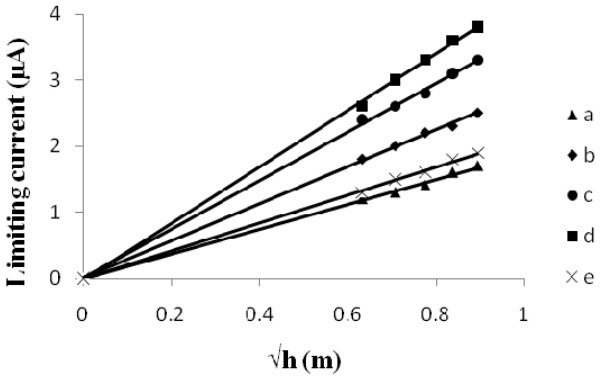


Figure 4. Effect of mercury column height (h) on limiting current of hydrazone [Hydrazone] = 1×10^{-3}M; pH = 8.1; Medium = Dimethylformamide (50% by volume)

Effect of concentration of the depolarizer on limiting current

The effect of concentration of hydrazones (a to e) on limiting current in the concentration range 0.25 to 2.00 mM has been studied in solutions of typical pH 4.1 and 8.1. The linear plots obtained between i_L and concentration shown in figures 5 and 6 reveal that the proposed method can be conveniently applied for the determination of small amount of hydrazones under study. The linear relationship between i_L and concentration supports the diffusion controlled nature of the reduction process.

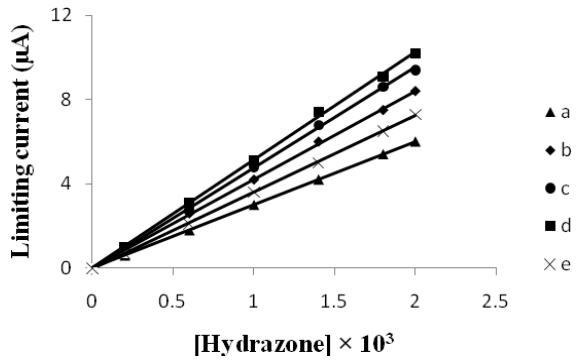


Figure 5: Effect of concentration of hydrazone on its limiting current
pH = 4.1; Medium = Dimethylformamide (50% by volume)

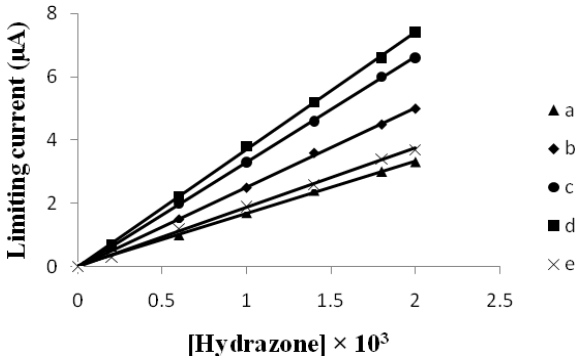


Figure 6: Effect of concentration of hydrazone on its limiting current
pH = 8.1; Medium = Dimethylformamide (50% by volume)

Irreversible nature of the wave

The wave was irreversible in the pH range 2.1 to 10.1 due to the bulky group attached at the end of the >C=N linkage[32]. The irreversible nature of the wave was established by semi log plots shown in figure 7 and by the shift of the half-wave potential values towards the more negative values with increase in the concentration of the depolarizer[33]. The irreversible nature of the wave was further confirmed by the decrease in heterogeneous rate constant values '$k^{o}_{f,h}$' and increase in activation free energy change values 'ΔG^{*}' with the increase in pH of the solution. The pertaining results are given in table 1.

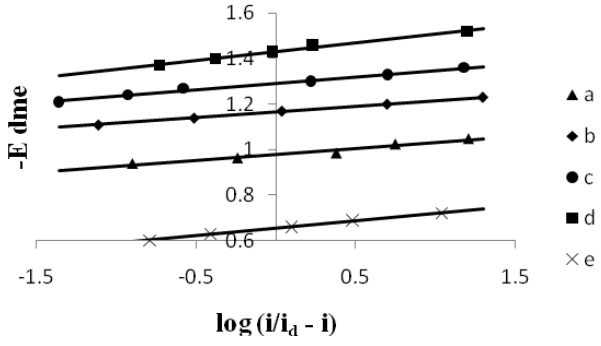


Figure 7: Semi log plot of hydrazones
pH = 4.1; Medium = Dimethylformamide (50% by volume)

Table 1. Polaroghaphic characteristics and kinetic parameters of hydrozones under study

[Hydrazone] = 1×10^{-3}M; Medium = Dimethylformamide (50% by volume)

pH	$-E_{1/2}$ V vs SCE	Limiting Current (μA)	$\Delta E_{1/2}/\Delta pH$	αn_a	Number of protons (P)	$D\times10^{2}$ m^2sec^{-1}	$I\times10^{-3}$	$k^{o}_{f,h}$ m sec^{-1}	ΔG^* KJ mol^{-1}
Propiophenone benzoicacid hydrazone									
2.1	0.70	3.9	0.08	0.86	1.3	3.19	2.17	2.91×10^{-12}	36.86
4.1	0.75	3.0	0.08	0.86	1.3	1.88	1.67	5.18×10^{-16}	46.32
6.1	1.12	2.3	0.08	0.86	1.3	1.11	1.28	1.34×10^{-18}	52.84
8.1	1.27	1.7	0.08	0.86	1.3	0.61	0.94	6.58×10^{-21}	58.66
10.1	1.27	1.7	0.08	0.86	1.3	0.61	0.94	6.58×10^{-21}	58.66
4'-methyl propiophenone benzoicacid hydrazone									
2.1	0.92	5.1	0.07	0.86	1.02	5.45	2.83	2.40×10^{-15}	44.64
4.1	1.17	4.2	0.07	0.86	1.02	3.69	2.33	4.59×10^{-19}	54.02
6.1	1.34	3.3	0.07	0.86	1.02	2.28	1.83	1.22×10^{-21}	60.50
8.1	1.48	2.5	0.07	0.86	1.02	1.31	1.39	8.52×10^{-24}	65.94
10.1	1.48	2.5	0.07	0.86	1.02	1.31	1.39	8.52×10^{-24}	65.94
4'-methoxy propiophenone benzoicacid hydrazone									
2.1	1.04	5.7	0.08	0.86	1.16	6.80	3.17	4.83×10^{-17}	48.91
4.1	1.3	4.8	0.08	0.86	1.16	4.83	2.67	6.75×10^{-21}	58.62
6.1	1.47	4.1	0.08	0.86	1.16	3.52	2.28	1.95×10^{-23}	65.02
8.1	1.61	3.3	0.08	0.86	1.16	2.28	1.83	1.45×10^{-25}	70.38
10.1	1.61	3.3	0.08	0.86	1.16	2.28	1.83	1.45×10^{-25}	70.38
4'-hydroxy propiophenone benzoicacid hydrazone									
2.1	1.18	6.2	0.08	0.86	1.16	8.05	3.44	4.84×10^{-19}	53.93
4.1	1.43	5.1	0.08	0.86	1.16	5.45	2.83	9.24×10^{-23}	63.30
6.1	1.60	4.6	0.08	0.86	1.16	4.43	2.55	2.81×10^{-25}	69.66
8.1	1.74	3.8	0.08	0.86	1.16	3.02	2.11	2.14×10^{-27}	74.98
10.1	1.74	3.8	0.08	0.86	1.16	3.02	2.11	2.14×10^{-27}	74.98
4'-chloro propiophenone benzoicacid hydrazone									
2.1	0.40	4.5	0.08	0.86	1.16	4.24	2.50	7.70×10^{-8}	25.73
4.1	0.65	3.6	0.08	0.86	1.16	2.71	2.00	1.43×10^{-11}	35.15
6.1	0.82	2.7	0.08	0.86	1.16	1.53	1.50	3.63×10^{-14}	41.67
8.1	0.97	1.9	0.08	0.86	1.16	0.76	1.05	1.69×10^{-16}	47.53
10.1	0.97	1.9	0.08	0.86	1.16	0.76	1.05	1.69×10^{-16}	47.53

Effect of temperature on the polarographic reduction of hydrazones under study

The polarograms of 4'– (substituted) propiophenone benzoic acid hydrazone in the media of pH 4.1 were recorded at 30°C, 40°C, 50°C and 60°C to study the effect of temperature on the limiting current and half-wave potentials. The compounds exhibit well defined single cathodic wave at all temperatures in the pH range of study. The diffusion current increases with increase in temperature and the temperature coefficient of diffusion current lies between 1.0 to 1.8% per degree. The values were in good agreement with the values reported in the literature for other similar compounds by Meites[33]. The results presented in table 2 reveal a decrease in αn_a values and a shift of half-wave potentials towards more negative values with the raise in temperature. The decrease in αn_a values was attributed to the decrease in α value which indicates that the transfer of electrons was increasingly difficult with the increase in temperature. The decrease in αn_a values[33-36] with the raise in temperature suggests the enhancing irreversible nature of the system and was further supported by shift of half-wave potentials towards more negative values. Similar observations were reported in the literature for other organic compounds [37,38].

Table 2. Effect of temperature on polarographic characteristics of hydrazones under study

[Hydrazone] = 1×10^{-3}M, pH = 4.1, Medium = Aqueous dimethylformamide (50% v/v)

Temperature k	$-E_{1/2}$ V vs SCE	Limiting Current (μA)	Temperature Coefficient	αn_a	$D\times10^2$ m^2sec^{-1}
Propiophenone benzoicacid hydrazone					
303	0.95	3.0	---	0.86	1.88
313	1.01	3.4	1.25	0.80	2.42
323	1.09	3.9	1.37	0.74	3.18
333	1.14	4.6	1.65	0.71	4.43
4'-methyl propiophenone benzoicacid hydrazone					
303	1.17	4.2	---	0.86	3.69
313	1.23	4.8	1.33	0.82	4.83
323	1.29	5.7	1.71	0.78	6.80
333	1.35	6.8	1.76	0.75	9.68
4'-methoxy propiophenone benzoicacid hydrazone					
303	1.30	4.8	---	0.86	4.83
313	1.36	5.3	1.00	0.82	5.88
323	1.43	5.9	1.07	0.78	7.29
333	1.47	6.6	1.12	0.76	9.12
4'-hydroxy propiophenone benzoicacid hydrazone					
303	1.43	5.1	---	0.86	5.45
313	1.47	5.6	0.94	0.84	6.57
323	1.54	6.2	1.02	0.80	8.05
333	1.60	6.9	1.07	0.77	9.97
4'-chloro propiophenone benzoicacid hydrazone					
303	0.65	3.6	---	0.86	2.71
313	0.69	4.1	1.30	0.80	3.52
323	0.74	4.8	1.57	0.74	4.82
333	0.79	5.7	1.72	0.69	6.80

Thermodynamic parameters

The formal rate constant and hence the other thermodynamic parameters were evaluated from different methods proposed by Meites-Israel[39], Oldham-Parry[40] and Gour-Bhargava[41] and are presented in table 3. The corresponding formulae for the calculation of kinetic parameter '$k^{o}_{f,h}$' are given below.

Meites-Israel's method

Meites-Israel assumed that diffusion to the electrode surface is linear.

$$E_{dme} = \frac{0.05915}{\alpha n_a} \log \frac{1.349\, k^{0}_{f,h} t^{1/2}}{D^{1/2}} - \frac{0.0542}{\alpha n_a} \log \frac{i}{i_d - i}$$

Oldham-Parry's method

Oldham-Parry have suggested alternatives to the usual log plots for the calculation of $k^{o}_{f,h}$.

$$E_{dme} = E_{1/2} - \frac{0.05915}{\alpha n_a} \log \left\{ 1.35\, k^{0}_{f,h} \frac{\sqrt{t}}{\sqrt{D}} \right\}$$

Gaur-Bhargava's method

Gaur-Bhargava assumed that diffusion to the electrode surface is spherical.

$$E_{dme} = \frac{0.05915}{\alpha n_a} \log \frac{1.349\, k^{0}_{f,h} t^{1/2}}{1.128\, D^{1/2}} - \frac{0.05690}{\alpha n_a} \log \frac{i}{i_d - i}$$

αn_a was calculated from the equation $\alpha n_a = -0.0517/(E_{3/4}-E_{1/4})$

It was observed that the formal rate constant '$k^{o}_{f,h}$' decreases with increase in temperature. The decrease in $k^{o}_{f,h}$ values suggests that the electrode reaction of the 4'–(substituted) propiophenone benzoic acid hydrazone rendered increasingly irreversible with the raise in temperature. This observation was in accordance with the conclusion arrived on the basis of αn_a values. The thermodynamic parameters enthalpy of activation (ΔH^*), free energy of activation (ΔG^*) and entropy of activation (ΔS^*) presented in table 3 reveal following points.

1) The positive values of ΔH^* indicate that the process was endothermic.
2) The positive values of ΔG^* indicate that the process was not spontaneous.
3) The negative values of ΔS^* indicate that the process was entropically unfavorable.

Table 3. Kinetic and thermodynamic parameters of polarographic reduction of hydrazone under study by various treatments

[Hydrazone] = 1×10^{-3}M; pH = 4.1; Medium = Dimethylformamide (50% by volume)

Parameter	Propiophenone benzoicacid hydrazone				4'-methyl propiophenone benzoicacid hydrazone				4'-methoxy propiophenone benzoicacid hydrazone			
Temperature (k)	303	313	323	333	303	313	323	333	303	313	323	333
Meites-Israel Treatment												
$K^0_{f,h}$ (m sec^{-1})	2.89×10^{-17}	2.61×10^{-17}	1.77×10^{-17}	1.39×10^{-17}	2.57×10^{-20}	1.80×10^{-20}	1.59×10^{-20}	1.10×10^{-20}	3.78×10^{-22}	3.14×10^{-22}	2.35×10^{-22}	2.00×10^{-22}
ΔH^* (KJ mol^{-1})	20.08	20.08	20.08	20.08	22.38	22.38	22.38	22.38	19.16	19.16	19.16	19.16
ΔG^* (KJ mol^{-1})	49.50	51.25	53.39	55.35	57.15	59.50	61.55	63.93	61.80	64.058	66.48	68.79
$-\Delta S^*$ (J k^{-1} mol^{-1})	105.35	107.86	111.41	114.22	123.05	126.44	129.53	133.05	148.99	151.71	154.80	157.31
Oldham-Parry Treatment												
$K^0_{f,h}$ (m sec^{-1})	2.95×10^{-17}	2.66×10^{-17}	1.80×10^{-17}	1.42×10^{-17}	2.63×10^{-20}	1.85×10^{-20}	1.63×10^{-20}	1.13×10^{-20}	3.89×10^{-22}	3.23×10^{-22}	2.42×10^{-22}	2.06×10^{-22}
ΔH^* (KJ mol^{-1})	19.92	19.92	19.92	19.92	22.97	22.97	22.97	22.97	19.16	19.16	19.16	19.16
ΔG^* (KJ mol^{-1})	49.46	51.25	53.35	55.35	57.15	59.46	61.55	63.93	61.76	64.02	66.44	68.74
$-\Delta S^*$ (J k^{-1} mol^{-1})	105.77	108.40	111.79	114.72	121.08	124.85	127.73	131.29	148.86	151.58	154.68	157.19
Gaur-Bhargava Treatment												
$K^0_{f,h}$ (m sec^{-1})	1.72×10^{-17}	1.54×10^{-17}	1.02×10^{-17}	0.79×10^{-17}	1.14×10^{-20}	0.79×10^{-20}	0.69×10^{-20}	0.48×10^{-20}	1.41×10^{-22}	1.16×10^{-22}	0.86×10^{-22}	0.72×10^{-22}
ΔH^* (KJ mol^{-1})	20.5	20.5	20.5	20.5	24.69	24.69	24.69	24.69	19.16	19.16	19.16	19.16
ΔG^* (KJ mol^{-1})	50.04	51.84	54.02	56.02	58.03	60.42	62.55	64.98	62.84	65.19	67.66	70
$-\Delta S^*$ (J k^{-1} mol^{-1})	105.77	108.40	112.04	114.97	118.32	122.46	125.52	129.28	152.46	155.31	158.40	160.95
Parameter	4'-hydroxy propiophenone benzoicacid hydrazone				4'-chloro propiophenone benzoicacid hydrazone							
Meites-Israel Treatment												
$K^0_{f,h}$ (m sec^{-1})	5.16×10^{-24}	3.81×10^{-24}	3.17×10^{-24}	2.61×10^{-24}	7.98×10^{-13}	6.69×10^{-13}	5.21×10^{-13}	4.20×10^{-13}				
ΔH^* (KJ mol^{-1})	19.16	19.16	19.16	19.16	18.58	18.58	18.58	18.58				
ΔG^* (KJ mol^{-1})	66.48	69.04	71.5	73.97	38.28	39.79	41.38	42.97				
$-\Delta S^*$ (J k^{-1} mol^{-1})	164.47	167.61	170.33	172.88	73.30	76.06	78.86	81.54				
Oldham-Parry Treatment												
$K^0_{f,h}$ (m sec^{-1})	5.34×10^{-24}	3.94×10^{-24}	3.29×10^{-24}	2.72×10^{-24}	8.07×10^{-13}	6.77×10^{-13}	5.27×10^{-13}	4.25×10^{-13}				
ΔH^* (KJ mol^{-1})	19.16	19.16	19.16	19.16	18.37	18.37	18.37	18.37				
ΔG^* (KJ mol^{-1})	66.44	68.99	71.46	73.97	38.28	39.79	41.38	42.97				
$-\Delta S^*$ (J k^{-1} mol^{-1})	164.30	167.48	170.20	172.88	74.01	76.73	79.53	82.17				
Gaur-Bhargava Treatment												
$K^0_{f,h}$ (m sec^{-1})	1.63×10^{-24}	1.18×10^{-24}	0.98×10^{-24}	0.78×10^{-24}	7.07×10^{-13}	5.86×10^{-13}	4.49×10^{-13}	3.57×10^{-13}				
ΔH^* (KJ mol^{-1})	19.16	19.16	19.16	19.16	17.82	17.82	17.82	17.82				
ΔG^* (KJ $mole^{-1}$)	67.74	70.37	72.89	75.4	38.41	39.96	41.55	43.18				
$-\Delta S^*$ (J k^{-1} mol^{-1})	168.57	171.92	174.59	177.15	76.23	78.99	81.75	91.96				

The millicoulometer of De Vries and Kroon[42] with mercury pool cathode was employed for the determination of the number of electrons involved in the reduction process. It is evident from table 4 that four electrons were involved in the reduction of 4'– (substituted) propiophenone benzoic acid hydrazone in Britton - Robinson buffers of pH 4.1 containing 50% (by volume) dimethylformamide.

Table 4. Millicoulometric data of propiophenone benzoic acid hydrazone
[Hydrazone] = 1×10^{-3}M, pH = 4.1, Medium = Aqueous dimethylformamide (50% v/v)

pH	Current (μA)	Time (sec)	No. of electronics
4.1	3.0	0	---
	2.8	7200	3.9
	2.7	10800	3.8

Effect of substituents on the polarographic behavior of the 4'– (substituted) propiophenone benzoic acid hydrazone

Generally structural correlation is done with substituent constant 'σ_P' for the compounds in aromatic series. $E_{1/2} - \sigma_P$ plots drawn for the compounds under investigation is presented in figure 8. The values of specific reaction constants 'ρ' calculated from the slope of $E_{1/2} - \sigma_P$ plots are shown in table 5. The ρ values were expected to be positive[43] as it involves the nucleophilic addition of electrons to the substrate. The ρ values obtained in the studies therefore confirm that the electron uptake process was potential determining step in all the reduction processes studied.

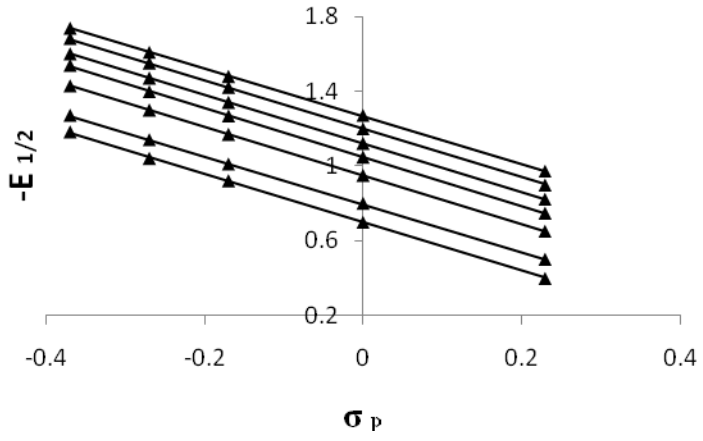


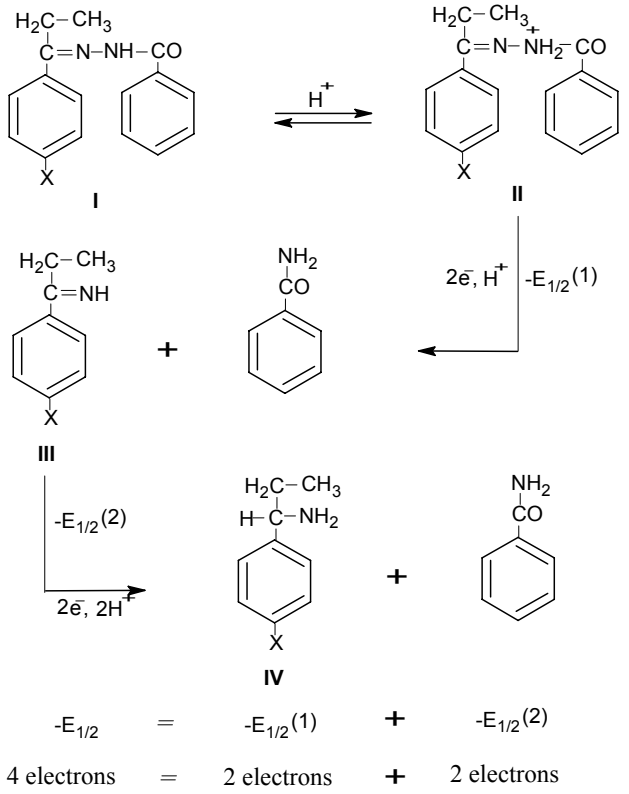
Figure 8. -E – σ_P plot of hydrazones (The top line at pH 8.1, the next at 7.1….. and the bottom line at pH 2.1) Medium = Dimethylformamide (50% by volume)

Table 5. Effect of pH on the reaction constant for the reduction of 4'-(substituted) propiophenone benzoicacid hydrazones

pH	ρ value
2.1	1.33
3.1	1.30
4.1	1.36
5.1	1.30
6.1	1.29
7.1	1.26
8.1	1.26
9.1	1.26
10.1	1.26

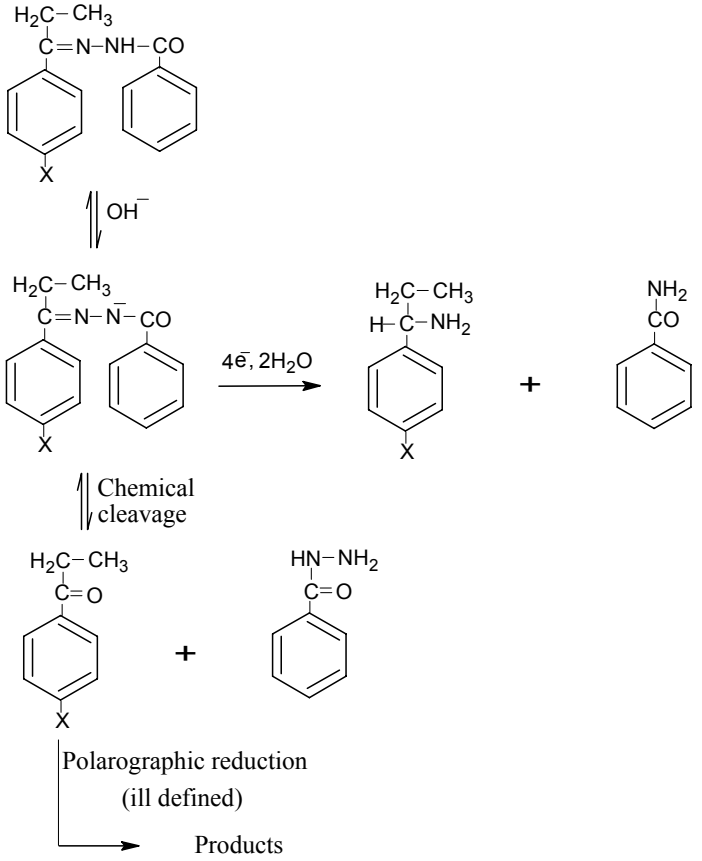
Reduction mechanism

From the above discussion it is clear that hydrazones 'a to e' were reduced at the dropping mercury electrode through a mechanism which involves the azomethine group. The azomethine moiety in the 4'– (substituted) propiophenone benzoic acid hydrazone (I) was protonated to yield protonated hydrazone form (II). Then the weak (=N – NH–) single bond of the hydrazone was cleaved[44,45] with the uptake two electrons and a proton. The unstable intermediate imine (III) produced in the above process was then reduced further to yield amine (IV) in a two electron process. It was reported that the above mentioned two steps of reduction occur at the same potential[46,47] and this fact substantiates the appearance of single four-electron wave as shown in scheme 1.



Scheme 1

In alkaline medium (pH > pKa) 4'– (substituted) propiophenone benzoic acid hydrazone exist in the anionic form and the later was susceptible to chemical cleavage partially into corresponding carbonyl compound as shown in scheme 2. The second wave was not differentiated in the present studies, probably due to the fact that the substituted propiophenones obtained during the chemical cleavage may be reduced at much higher negative potential which was nearly same as the decomposition potential of the buffer solution.



Scheme 2

Conclusion

The five hydrazones (a, b, c, d and e) reported in this article gave a well defined single polarographic wave. The reduction process was found to be irreversible and diffusion controlled with the involvement of protons. Based on the results obtained, the authors proposed a mechanism for the electrode reaction at the dropping mercury electrode and the same may be used for pharmacokinetic studies involving these hydrazones.

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