

Polarographic Studies on the Kinetics of the Electrode Reaction of 4-Benzoyl-1,5 Diphenyl Pyrazole-3-Carboxylic Acid

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The polarographic behavior of 4-Benzoyl-1,5 diphenyl pyrazole-3- Carboxylic acid (BDPPCA) in aqueous ethanol solution (76 % v/v) at 25 °C was studied as a function of pH using Mcl buffer solution. One well-defined wave was obtained in the pH range of 3.3-5.4. This wave, corresponding to two electron reduction processes, was irreversible and diffusion controlled. However, in the pH range of 5.4-7.4 a single reversible and diffusion-controlled wave involving two electrons resulted. The kinetic parameters ($n_a, k_{f,h}^\circ$) were calculated by Koutecky's method. A tentative mechanism was put forward for the reduction process of depolarizer. Furthermore, the effects of different supporting electrolytes on the kinetics of the irreversible electrode reaction of BDPPCA were investigated.

Introduction

Most pyrazole derivates have been studied polarographically in non-aqueous media¹⁻³. The polarographic behavior of BDPPCA, a pyrazole derivative, has been studied both in aqueous and in non-aqueous media⁴⁻⁵. We have previously reported the investigations of the polarographic reduction of BDPPCA with special emphasis on the kinetics and mechanism of the electrode process⁶. In the present study, the effect of the concentration and nature of different supporting electrolytes on the reduction process was investigated.

Experimental

4-Benzoyl-1,5 diphenyl pyrazole-3-carboxylic acid was prepared by recrystallization from absolute methanol before use⁷. NaCl, NaNO₃, NH₄Cl, LiCl, Na₂SO₄ (each 0.1 mole dm⁻³) were used as the supporting electrolytes. Polarograms were recorded with a Metrohm E-261 Polarograph. All measurements were made at 25 °C. The purified nitrogen was bubbled through the electrolyte in order to remove the oxygen. The potentials were measured against a saturated calomel electrode (SCE). The concentration of supporting electrolytes in ethanol solution (76% v/v) was maintained at 4.44.10⁻⁴ mole dm⁻³.

The numbers of electrons (n) involved in the reduction of BDPPCA at different pH values were determined by Coulomb counter (Keithley 6517). From the value of n , the diffusion coefficients of BDPPCA at different pH values and also in the presence of increasing concentrations of various supporting electrolytes were calculated using the Ilkovic Equation. The potential-dependent rate constant $k_{f,h}$ was calculated by Koutecky's method^{8,9}. The kinetics parameters ($n_a, k_{f,h}^\circ$) were calculated from the plots of $\log k_{f,h}$ vs E_{de} ¹⁰. Throughout the measurements, the current at the end of the drop (ie, maximum current) was recorded¹¹⁻¹². The dme had the following characteristics:

$$m = 2.35 \text{ mg s}^{-1}; t = 3.55 \text{ s}; m^{2/3} t^{1/6} = 2.19 \text{ mg}^{2/3} \text{ s}^{-2/3} (\text{in } 0.1 \text{ mole dm}^{-3} \text{ KNO}_3 \text{ in open circuit});$$

$$h_{curr} = 39.2 \text{ cm}$$

Results and Discussions

For current-voltage curves of BDPPCA in the pH range of 3.3-5.4, the first step was found to be diffusion controlled as the plot of $\log i$ vs $\log t$ was linear and passed through the origin. The common tests of irreversibility in cyclic voltammetry were also used¹³⁻¹⁵. The nature of the cyclic voltammogram showed that the anodic portion was completely absent. The absence of the anodic peak may be ascribed to the fact that the product obtained in the first step (cathodic scan) of the carboxyl group of BDPPCA did not oxidize in the reverse cycle and hence no peak was observed in the anodic portion, indicating the irreversible nature of the wave. The values of the kinetics parameters $n_a, k_{f,h}^\circ$ of the irreversible electrode reaction of BDPPCA were calculated and presented in Table 1 and in Figure 1, 2. An emphasis was made on determining the stoichiometry of the rate-determining step. The proton number (p) involved in the rate-determining step of the reduction of the depolarize has been calculated from the slope of $E_{1/2}$ vs pH plots given by the following equation at 25°C

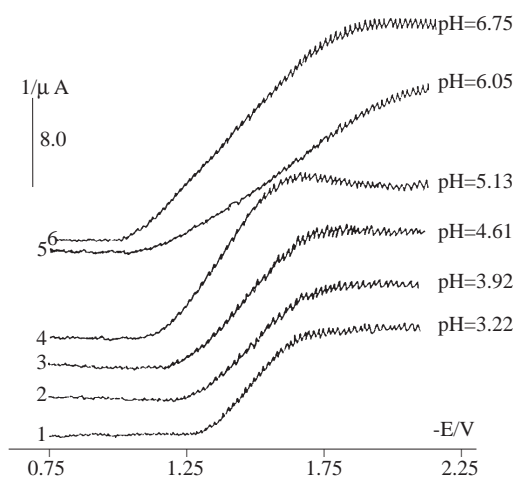


Figure 1. Polarographs of the BDPPCA $4.44 \cdot 10^{-4} \text{ mol dm}^{-3}$ in aqueous ethanol solution (76 % v/v)+0.1 mol dm^{-3} LiCl at 25°C

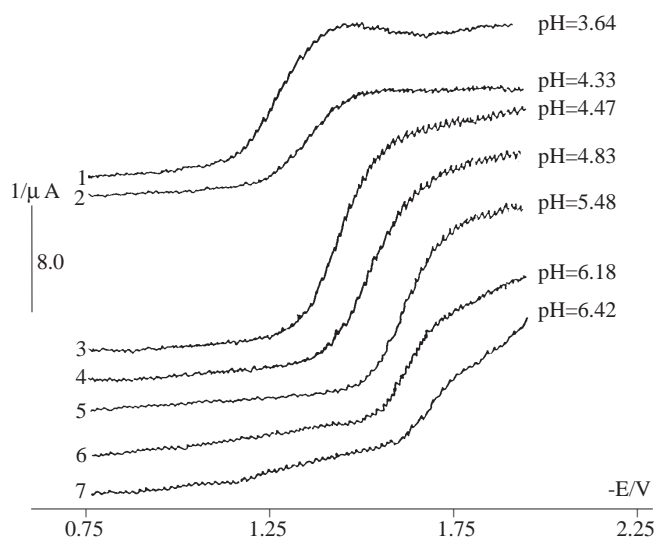


Figure 2. Polarographs of the BDPPCA $4.44 \cdot 10^{-4}$ mol dm^{-3} in aqueous ethanol solution (76 % v/v)+0.1 mol dm^{-3} Na_2SO_4 at 25°C

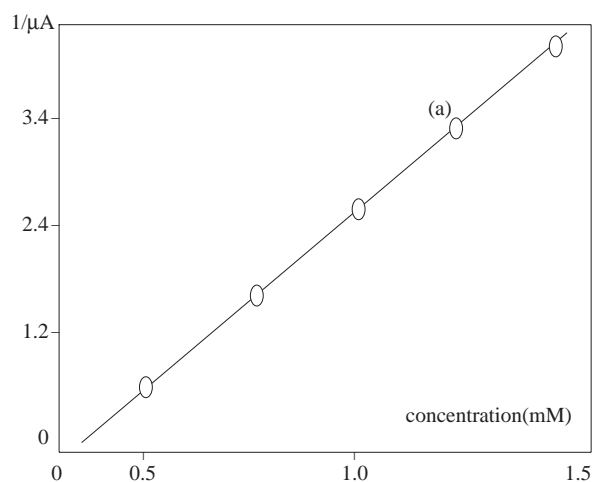


Figure 3. Polarography cathodic limiting current vs concentration plot for BDPPCA in aqueous solution (76 % v/v) at 25°C (a) diffusion

$$\frac{\delta E_{1/2}}{\delta \text{pH}} = \left(\frac{0.05915}{\alpha n a} \right)_p$$

$$E_{1/2} - \frac{0.05915}{\alpha n} \log \frac{1.349 k_{f,h}^0 t^{1/2}}{D_0^{1/2}}$$

t = drop time of mercury

D_0 = Diffusion coefficient of reduced species (Determined from the Ilkovic equation)

$$E = E_{1/2} - \frac{0.05915}{\alpha n} \log \frac{I_d - I}{I}$$

n was found from the above equation by plotting $E_{1/2}$ vs $\log \frac{I_a - I}{I} \log k_{f,h}^\circ = \frac{E_{1/2} \alpha n}{0.05915} - \log 1.349 - 1/2 \log t + 1/2 \log D_0$, from this equation $k_{f,h}^\circ$ was found. In order to determine the type of reduction current for BDPPCA, the limiting current (I_d) was plotted vs concentration increase which is shown at constant Hg-column height in Figure 3. The relationship between i_d and Hg-column height indicate that i_d does not change vs Hg-column height, as can be seen in Figure 4. According to the graph, the limiting current is indeed the diffusion current.

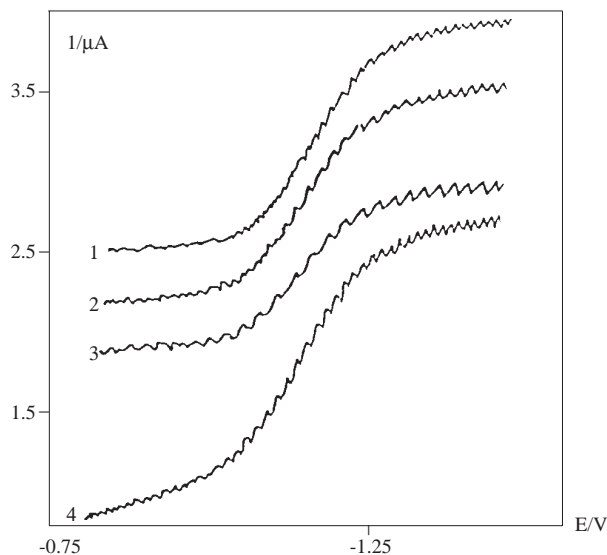
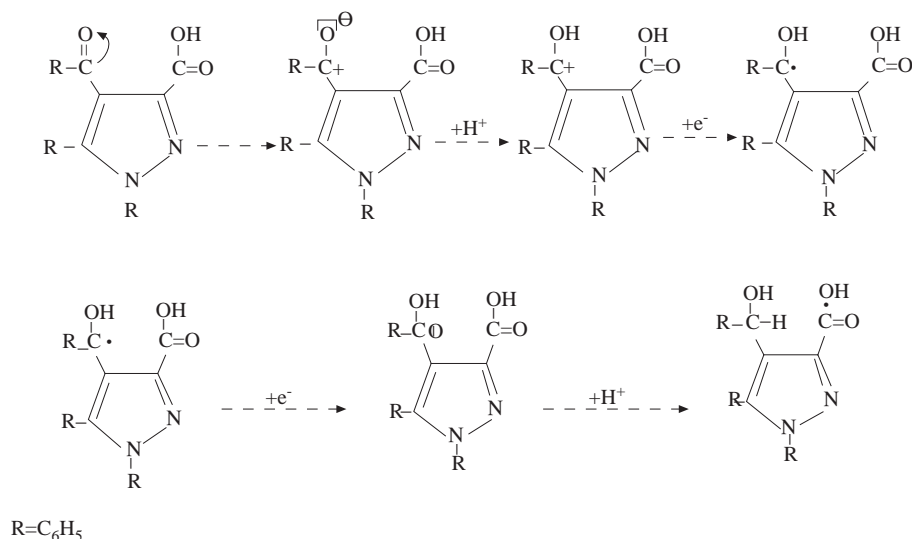


Figure 4. Polarographs of the BDPPCA in the same concentration and at different Hg-column heights (1:20 cm; 2:30 cm; 3:40 cm; 4:50 cm)

The number of electrons involved in the each step (ne) is 1, on the basis of the above-mentioned stoichiometry of the rate-determining step for different pH values. The mechanism shown below can be proposed for the polarographic reduction of BDPPCA as follows:



Effects of the concentration and nature of different supporting electrolytes on the kinetics of the electrode reaction of BDPPCA:

Table 1. Polarographic and kinetic parameters of the electrode reaction of BDPPCA at different pH values (Mcl buffer)

Supporting electrolytes	pH	$I_d(\mu A)$	$-E_{1/2}[V(SCE)]$	Slope (mV)	$DX10^{-6}$ (cm^2s^{-1})	αn_a	$k_{f,h}^\circ (cms^{-1})$
NaNO ₃	3.31	3.25	1.078 V	196	5.6	0.31	6.65×10^{-11}
	3.89	2.15	1.094"	148	2.3	0.35	1.17×10^{-19}
	4.52	1.75	1.142"	111	1.4	0.53	1.65×10^{-18}
	5.00	1.60	1.182"	105	1.4	0.56	5.27×10^{-17}
	5.83	1.50	1.246"	91	4.1	0.65	1.48×10^{-17}
	6.98	0.90	1.294"	75	2.0	0.78	9.58×10^{-14}
	7.40	0.70	1.296"	66	1.0	0.89	8.16×10^{-13}
NaCl	3.35	2.06	1.070"	333	2.1	0.17	2.43×10^{-19}
	3.95	1.98	1.102"	303	2.1	0.19	5.38×10^{-17}
	4.50	1.46	1.114"	260	1.4	0.22	6.65×10^{-16}
	4.95	1.34	1.190"	257	1.2	0.23	6.46×10^{-16}
	5.88	1.20	1.254"	223	3.6	0.26	5.06×10^{-15}
	7.00	0.90	1.302"	220	2.6	0.27	2.75×10^{-15}
	7.43	0.64	1.326"	181	1.4	0.32	1.32×10^{-13}
LiCl	3.22	2.75	1.084"	171	4.0	0.34	7.05×10^{-23}
	3.92	1.75	1.110"	116	1.6	0.51	2.85×10^{-18}
	4.61	1.50	1.166"	91	4.8	0.65	1.35×10^{-14}
	5.13	1.40	1.206"	82	4.1	0.72	5.72×10^{-14}
	6.05	1.26	1.270"	84	3.6	0.70	2.66×10^{-14}
	6.75	0.76	1.310"	76	1.2	0.77	1.57×10^{-10}
	7.38	0.48	1.370"	45	0.5	1.31	1.98×10^{-13}
NH ₄ Cl	3.17	3.50	1.102"	205	6.5	0.29	4.59×10^{-26}
	4.02	2.75	1.158"	183	4.0	0.32	1.52×10^{-24}
	4.71	1.50	1.190"	56	1.5	0.69	1.75×10^{-18}
	5.32	1.60	1.222"	103	1.2	0.57	4.74×10^{-17}
	6.36	1.50	1.270"	94	4.6	0.63	7.98×10^{-17}
	7.35	1.40	1.350"	86	4.3	0.69	8.23×10^{-16}
	7.80	1.40	1.382"	83	4.1	0.71	4.25×10^{-16}
Na ₂ SO ₄	3.64	1.10	0.882"	104	1.6	0.57	1.41×10^{-13}
	4.33	0.80	0.762"	71	1.0	0.83	3.11×10^{-12}
	4.47	1.70	0.555"	62	1.7	0.95	1.36×10^{-9}
	4.83	2.05	0.750"	63	1.5	0.94	0.72×10^{-9}
	5.48	1.50	0.775"	48	4.1	1.23	1.54×10^{-9}
	6.18	1.20	0.800"	40	3.0	1.47	1.11×10^{-9}
	6.42	1.10	0.785"	49	2.1	1.21	1.25×10^{-9}

The effects of the concentrations and nature of different supporting electrolytes, viz. NaNO₃, NH₄Cl, NaCl, LiCl and Na₂SO₃ on the kinetics of the electrode reaction of BDPPCA was studied at pH: 5.0. The kinetic parameters (α , n_a and $k_{f,h}^\circ$) of the electrode reaction were calculated at different concentrations (0.1-1.0 mole dm⁻³) of the polarizer. It was found that the values of α , n_a and $k_{f,h}^\circ$ had a tendency to increase

with increasing NaNO_3 , NaCl and Na_2SO_4 concentrations, while a decrease occurred with increasing LiCl , and NH_4Cl concentrations, thereby showing that the electrode reaction of BDPPCA became less irreversible with NaNO_3 , NaCl and Na_2SO_4 . On the other hand, it became irreversible with increasing concentrations of LiCl and NH_4Cl . The positive shift in $E_{1/2}$ with increasing concentrations led to the above conclusions.

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