

Polarographic Reduction of Furfural Semicarbazone

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Polarographic reduction of furfural semicarbazone in acid media is diffusion-controlled and occurs via protonation, at different sites in the heterocyclic ring. While protonation at C-3 leads to the ring-cleaved product, protonation at C-5 gives reduction product with furan ring in tact.

Zuman and Fleet¹ studied the polarographic reduction of a wide variety of semicarbazones of carbonyl compounds except that of furfural semicarbazone.

This and many of its derivatives such as nitrofurfural semicarbazone find wide applications in the manufacture of antiseptic ointments. Semicarbazones have also been used in our laboratories for the polarographic determination of transition metal ions. This prompted us to undertake the title investigation.

The furfural semicarbazone was prepared² in the laboratory and recrystallised from aq. ethanol, m.p. 200-201° (lit m.p. 202°). All other chemicals used were of AR grade and wherever necessary purified using standard procedures. Polarograms were recorded at 30° ± 0.1°C employing DC pen recording polarograph (ELICO Private Limited, Hyderabad). A Lingane type of H-cell with SCE in the narrow limb was employed and the d.m.e. had the following characteristics: $\tau = 3.0$ s; $m = 1.93$ mg S⁻¹, $h = 85$ cm at 0.0 V (vs SCE in water).

The effect of varying pH on the $E_{1/2}$ in buffered solutions (sodium acetate + hydrochloric acid, pH 1 to 3; sodium acetate + acetic acid, pH 4 to 7; and ammonium chloride + ammonia solution, pH 8 to 10) has been studied. A single wave is observed in the pH range 1 to 10 and $E_{1/2}$ varies linearly with pH in the range 1 to 7 (Table 1). The effects of the height of mercury column and concentration of the depolariser on wave height indicate that the wave is diffusion-controlled. Semi-logarithmic analysis of the polarogram shows the irreversible nature of the wave. As is expected, the reduction of semicarba-

Table 1—Effect of pH on $E_{1/2}$ and Wave Height

pH	$-E_{1/2}$ (V vs SCE)	Wave height (cm)	α_n
1	0.72	11.6	1.03
2	0.80	14.2	1.03
3	0.88	15.0	1.03
4	0.96	14.5	1.03
5	1.05	14.2	1.03
6	1.12	12.2	1.03
7	1.22	6.9	1.03
8	1.63	10.5*	—
9	1.65	9.0*	—
10	1.68	8.5*	—

*Waves are ill-defined and approximate values are given.

Table 2—Effect of Varying Hydrochloric Acid Concentration on $E_{1/2}$ and Wave Height in Unbuffered KCl Solutions

[KCl] = 0.1 M; [FAS] = 1×10^{-3} M; [HCl] = 1×10^{-2} M; total volume = 25 ml

Volume of HCl (ml)	pH (measured)	$-E_{1/2}$ (V vs SCE)	Wave height (cm)
1.0	3.99	0.94	1.8
1.5	3.71	0.94	3.8
2.0	3.56	0.94	5.4
2.5	3.44	0.94	7.2
3.0	3.37	0.94	9.1
4.0	3.24	0.94	11.7
5.0	3.10	0.94	15.8
7.0	2.96	0.94	16.4
8.0	2.89	0.92	16.5
10.0	2.79	0.91	16.2
15.0	2.62	0.89	15.8

zone occurs at more positive potentials than that of furfural. It is known that semicarbazones undergo four-electron reductive cleavage in general. But many instances are reported^{3,4,7} where the limiting current does not correspond to the number of electrons consumed in the reductive process. Such systems have been classified into four types.

(i) Where the maximum value of the limiting current is not reached due to the protonation equilibrium not being fully attained under the experimental conditions; (ii) where the semicarbazide derivatives (RR'CHNHNHCONH₂) are formed in increasing proportion during reduction; (iii) where a substituent such as -NH₂, a group in the depolariser is susceptible to facile protonation; and (iv) where simultaneous reduction of bi- and mono-protonated forms is possible.

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