

Cyclic Voltammetric Reduction of 2-Acetylpyridine Semicarbazone at Glassy Carbon Electrode

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Abstract: Electrochemical reduction behavior of 2-acetylpyridine semicarbazone is studied on glassy carbon electrode in CH₃OH-Britton Robinson buffer at pH 5, 7 & 9 using cyclic voltammetry. Single irreversible reduction wave is observed due to the reduction of semicarbazone moiety. The effect of change in pH and sweep rate is evaluated. The electrode process is found to be irreversible and diffusion controlled. Kinetic parameters are calculated from cyclic voltammetric measurements.

Keywords: 2-Acetylpyridine semicarbazone, GC electrode, B-R buffer and Cyclic voltammetry.

INTRODUCTION

Semicarbazones have been a subject of interest in recent decades due to their biological activity, good complexing properties and analytical applications.¹⁻⁷ Systematic perusal of earlier literature reveals that inspite of the variegated importance associated with semicarbazone compounds, relatively few reports exist on their electrochemical behavior.⁸⁻¹⁷ A thorough literature survey reveals that there is no report on the cyclic voltammetric study of 2-Acetylpyridine semicarbazone (2-AcPySC). In the presents work we have studied the 2-AcPySC at glassy carbon electrode using cyclic voltammetric technique with a view to investigate some important aspects as mechanism of electrode process and effect of varying condition on redox behavior of the compound. The kinetic parameters such as charge-transfer coefficient (α_n), diffusion coefficient ($D_0^{1/2}$) and rate constant ($K_{f,h}^0$) have been calculated.

EXPERIMENTAL

All chemicals employed were of analytical grade. Methanol was freshly distilled prior to use. 2-Acetylpyridine semicarbazone(2-AcPySC) was

synthesized by standard procedure available in literature.¹⁸ The cyclic voltammetric data were recorded with a fully computer controlled Basic Electrochemistry System (model ECDA 001). A three electrode combination system was used. This consisted of a glassy carbon (GC) working electrode, an Ag/AgCl reference electrode and a Pt wire auxiliary electrode. An elico digital pH meter was employed for pH measurements and all measurements were carried out at laboratory temperature.

Glassy carbon electrode was cleaned prior to the modification polishing with 0.1 μ m alumina on a polishing cloth using double distilled water as the lubricant. The activity of electrode was tested using solution of ferricyanide/ferrocyanide in 0.1M KCl.¹⁹

The stock solutions of 2-AcPySC (1×10^{-2} M) was prepared in methanol. Britton-Robinson buffer was prepared in doubly distilled water. In the typical cyclic voltammetric experiment, reaction mixture consisted of compound solution, methanol (the minimum volume necessary to keep the compound in the solution) and buffer solution (keeping the overall volume constant 10 ml) was taken. Before recording the current voltage curve, the solution was deoxygenated by purging a stream of nitrogen gas for

15 min prior to the experiments in order to remove dissolved oxygen from the media. The three electrodes were connected to the electrochemical cell. Required potential scan rates, current sensitivity, initial potential and final potential were applied and resulting current measured as a function of applied potential.

RESULT AND DISCUSSION

The 2-acetylpyridine semicarbazone (2-AcPySC) has been characterized on the basis of elemental and spectral analysis. The cyclic voltammograms of 2-AcPySC were recorded with an initial potential (E_i) +1400 to +1500mV and switching potential (E_s) between -1200 to -1300 mV at different scan rates 50,100,200,300,400 and 500mV/s in aqueous methanolic solutions (**fig 1-3**). Double cyclic voltammograms were also recorded to monitor the fate of products generated in first cycle. The

electrochemical reduction behavior of 2-acetylpyridine semicarbazone (2-AcPySC) was also studied at three different pH values 5, 7 and 9. All the voltammetric data are given in table 1-3. The compound exhibits a well defined single cathodic peak while no peak is obtained in reverse scan. Similar behavior was observed in all the cyclicvoltammograms at different scan rate and in the range of pH (5, 7 & 9). The peak potential (E_{pc}) value shifted in the more negative potential with an increase in the scan rate (v) indicating the electrochemical process was irreversible. The peak potential shift was higher when the scan rate increased. This means that under these conditions the electrochemical process is more irreversible. Peak current (I_{pc}) also increases as the scan rate increased. The current function ($I_{pc}/v^{1/2}$) has been found to be fairly constant with respect to sweep rate indicating that the electrode process is diffusion controlled.²⁰⁻²⁹

Fig 1 Cyclic voltammograms of 1mM 2-Acetylpyridinesemicarbazone (2-AcPySC) in CH₃OH-BR buffer at pH 5

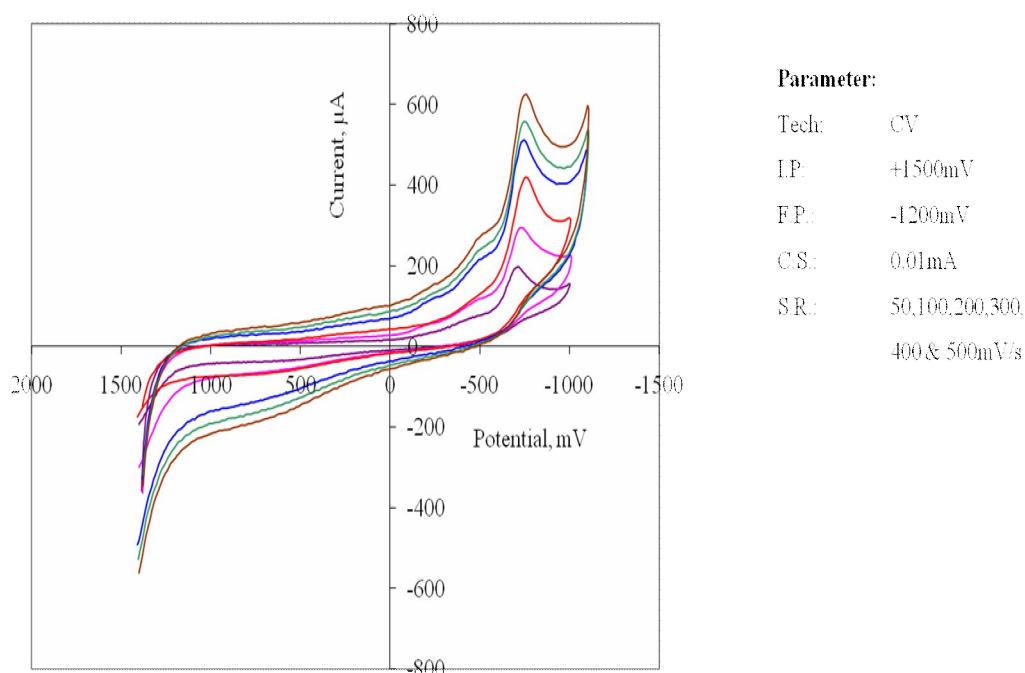
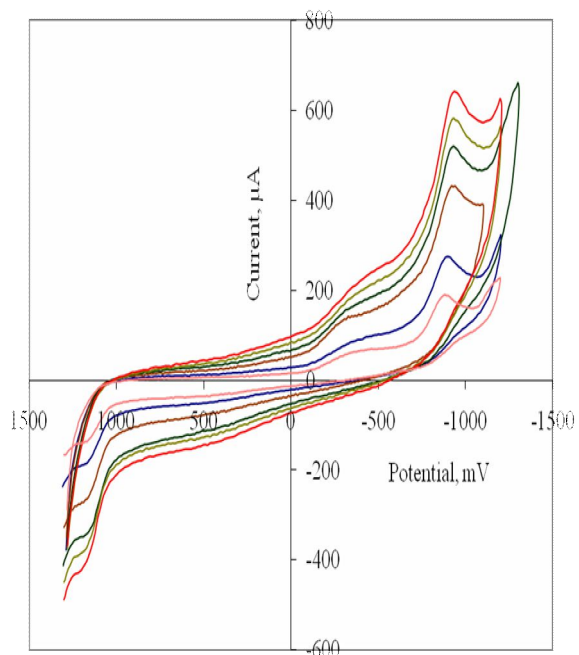


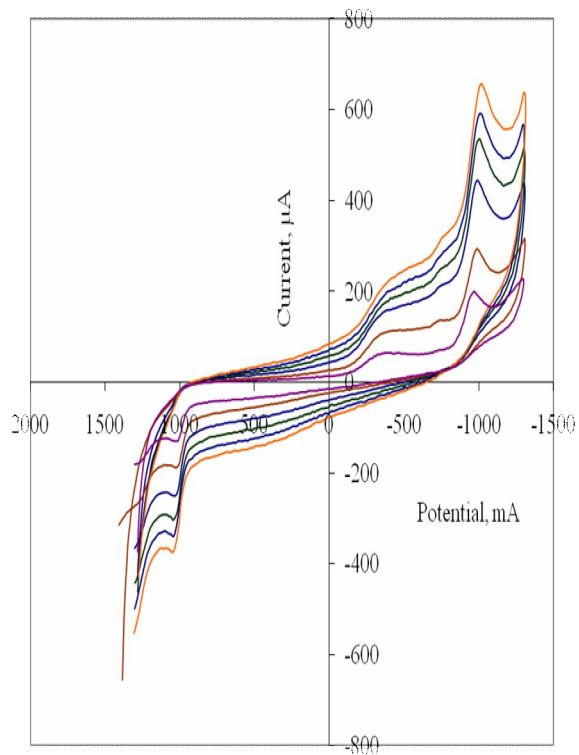
Fig 2 Cyclicvoltammograms of 1 mM 2-Acetylpyridine semicarbazone (2-AcPySC) in CH₃OH-BR buffer at pH 7



Parameters:

Tech: CV
 I.P. -1400mV
 F.P. -1200mV
 C.S. 0.01 mA
 S.R. 50,100,200,300,400
 & 500mV/S

Fig 3 Cyclicvoltammograms of 1mM 2-Acetylpyridinesemicarbazone (2-AcPySC)in CH₃OH-BR buffer at pH 9



Parameters:

Tech: CV
 I.P. +1400mV
 F.P. -1300mV
 C.S. 0.01mA
 S.R. 50,100,200,300,
 400&500 Mv/S

Table 1 Effect of sweep rate on voltammetric parameters of 1 mM 2-Acetylpyridine semicarbazone (2-AcPySC) in aqueous methanol solution containing B-R buffer at pH 5 (Fig 1)

Initial potential E_i : +1500 mV Working Electrode : Glassy Carbon
 Switching potential E_s : -1200mV Reference Electrode : Ag/AgCl/KCl
 Auxiliary Electrode : Platinum

v mV/s	E_{pc} mV	I_{pc} μA	$E_{1/2}$ mV	$E_{p/2}$ mV	$I_{p,c}/v^{1/2}$	α_n	$D_0^{1/2} \times 10^{-3}$ $cm^2.s^{-1}$	$K_{f,h}^{\circ}$ $cm.s^{-1}$
50	-711	1.98	-628	-591	0.2800	0.3976	1.39	4.43×10^{-8}
100	-731	2.94	-651	-612	0.294	0.4009	1.46	4.40×10^{-8}
200	-766	3.94	-673	-603	0.2786	0.2927	1.62	8.61×10^{-7}
300	-749	5.11	-662	-594	0.2950	0.3078	1.67	8.72×10^{-7}
400	-744	5.58	-665	-594	0.279	0.3181	1.56	7.51×10^{-7}
500	-759	6.25	-663	-610	0.2795	0.3202	1.55	6.56×10^{-7}

Table 2 Effect of sweep rate on voltammetric parameters of 1 mM 2-Acetylpyridine semicarbazone (2-AcPySC) in aqueous methanol solution containing B-R buffer at pH 7 (Fig 2)

Initial potential E_i : +1400mV Working Electrode : Glassy Carbon
 Switching potential E_s : -1200mV Reference Electrode : Ag/AgCl/KCl
 Auxiliary Electrode : Platinum

v mV/s	E_{pc} mV	I_{pc} μA	$E_{1/2}$ mV	$E_{p/2}$ mV	$I_{p,c}/v^{1/2}$	α_n	$D_0^{1/2} \times 10^{-3}$ $cm^2.s^{-1}$	$K_{f,h}^{\circ}$ $cm.s^{-1}$
50	-878	1.90	-797	-729	0.2687	0.3202	1.49	4.52×10^{-8}
100	-894	2.74	-814	-703	0.274	0.2498	1.72	6.20×10^{-7}
200	-920	4.31	-818	-683	0.3048	0.2013	2.14	4.30×10^{-6}
300	-930	5.20	-830	-702	0.3022	0.2092	2.07	3.60×10^{-6}
400	-932	5.81	-844	-711	0.2905	0.2159	1.97	3.11×10^{-6}
500	-935	6.43	-850	-711	0.2875	0.2130	1.96	3.73×10^{-6}

Table 3 Effect of sweep rate on voltammetric parameters of 1 mM 2-Acetylpyridine semicarbazone (2-AcPySC) in aqueous methanol solution containing B-R buffer at pH 9 (Fig 3)

Initial potential E_i : +1400mV Working Electrode : Glassy Carbon
 Switching potential E_s : -1300mV Reference Electrode : Ag/AgCl/KCl
 Auxiliary Electrode : Platinum

v mV/s	E_{pc} mV	I_{pc} μA	$E_{1/2}$ mV	$E_{p/2}$ mV	$I_{p,c}/v^{1/2}$	α_n	$D_0^{1/2} \times 10^{-3}$ $cm^2.s^{-1}$	$K_{f,h}^{\circ}$ $cm.s^{-1}$
50	-970	2.00	-910	-860	0.2828	0.4337	1.35	2.07×10^{-10}
100	-986	2.94	-926	-838	0.294	0.3223	1.63	1.67×10^{-8}
200	-989	4.44	-927	-838	0.3139	0.2447	2.00	4.85×10^{-7}
300	-1006	5.36	-935	-819	0.3094	0.2551	1.93	3.31×10^{-7}
400	-109	5.93	-950	-778	0.2965	0.2065	2.05	2.40×10^{-6}
500	-1013	6.57	-946	-801	0.2938	0.2250	1.95	1.24×10^{-6}

The effect of pH upon the reduction of 2-AcPySC was investigated (table 1-3). Peak potential values of the compound are found to be changed with the pH value of the solution. This dependence of the peak potential on pH indicating that proton transfer also takes place in the electrode reaction²⁷. The peak potential shifts in more negative values depending upon the pH of the solution. This means that the reduction is easier in acidic media and difficult in media where the proton

concentration is low. The ease of reduction is found to be more in acidic pH than in alkaline pH which may be because of the formation of easily reducible protonated intermediate.

Thus, the kinetic parameters such as charge-transfer coefficient (α_n), diffusion coefficient ($D_0^{1/2}$) and rate constant ($K_{f,h}^{\circ}$) have been calculated for irreversible and diffusion controlled reduction by using following equations²⁰⁻²³ and reported in table (1-3).

$$\left| E_p - E_{p/2} \right| = \frac{1.857RT}{\alpha_n F} = \left(\frac{47.7}{\alpha_n} \right) mV \quad (1)$$

$$I_p = 3.01 \times 10^5 n (\alpha_n)^{1/2} A C D_0^{1/2} \nu^{1/2} \quad (2)$$

$$E_p = -\frac{RT}{\alpha_n F} \left[0.78 + \ln \left(\frac{D_0^{1/2}}{K_{f,h}^\circ} \right) + \ln \left(\frac{\alpha_n F \nu}{RT} \right)^{1/2} \right] \quad (3)$$

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CONCLUSION

The result obtained in the present study shows that 2-AcPySC presently investigated undergoes easily reduction. Keeping in view of feasibility of the site of reduction and on the basis of cyclic voltammetric results, same reduction mechanism may be suggested for electroreduction of 2-AcPySC similar that reported in the literature⁹⁻¹³ which finds supports from the E_{pc} and $E_{1/2}$ shifts towards negative potential with increasing pH, as protons are consumed in the reduction.

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