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Polarographic and Cyclic Voltammetric Reduction of *p*-Chlorobenzaldehyde Isonicotinoylhydrazone

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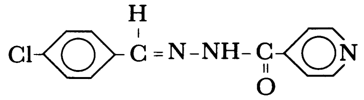
Synopsis. *p*-Chlorobenzaldehyde isonicotinoylhydrazone (*p*-Cl-BAINH) exibits a single wave in acid buffered solutions (pH 2—6) and two waves in alkaline buffered solutions (pH 7—9). However, the compound exhibits three cathodic peaks in acid solution and two cathodic peaks in alkaline solutions. The electrode reactions are attributed to the reductive cleavage of =N-N- linkage and the reduction of the amide formed in the cleavage.

Isonicotinohydrazide derivatives of carbonyl compounds are used extensively as theraptic agents.[1—4] *p*-Chlorobenzaldehyde isonicotinoylhydrazone (*p*-Cl-BAINH) with the following structure



p-Cl-BAINH

is one of such compounds. This compound offers interesting features for electrochemical reduction studies since it possesses more than one reducible sites in its molecule. The authors have therefore undertaken polarographic and cyclic voltammetric studies in solutions of pH 2 to 9. The results are communicated here.

Experimental

p-Cl-BAINH was prepared by refluxing a mixture (1:1) of *p*-chlorobenzaldehyde and isonicotinohydrazide for 2 h. The product was purified by repeated recrystallization from hot aqueous ethanol. The compound was characterized by infrared spectral data and melting point (measured value 217 °C, lit, 217—218 °C). All the other chemicals used in the investigations were of analytical reagent grade.

Current-voltage curves were recorded in Britton-Robinson buffers (pH 2—9) with a DC pen recording polarograph (CL 25, ELICO, India). The dropping mercury electrode had the following characteristics: t=3.0 s, m=1.93 mg s^{-1} at a height of 85 cm of mercury column in water under open circuit conditions. Cyclic voltammograms were recorded with a polarographic analyzer (model 174 A, Applied Research Company of Princeton, USA) coupled with an X-Y recorder (model RE 0074) and universal programmer (model 175). Hanging mercury drop electrode (HMDE, Metrohm model 9323), platinum wire electrode and SCE were used as working electrode, counter electrode, and reference electrode respectively. The results are presented in Tables 1 and 2.

Results and Discussion

Electrochemical Reduction in Acid Solutions. *p*-Cl-BAINH exhibits a single polarographic wave in acid solutions (pH 2—6). Semi-logarithemic analysis of the wave reveals that the wave is irreversible. The limiting current varied linearly with the concentration of the hydrazone and with the square root of the mercury column height indicating that the wave is diffusion-controlled. Half-wave potential shifts towards more negative values with increase in pH. This indicates that protons are taking part in the reduction process.

Table 1. Polarographic Reduction Waves of *p*-Cl-BAINH (4×10^{-4} M[a])in 20% Aqueous *N*,*N*-Dimethylformamide

pH	$-E_{1/2}$/V vs. SCE	
	First wave	Second wave
2.0	0.78	—
3.0	0.87	—
4.0	0.89	—
5.0	0.97	—
6.0	1.03	—
7.0	1.08	1.25
8.0	1.14	1.28
9.0	1.18	1.29

a) 1 M=1 mol dm^{-3}.

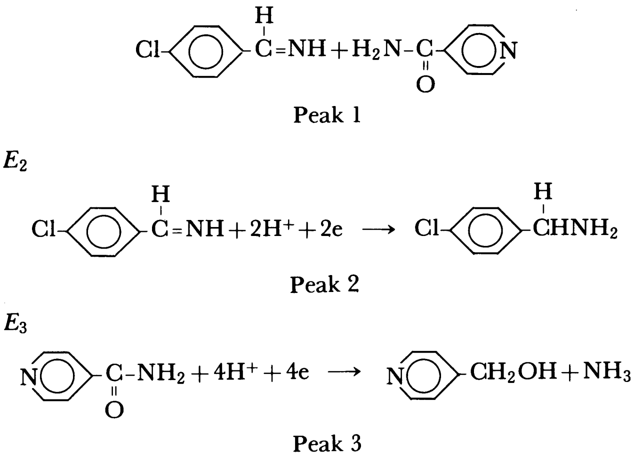
Table 2. Cyclic Voltammetric Peak Potentials of *p*-Cl-BAINH (4×10^{-4} M) in 20% Aqueous *N*,*N*-Dimethylformamide.

Sweep rate / V s^{-1}	$-E_{pc}$ I/V	$-E_{pc}$ II/V	$-E_{pc}$ III/V
	pH 4.0		
0.020	0.84	0.89	0.95
0.050	0.85	0.91	0.96
0.100	0.86	0.92	0.97
	pH 8.0		
0.020	1.15	1.28	—
0.050	1.16	1.30	—
0.100	1.17	1.31	—

The cyclic voltammogram of the hydrazone shows three cathodic peaks in acid solutions in the forward scan. In the reverse scan, no peak is observed. This indicates the irreversible nature of the electrode process. This is also confirmed by the negative shift in the peak potentials with increasing sweep rates.

The total mumber of electrons involved in the polarographic process is established experimentally to be 8. On the basis of the three peaks observed in cyclic voltammogram and the number of electrons involved in the single reduction wave noticed and on the basis of the reported behavior in the literature[5] of semicarbazones (compounds bearing structural relationship with the present hydrazone) it is proposed that the single polarographic wave observed is a composite wave representing the reductive cleavage of =N-N-linkage and the reduction of the imine and the amide formed in the cleavage. The appearance of a single wave suggests that these reduction steps take place at potentials very close to each other. This is clear from the almost same potentials of the peaks in the cyclic voltammogram. Bulk electrolysis and subsequent chemical identification of the products in acid solutions revealed the presence of amine and alcohol. The electrolysis was carried out in solutions of pH 4 at an applied voltage of −1.2 V vs. SCE with mercury pool as cathode. The catholyte after electrolysis was concentrated and extracted with ether. The extract responded to the tests for the primary amine (diazotization and coupling with 2-naphthol) and for the primary alcohol (oxidation and condensation with 2,4-dinitrophenylhydrazine).

E_1 *p*-Cl-BAINH + $2H^+$ + 2e →



$E_1 \approx E_2 \approx E_3$ in acidic solutions
E_1, E_3 in alkaline solutions
(E: Half-wave potential).

Electrochemical Reduction in Alkaline Solutions. *p*-Cl-BAINH exhibits two polarographic waves in alkaline solutions. The effect of mercury column height and concentration on the wave height suggests that the waves are diffusion-controlled. The wave is found irreversible by the semi-logarithemic analysis.

The cyclic voltammogram of the compound exhibits two cathodic peaks in the forward scan. In the reverse scan, no peak is observed. This fact indicates the irreversible nature of the electrode process. This is also confirmed by the negative shift in the peak potentials with increasing sweep rates.

It was reported that semicarbazones undergo reductive cleavage of =N–N– linkage and the imine formed in the cleavage is resistant to further reduction.[6] Imine undergoes reduction only in the protonated form. The absence of imine reduction in alkaline solution can therefore be attributed to the significant decrease in the recombination rate. It was reported that amides undergo reduction to the corresponding alcohols.[7] Bulk electrolysis and subsequent identification reveal the formation of alcohol as well as the aldehyde in alkaline solutions. The aldehyde, formed is attributed to the decomposition of Ar-CH=NH to Ar-CHO in alkaline solution. The two waves appeared therefore indicate the =N–N– cleavage (first wave) and the amide reduction (second wave), respectively. The reduction of the amide being made difficult in alkaline solutions is understood since protonated amide alone is susceptible to reduction. The appearence of two peaks with potentials similar to the half-wave potentials supports the mechanism proposed.

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