



Electrochemical Studies of 1,5-Diphenylcarbazide

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Electrochemical behaviour of 1,5-diphenylcarbazide has been investigated to determine the redox process at hanging mercury electrode by using differential pulse voltammetry and cyclic voltammetry. A series of studies were performed with various parameters such as pH, different supporting electrolyte and photochemical oxidation process. Studies performed in both acidic and alkaline buffer solutions revealed cathodic reduction of the carbonyl group (C=O) present in the compound at -1.20 V vs. S.C.E. proton abstraction in alkaline buffer solution resulted in cathodic reductions of both the oxidation products of 1,5-diphenylcarbazide at -0.3 V and -0.6 V vs. S.C.E. Studies performed in supporting electrolytes such as, KNO₃ and HClO₄ showed the oxidation prone sensitive nature of 1,5 diphenylcarbazide towards the oxidizing ability of anions like NO₃⁻ and ClO₄⁻ present in supporting electrolyte. Photochemical oxidation was triggered at lower concentrations of 1,5-diphenylcarbazide, which oxidizes to 1,5-diphenylcarbadiazone. It subsequently reduces to 1,5-diphenylcarbazone and 1,5-diphenylcarbazide.

Key Words: 1,5-Diphenylcarbazide, 1,5-Diphenylcarbazone, 1,5-Diphenylcarbadiazone, Differential pulse voltammetry, Cyclic voltammetry.

INTRODUCTION

1,5-Diphenylcarbazide is considered as an important substance for detection and determination of one of the most hazardous environmental pollutant known as hexavalent chromium. Goldoni *et al.*¹ used 1,5-diphenylcarbazide for the determination of hexavalent chromium in exhaled breath condensate of workers in chrome plating industry. 1,5-Diphenylcarbazide was used by Moghimi² as a modifier in octadecyl-bonded silica membrane disks for trace level detection of copper ions in different water samples. In plant physiological studies conducted by Dean and Pocock³, 1,5-diphenylcarbazide has been utilized as an alternative source of electron donor to restore electron transport through heat-treated chloroplast. Ramirez *et al.*⁴ carried out kinetic and thermodynamic studies of diphenylcarbazide in aqueous solution of different pH spectrophotometrically. Abbaspour and Izadyar⁵ used 1,5-diphenylcarbazide as chromium ionophore in fabrication of composite multi-walled carbon nanotube (MWNT) polyvinylchloride (MWNT-PVC) based potentiometric sensor. Molecular simulation and self-assembled monolayer study of 1,5-diphenylcarbazide on a copper surface are also available in literature⁶. Swiecicka and Garbos⁷ used 1,5-diphenylcarbazide for post column reaction with chromium(VI) for trace level detections present in bottled

mineral water and spring water by using high performance ion chromatography technique. Zhai *et al.*⁸ used 1,5-diphenylcarbazide doped in magnetic nanoparticles for trace level detection of mercury ions present in aqueous solutions by using solid phase extraction method. Complexation studies of osmium⁹, rhodium and iridium¹⁰ were performed by using 1,5-diphenylcarbazide and also its oxidation products such as, 1,5-diphenylcarbazone and 1,5-diphenylcarbadiazone were used for analytical determination of molybdenum¹¹ and chromium¹². Attempts were also made to study the electrochemical behaviour of 1,5 diphenylcarbazide in HClO₄ as supporting electrolytes¹³.

However owing to the complexity of problem, the present work focuses on systematic representation of mechanisms involved during oxidation-reduction process in different buffer solutions, supporting electrolytes and lower concentrations of 1,5-diphenylcarbazide by differential pulse voltammetry and cyclic voltammetry.

EXPERIMENTAL

The voltammetric system used for the studies was metrohm ion analysis PGSTAT 30 version 757VA computrace 1.0 software with metrohm 663 VA Standard electrode system installed for analysis. Metrohm three-electrode system 6.1246.020 comprising of saturated calomel electrode as a

reference electrode, platinum electrode as a counter electrode and hanging mercury drop electrode as a working electrode was used throughout the experiment.

Deionized water was used to prepare all the solutions. The 1,5-diphenylcarbazine used for this study was of HPLC Grade. This product was repeatedly recrystallized with absolute alcohol, till a pure white crystalline solid with melting point of 170 °C was obtained. Thin layer chromatographic method¹⁴ was used to ascertain that compound is free from impurities such as, 1,5-diphenylcarbazone and 1-phenylsemicarbazide. All A.R. grade chemicals were used. All the solutions of 1,5-diphenylcarbazine used throughout the entire course of work were prepared in glacial acetic acid.

Voltammetric study of 1,5-diphenylcarbazine in buffered solutions: Differential pulse voltammetric and cyclic voltammetric studies were performed in buffer solution¹⁵ of pH 2.07 and 10.00 (Tables 1 and 2). Blank measurements were carried out with 18 mL of buffer solutions and 2 mL of 1 mol dm⁻³ sodium acetate as supporting electrolytes and concentration of 1,5-diphenylcarbazine as sample was kept as 2.91 × 10⁻³ mol dm⁻³ during the analyses.

Voltammetric study of 1,5-diphenylcarbazine in different supporting electrolyte: Differential pulse voltammetric study of 2.91 × 10⁻⁴ mol dm⁻³ of 1,5-diphenylcarbazine were carried out in 0.1 mol dm⁻³ of KNO₃ and HClO₄ as supporting electrolytes in unbuffered condition containing 18 mL of deionized water and 2 mL of supporting electrolyte as blank.

Photochemical oxidation-reduction study of 1,5-diphenylcarbazine: Photochemical oxidation-reduction studies of 1,5-diphenylcarbazine were performed by subjecting a stock solution of 0.005 mol dm⁻³ of 1,5-diphenylcarbazine to sunlight for the duration of 15 min. The electrochemical analyses by using differential pulse voltammetry were performed in the concentration range of 4.95 × 10⁻⁵ to 1.92 × 10⁻⁴ mol dm⁻³ with an increment of 4.7 × 10⁻⁵ mol dm⁻³ during every analysis. This study was carried out in 18 mL buffer solution of pH 2.07 and 2 mL of 0.1 mol dm⁻³ sodium acetate as supporting electrolyte.

RESULTS AND DISCUSSION

Electrochemical reduction of carbonyl group (C=O) present in 1,5-diphenylcarbazine was observed at the reduction potential of -1.2 V vs. S.C.E. in both acidic and basic buffer solutions. Fig. 1. shows cathodic reduction of oxidation products of 1,5-diphenylcarbazine formed due to abstraction of proton by hydroxyl ion in alkaline buffer medium, which was observed in the form of two additional peaks, first peak at reduction potential of -0.3 V and the second peak at -0.5 V vs. S.C.E. This process of oxidation taking place in alkaline medium is believed to be very fast as no anodic peaks were observed in the voltammograms. Cyclic voltammetric study of 1,5-diphenylcarbazine revealed a complete irreversible process in acidic medium (Fig. 2) and a quasi-reversible process in alkaline medium as both the cathodic and anodic peaks were not equal (Fig. 3).

The possible mechanism occurred during electrochemical studies in alkaline medium is proposed (**Scheme-I**). The irreversibility of cyclic voltammograms in acidic medium

(Table-1) is correlated to the transfer coefficient by means of the following equation¹⁶:

$$E_p - E_{p/2} = 0.048 / \alpha n \alpha$$

Reversibility of the electrode process in alkaline buffer solution (Table-2) is calculated by using the following equation:

$$E_{pa} - E_{pc} = 0.057/n$$

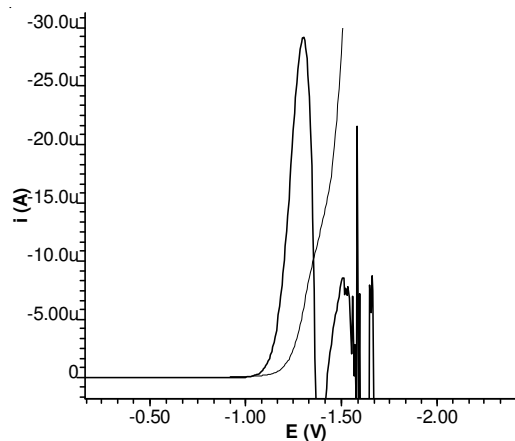


Fig. 1. Typical differential pulse voltammogram of 2.91 × 10⁻³ mol dm⁻³ of 1,5-diphenylcarbazine recorded at 15 mV s⁻¹ of scan rate in buffer solution of pH 2.07

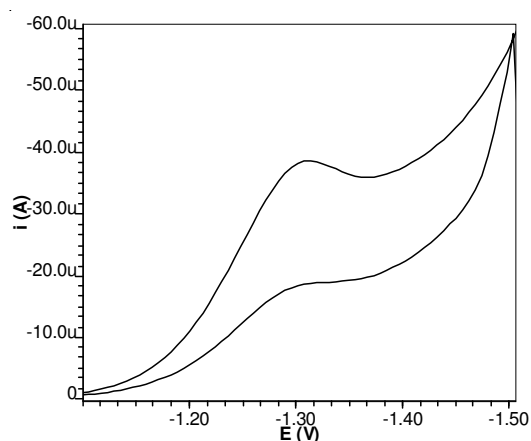


Fig. 2. Typical cyclic voltammogram of 2.91 × 10⁻³ mol dm⁻³ of 1,5-diphenylcarbazine recorded at 40 mV s⁻¹ of scan rate in buffer solution of pH 2.07

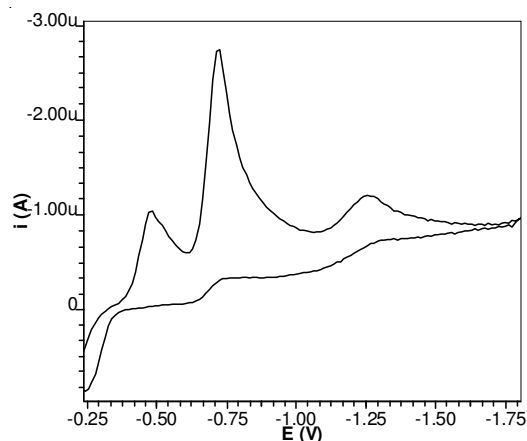
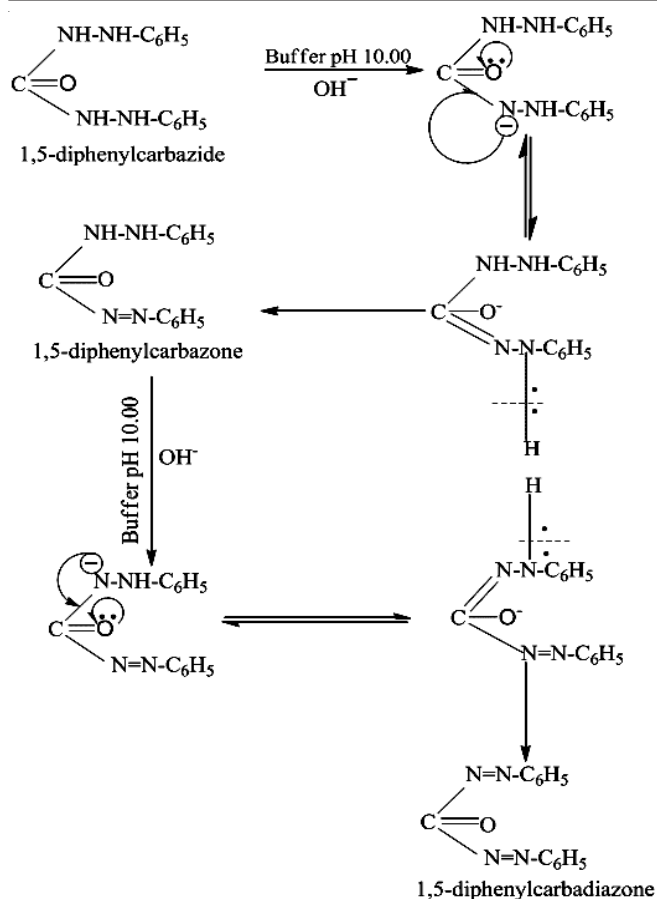


Fig. 3. Typical cyclic voltammogram of 2.91 × 10⁻³ mol dm⁻³ of 1,5-diphenylcarbazine recorded at 40 mV s⁻¹ of scan rate in buffer solution of pH 10



Scheme-I: Proposed mechanism for 1,5-diphenylcarbazide undergoing abstraction of a proton by the hydroxyl ions in alkaline medium of pH 10

Scan rate (mV/s)	2.07 ($E_p - E_{p2}$)	2.07 (α_{n_2})
20	0.05	0.96
40	0.09	0.53
60	0.05	0.96
80	0.09	0.53
100	0.10	0.48

Scan rate (mV/s)	ΔE_{p1}	ΔE_{p2}	n_1	n_2
20	0.210	0.130	0.271	0.438
40	0.230	0.105	0.247	0.542
60	0.230	0.107	0.247	0.532
80	0.240	0.094	0.237	0.606
100	0.240	0.120	0.237	0.475

Electrochemical studies of 1,5-diphenylcarbazide carried out with KNO_3 and HClO_4 as supporting electrolytes reveals the presence of two cathodic peaks. The reduction potentials of these peaks were also found to be similar to those of oxida-

tion products of 1,5-diphenylcarbazide (Fig. 4). This indicates that anions, NO_3^- and ClO_4^- present in supporting electrolytes are capable of oxidizing 1,5-diphenylcarbazide. The possible mechanism taking place during interaction of 1,5-diphenylcarbazide with both the supporting electrolytes are proposed in (Scheme-II) for KNO_3 and (Scheme-III) for HClO_4 .

Exposure of 1,5-diphenylcarbazide stock solution to sun light leads to change of the colour from colourless to light pink, indicating some transitional photochemical reactions. Electro analytical studies of these reactions by differential pulse voltammetry showed a composite oxidation-reduction peak as shown in Fig. 5 between the potential range of -1.0 V to -1.4 V. It indicates that 1,5-diphenylcarbazide is getting oxidized to one of its oxidation products, which further reduced to 1,5-diphenylcarbazide. There is presence of two additional peaks as shown in Fig. 6. First peak is due to 1,5-diphenylcarbazone with the increasing current at the reduction potential of -0.3 V and second peak is because of 1,5-diphenylcarbadiazone with decreasing current at the reduction potential of -0.5 V. It indicates that 1,5-diphenylcarbazide is getting oxidized to its second oxidation product 1,5-diphenylcarbadiazone and 1,5-diphenylcarbadiazone is getting reduced to 1,5-diphenylcarbazone. 1,5-Diphenylcarbazone further gets reduced to 1,5-diphenylcarbazide. Thus a complete reversible oxidation-reduction reaction was observed during the photochemical studies as shown in Scheme-IV.

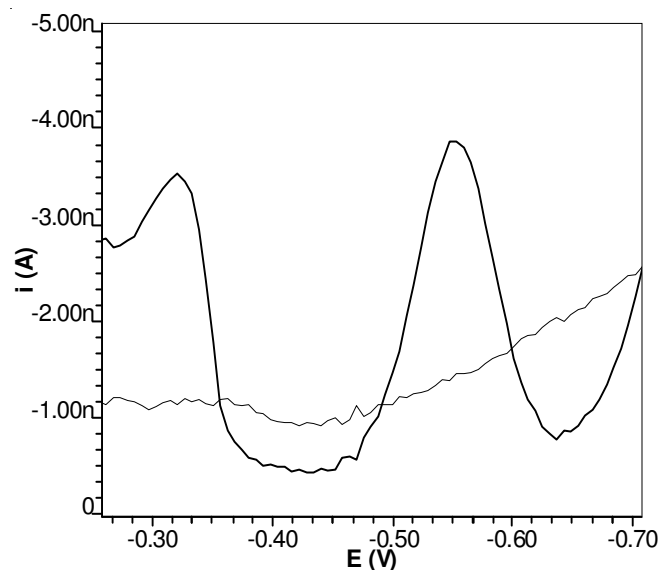
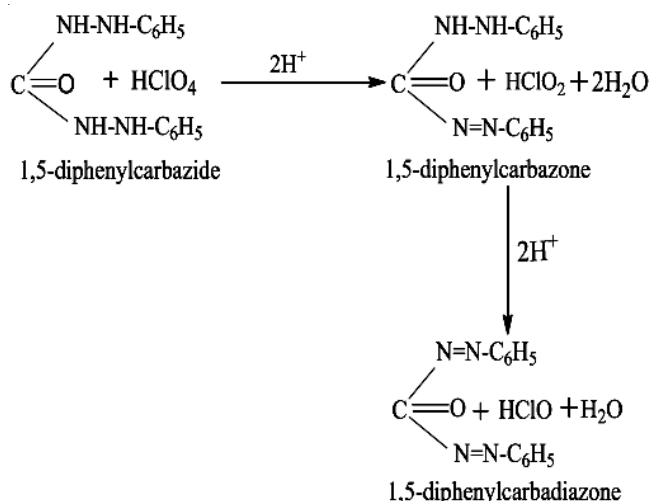


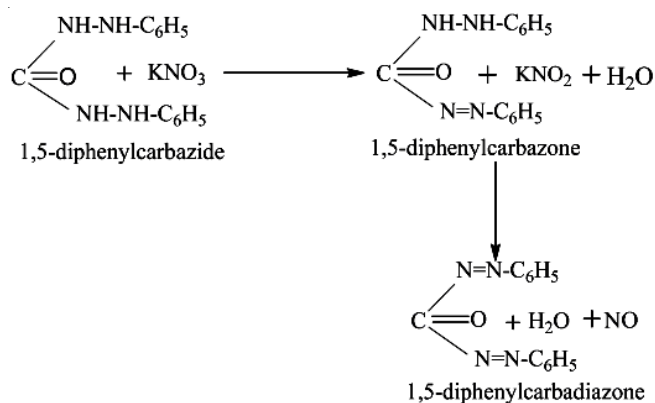
Fig. 4. Typical differential pulse voltammogram obtained with $2.91 \times 10^{-4} \text{ mol dm}^{-3}$ of 1,5-diphenylcarbazide in $0.1 \text{ mol dm}^{-3} \text{ KNO}_3$ as supporting electrolyte and recorded at 15 mV s^{-1} of scan rate in unbuffered solution

Conclusion

1,5-Diphenylcarbazide is well known organic compound used in detection and identification of many hazardous substances important from environmental point of view. 1,5-Diphenylcarbazide was found to be very sensitive towards supporting electrolytes, buffer solutions and sunlight while performing this work. On the other hand, the above mentioned redox processes of 1,5-diphenylcarbazide with its oxidation products can be used. This peculiar characteristic of 1,5-diphenyl-



Scheme-II Proposed mechanism for 1,5-diphenylcarbazide undergoing oxidation in presence of HClO_4 as supporting electrolyte in unbuffered solution



Scheme-III Proposed mechanism for 1,5-diphenylcarbazide undergoing oxidation in presence of KNO_3 as supporting electrolyte in unbuffered solution

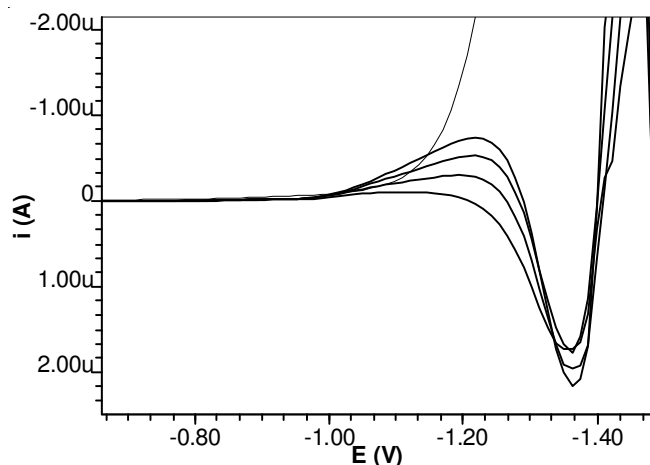


Fig. 5. Typical composite oxidation-reduction obtained during photochemical study of 4.95×10^{-5} to 1.92×10^{-4} mol dm^{-3} of 1,5-diphenylcarbazide recorded at 15 mV s^{-1} of scan rate in buffer solution of pH 2.07

carbazide can be utilized for determination of many metal ions inspite of using 1,5-diphenylcarbazide, 1,5-diphenylcarbazone and 1,5-diphenylcarbadiazone separately.

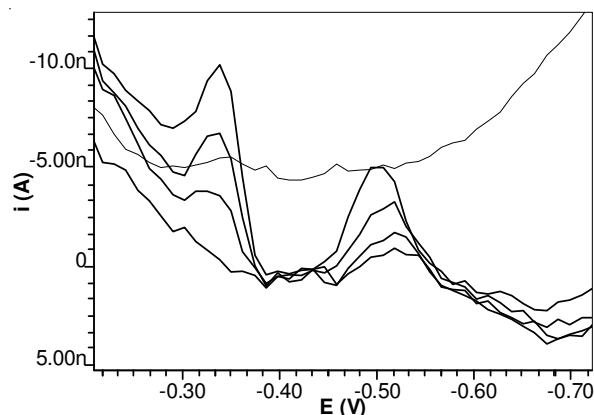
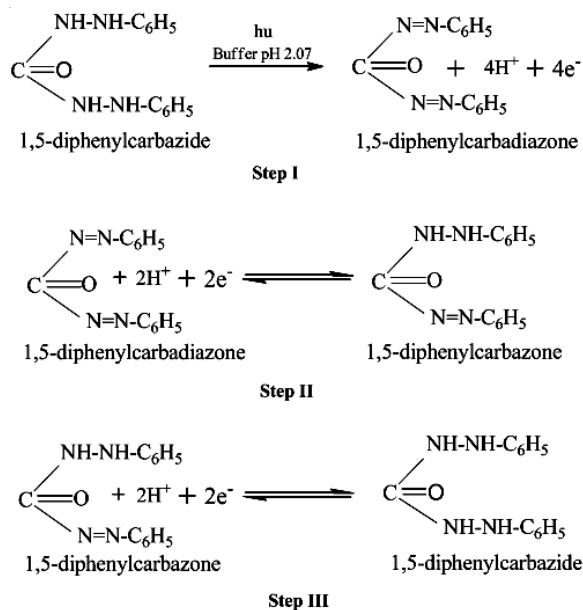


Fig. 6. Typical differential pulse voltammogram of oxidation products of 1,5-diphenylcarbazide obtained during photochemical study of 4.95×10^{-5} to 1.92×10^{-4} mol dm^{-3} of 1,5-diphenylcarbazide recorded at 15 mV s^{-1} of scan rate in buffer solution of pH 2.07



Scheme-IV Proposed mechanism for 1,5-diphenylcarbazide undergoing photochemical oxidation- reduction in presence of sunlight in buffer solution of pH 2.07

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