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POLAROGRAPHIC BEHAVIOUR OF *p*-NITRO ACETOPHENONE ISONICOTINOYL HYDRAZONE (*p*-NO_2APINH)

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The polarographic behaviour of *p*-nitro acetophenone isonicotinoyl hydrazone (*p*-NO_2APINH) is studied at the dropping mercury electrode in the *p*H range 2 to 12 in aqueous solutions containing dimethylformamide (20 per cent V/V). The compound exhibited four waves in the *p*H range 2 to 5 and three waves in the *p*H range 6 to 12. The first and second waves are ascribed to the four electron reduction of nitro group to hydroxylamine and the reductive cleavage of = N—N— linkage present in the hydrazone respectively. The third and fourth waves are shown to be due to the reduction of the amide and the imine, the products formed during the reduction processes corresponding to the first and second waves.

Key Words: Polarography; *p*-Nitro Acetophenone Isonicotinoyl Hydrazone (*p*-NO_2 APINH); Dimethylformamide

INTRODUCTION

POLAROGRAPHIC determination of carbonyl compounds or the determination of metal ions *via* the complexation with carbonyl compounds is generally carried out employing the carbonyl derivatives rather than the carbonyl compounds directly. Oximes, hydrazones and semicarbazones are amongst the chief carbonyl derivatives employed for the purpose. The polarographic behaviour of the hydrazone derivatives is generally similar to that of the parent ketone. They usually undergo four-electron-reduction to the corresponding amine. It was reported that various hydrazone derivatives exhibit more number of waves and these were time-dependent. The multiplicity and the time dependency of the waves have been ascribed to the equilibria existing between the hydrazone, azo and ene hydrazine forms.[1–4] However, no evidence has been found for the existence of the ene-hydrazine form in aprotic media. Hence, O'Connor[5] ascribed the multiplicity of waves to adsorption and kinetic phenomena. But the origin of the multiplicity of the waves is still not clear. Abdul Huq[6] and Murali Mohan and Brahmaji Rao[7–9] employed resacetophenone isonicotinoyl hydrazone in the catalytic polarographic determination of sub microgram quantities of Fe(III), Mo(VT), V(V). Isonicotinoyl hydrazide derivatives of substituted aromatic

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carbonyl compounds are found to possess similar activity. However, their suitability in such applications depend largely on the position of their polarographic reduction waves on the potential axis *vis-a-vis* the position of the metal ion waves. It is for this reason a detailed polarographic investigation on such compounds is a pre-requisite to establish the usefulness or otherwise of the compounds as analytical reagents. The polarographic behaviour of metal ions is well known. Preliminary studies suggested that *p*-nitroacetophenone isonicotinoyl hydrazone (*p*-NO_2APINH) is a promising reagent. In view of the paucity of information on the polarographic reduction behaviour of isonicotinoyl hydrazide derivatives of carbonyl compounds in particular and hydrazones in general the authors have taken up the detailed study of the title compound. The reduction of *p*-NO_2 APINH at the dropping mercury electrode in the *p*H range 2 to 12 is therefore studied and the results are communicated here.

Experimental

p-Nitroacetophenone isonicotinoyl hydrazone (*p*-NO_2APINH) is prepared by refluxing a mixture of *p*-nitroacetophenone and isonicotinoyl hydrazide for 3. hours. All other chemicals used in the investigations are of AnalaR grade. Current-voltage curves are recorded in Britton-Robinson buffers with ELICO Pen Recording Polarograph. The dropping mercury electrode with the following characteristics is used in the studies — $t = 3.0$s, $m = 1.93$mg sec^{-1}, $h = 85$cm at OV *vs* SCE in water.

Results and Discussion

The hydrazone exhibited in general three waves in the *p*H range of study namely 2 to 12. However, an additional fourth wave is noticed in the *p*H range 2 to 5.

First Wave

Semi-logarithmic analysis plot revealed 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 indicating that the wave is diffusion controlled. The half-wave potential increased linearly with *p*H indicating that protons are involved in the rate determining step. The number of protons involved is found to be 0.48, from the slopes of $E_{1/2}$ — *p*H and E_{dme} *vs* log $i/i_d - i$ plots. This suggests that protons are involved in heterogeneous rate process. The position of the wave on the potential axis (-0.21 to -0.81 V) suggests that this wave is due to the reduction of the nitro group present in the hydrazone.

Second Wave

The wave appears in the potential region -0.69 to -1.50 volts *vs* SCE. The limiting current shows a linear dependence on the concentration of the hydrazone and the square root of mercury column height. These observations indicate the diffusion-controlled nature of the wave. Semi-logarithmic analysis

of the wave indicates that the wave is irreversible. $E_{1/2}$ varied linearly with pH and the number of protons involved in the rate limiting process is found to be 0.9. This also suggests a heterogeneous transfer process. The position on the potential axis and the characteristics of the second wave are similar to those of the first wave of isonicotinoyl hydrazide reported by Lund.[10] It is therefore, assumed that this wave is due to the cleavage of the = N — N— linkage as proposed by Lund.

TABLE I

Polarographic half-wave potentials of p-nitroacetophenone isonicotinoyl hydrazone in Britton-Robinson buffers (pH 2–12)

[p-NO_2APINH] = 4 × 10^{-4}M Medium = 20% aqueous DMF (by volume)

pH	I wave		II wave		III wave		IV wave	
	$-E_{1/2}$ V *vs* SCE	Wave height μA	$-E_{1/2}$ V *vs* SCE	Wave height μA	$-E_{1/2}$ V *vs* SCE	Wave height μA	$-E_{1/2}$ V *vs* SCE	Wave height μA
2.0	0.21	3.6	0.69	3.0	0.84	5.7	1.02	3.2
3.0	0.28	3.6	0.77	2.7	0.96	4.5	1.14	2.7
4.0	0.36	3.6	0.91	2.7	1.08	4.3	1.30	2.7
5.0	0.40	3.5	0.96	2.7	1.20	4.0	1.34	2.7
6.0	0.48	3.3	1.11	2.7	1.34	3.5	—	—
7.0	0.54	3.1	1.20	2.4	1.47	2.7	—	—
8.0	0.59	2.9	1.30	2.4	1.50	2.6	—	—
9.0	0.63	2.8	1.34	2.4	1.56	2.7	—	—
10.0	0.72	2.9	1.39	2.4	1.65	2.7	—	—
11.0	0.78	2.9	1.44	2.4	1.65	2.7	—	—
12.0	0.81	2.9	1.50	2 4	1.65	2.6	—	—

Third Wave

The wave appeared in the voltage region —0.84 to —1.65 volts *vs* SCE. The linear proportionality observed between the limiting current and the concentration of the hydrazone or the square root of mercury column suggests the diffusion controlled nature of the wave in acid pHs. $E_{1/2}$ varied with pH in acid solutions indicating the participation of protons in this medium. In alkaline medium the wave showed a linear dependence of the limiting current on the concentration and a non-linear dependence on the square root of mercury height. These observations suggest that the wave is not diffusion-controlled in this medium. Further $E_{1/2}$ is independent of pH. The limiting current in alkaline pH's is much less than that in acid pHs. These facts suggest that in alkaline medium the amide is stabilised.

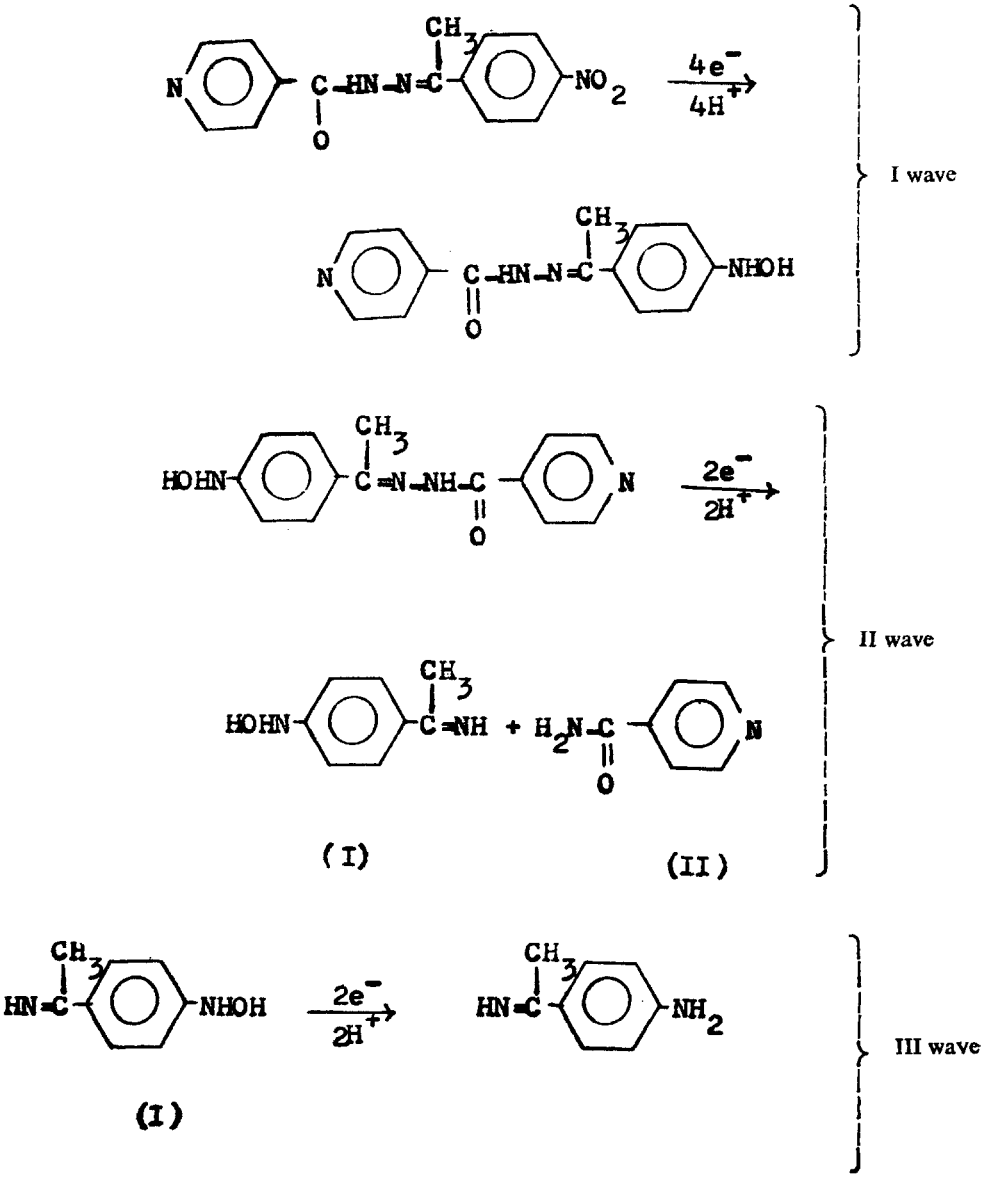
Fourth Wave

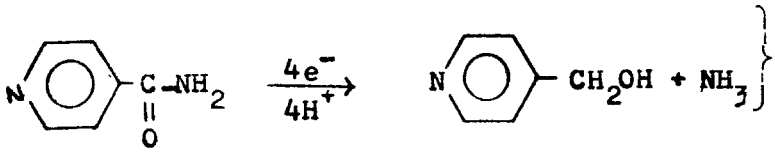
The wave is present in the pH range 2–5 only in the potential region —1.02 to —1.34 volts *vs* SCE. Semi-logarithmic analysis and the dependence of limiting

current on mercury column height indicate that the wave is irreversible but diffusion-controlled. From the position of the wave and the number of electrons involved, the wave is ascribed to the reduction of the protonated imine.

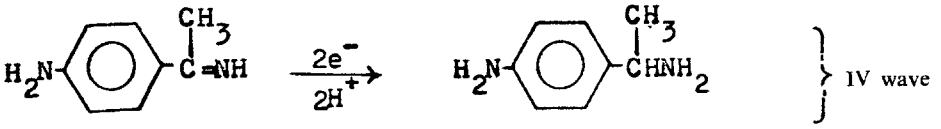
The number of electrons involved in the reduction of the four waves is established to be four, two, six and two respectively in the acid medium. On the basis of the position of the waves on potential axis, the number of electrons

Acid Medium

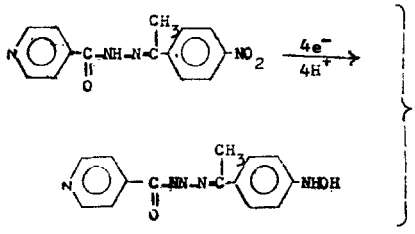


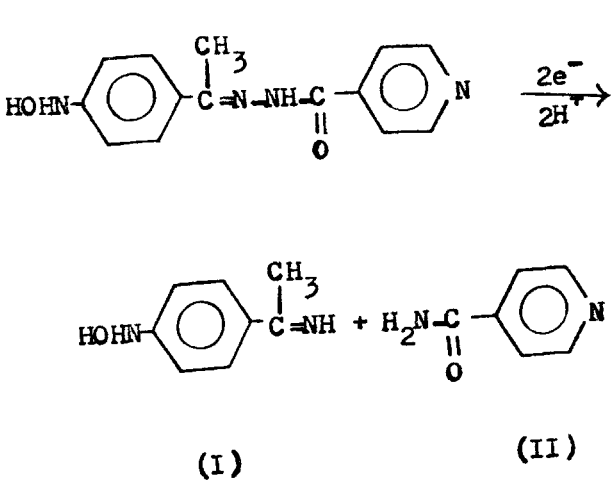


(II)



Alkaline Medium





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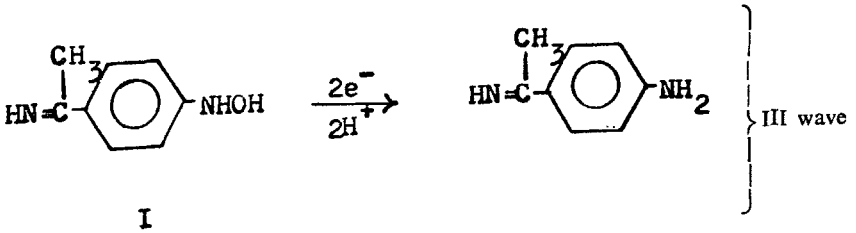

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consumed in the reduction and the earlier reports in the literature, the above scheme is proposed for the reduction of *p*-nitroacetophenone isonicotinoyl hydrazone.

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