Cyclic Voltammetric Study of Gallacetophenone Hydrazones

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The voltammetric behaviour of GAPINH and GAPSH has been studied in universal buffer systems of pH 2.0 to 12.0 by cyclic voltammetry, controlled potential electrolysis and the reduction mechanism is proposed.

Most of the salicyl hydrazones [1-3] and isonicotinoyl hydrazide derivatives [4-6] of carbonyl compounds are used extensively as anti tuberculosis and other therapeutic agents. The therapeutic action is generally related the redox behaviour of the compound.

The electrochemical reduction behaviour of Gallacetophenone Isonicotinoyl hydrazone (GAPINH) and Gallacetophenone salicyl hydrazone (GAPSH) in aqueous buffered media are reported here to arrive at information on the kinetic and mechanistic aspects.

EXPERIMENTAL

Gallacetophenone hydrazones were prepared by heating equimolar amounts of corresponding hydrazides with Gallacetophenone in aqueous ethanol medium [7]. The separated products were filtered and recrystallized from ethanol. The purity of the reagents were checked by TLC and their melting points. Reagent stock solution was prepared in ethanol.

The supporting electrolytes of pH range 2.0 - 12.0 [8] were prepared using 0.2 M boric acid, 0.05 citric acid and 0.1M trisodium orthophosphate. All the chemicals used were of analytical grade. A 1.0 ml volume of the stock solution was taken in a palarographic cell, 9.0 ml of the appropriate buffer of selected pH was added and the solution was purged with O_2 - free nitrogen gas for 10 min. prior to each run.

Elico recording polarograph, model CL-25, Brinkmann Bank was used for cyclic voltammetric recording, the millicoulometer set up supplied by Raselkis (Budapest) for millicoulometry and pH meter model LI-10 of Elico (pvt) Ltd., India for pH measurements.

RESULTS AND DISCUSSION

The cyclic voltammogram of GAPINH (Fig.1) and GAPSH showed three cathodic peaks in acid solutions in the forward scan. No peak is observed in reverse scan indicating irreversible nature of the electrode process. This is also confirmed by the negative shift in the peak potentials with increasing sweep rates. The reduction process is found to be diffusion controlled and adsorption-free as inferred by the i_p *vs* $v^{1/2}$ linear plot passing through the origin.

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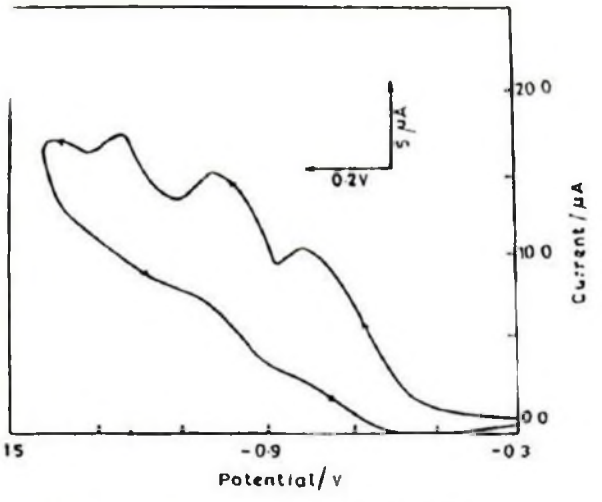


Fig.1:Typical cyclicvoltammogram of 2,3,4-Trihydroxy Acetophenone Isonicotinoyl hydrazone in pH=4 concentration : 0.5 mM ; Scan rate : 40 mVs^{-1}

Both the compounds exhibit two cathodic peaks in alkaline solution. In reverse scan no peak is observed. The characteristics of the waves / peaks are same as in the acid solutions. The reduction potentials in different media are presented in Table 1. The number of electrons involved in the eletrode process is estimated by millicoulometric study [9] and found to be two for first, second & third peaks in acidic medium and two & four for first and second peaks in basic medium respectively.

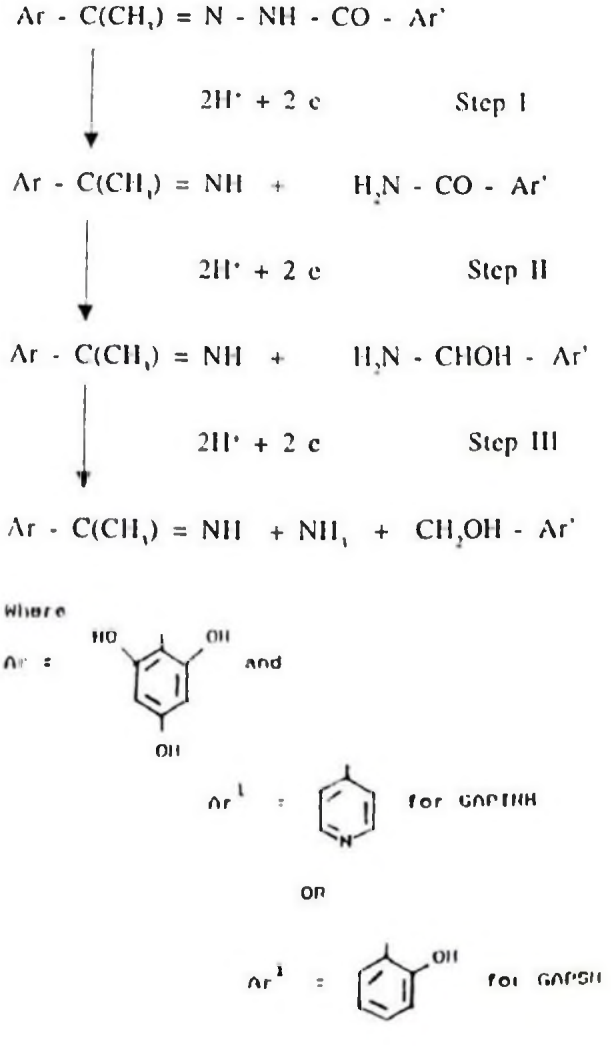
The first wave in both acid and alkaline regions is ascribed to the redutive cleavage = N - NH - linkage involving two electrons. While the second wave in acid medium is ascribed to reduction of amide to secondary alchohol and third as due to further reduction of C-N bound to give primary alcohol and ammonia, the second wave in alkaline media is attributed to the reduction of the amide directly to alcohol in a four electron step. This assignment is based on the position of the wave on the potential axis and the product analysis obtained by controlled potential electrolysis experiments.

Table 1

Half wave Potentials (V *vs* SCE) of GAPINH & GAPSH at Different pH Values

Medium of pH	GAPINH (wave) I	II	III	GAPSH (wave) I	II	III
2	0.74	0.92	1.15	0.77	0.96	1.20
4	0.82	1.06	1.27	0.87	1.09	1.30
6	0.91	1.14	1.36	0.96	1.18	1.41
8	1.01	1.23	-	1.05	1.28	-
10	1.09	1.32	-	1.13	1.36	-
12	1.18	1.39	-	1.21	1.43	-

Reduction Scheme in Acidic Media



In basic medium the first step remains the same but the second step corresponds to steps II and III together.

GAPINH is found to be reduced more easily than GAPSH (See Table 1). This is because GAPINH contains electron withdrawing nitrogen atom in the second ring whereas GAPSH contains electron releasing hydroxyl group. The feasibility of reduction of GAPINH compared with GAPSH can also be explained on the basis of their molecular weights.

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