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Electrochemical Study of Direct and Indirect Oxidation of 1,5- Diphenyl-carbazide in Water Mixed Solvent Systems by Differential Pulse Voltammetry

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Abstract

Direct and indirect oxidation of 1,5-diphenylcarbazide have been studied at hanging mercury drop electrode with differential pulse voltammetric technique. Direct oxidation of 1,5- diphenylcarbazide with $KMnO_4$ resulted in formation of 1,5-diphenylcarbazone in the system at the reduction potential of –0.3 Volts. Oxidation study with $K_2Cr_2O_7$ resulted in formation of 1,5-diphenylcarbazone at the reduction potential of -0.3 Volts along with formation of 1,5-diphenylcarbadiazone at the reduction potential of -0.6Volts in the system. Thus indicates that $KMnO_4$ can be utilized for controlled step oxidation of 1,5- diphenylcarbazide, whereas, $K_2Cr_2O_7$ can be utilized for maximum oxidation of 1,5-diphenylcarbazide. Indirect oxidation of 1,5-diphenylcarbazide was studied by dissolving 1,5-diphenylcarbazide in water mixed solvent systems for aerial oxidation due to formation of 1,5-diphenylcarbazone occurred and detected at the reduction potential of –0.3Volts.

Keywords:

1,5-diphenylcarbazide; 1,5-diphenylcarbazone; 1,5-diphenylcarbadiazone; aerial oxidation; mixed solvent system

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1. Introduction

1,5-diphenylcarbazide is a compound which has been widely used for biological, chemical and electro-analytical purpose. 1,5-diphenylcarbazide and its oxidation products such as, 1,5-diphenylcarbazone and 1,5-diphenylcarbadiazone have been extensively used for analytical determination of many metal ions such as chromium[1-5], mercury [6-7] and osmium [8-9]. Use of 1,5-diphenylcarbazide as an artificial electron donor for restoration of electron transport through chloroplast has been reported [10]. 1,5-diphenylcarbazide is also known to be utilized for the detection and determination of Cr(VI) and Cr (III) from the effluents of industries, where chrome plating or chromic acid are frequently used which are considered as frequent source for causing water pollution and air pollution[11]. Polarographic and chronovoltammetric reductions of 1, 5-diphenylcarbazide (DPCI) and its oxidation products such as 1,5-diphenylcarbazone (DPCO) and 1,5-diphenylcarbadiazone (DPCDZ) have been reported and during the analysis it was also reported that 1,5-diphenylcarbazide (DPCI) gets oxidized to 1,5-diphenylcarbazone (DPCO) and then to 1,5-diphenylcarbadiazone in two stages [12-13]. Electrochemical behavior of 1,5-diphenylcarbazide in 0.3 mol L^{-1} $HClO_4$ and its use in determination of Cr (VI) and Cr (III) by

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using carbon paste electrode and graphite electrode has also been reported [14-15]. The work presented in first part of this paper gives a detail studies on the oxidative behavior of 1,5-diphenylcarbazide and its oxidation products in presence of $K_2Cr_2O_7$ and $KMnO_4$. Second part of the study deals with aerial oxidation study of 1,5-diphenylcarbazide in water mixed solvent system.

2. Experimental

2.1. Chemicals and reagents

1,5-diphenylcarbazide used for this study was of analytical reagent grade. It was repeatedly recrystallized from absolute alcohol, till a pure white crystalline solid with melting point of 170^0C was obtained. Purity of 1,5-diphenylcarbazide was tested by using thin layer chromatographic method[16]. The compound was found to be free from impurities such as, 1,5-diphenylcarbazone and 1-phenylsemicarbazide. All chemicals used were of analytical reagent grade. All the solutions were prepared in double distilled/deionised water.

2.2. Apparatus

For all differential pulse voltammetric measurements, the system used 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 the hanging mercury drop electrode as a working electrode was used. The capillary of drop size 04 with the surface area of 0.40 mm^2 was used. The time of purging was 180 s and the time of equilibrations was 20 s.

2.3. Procedure

0.605 mg of pure 1, 5-diphenylcarbazide was weighed and dissolved in 50 cm^3 of glacial acetic acid to provide a 0.05 mol L^{-1} solution. This solution was used as the stock solution of 1,5-diphenylcarbazide. 1 mol L^{-1} of sodium acetate solution was prepared and used as the supporting electrolyte. These analyses were carried out in buffer solution of pH 2.07, comprising of 0.05 mol L^{-1} HCl and 0.09 mol L^{-1} KCl. In all the differential pulse voltammetric analyses, blank voltammograms were recorded with 18 cm^3 of the buffer solution, 2 cm^3 of 1 mol L^{-1} of sodium acetate as supporting electrolyte and to this blank solution 5 cm^3 of 0.05 mol L^{-1} of the stock DPCI solution was added and voltammograms were recorded. Further to this solution increasing concentration of 0.005 mol L^{-1} of $KMnO_4$ was added and effect caused by addition of $KMnO_4$ was recorded. Similarly differential pulse voltammetric measurements were also carried out by using increasing concentration of 0.005 mol L^{-1} of $K_2Cr_2O_7$ on 5cm^3 of 0.05 mol L^{-1} of the stock DPCI solution.

2.4. Direct Oxidation of 1,5-diphenylcarbazide in presence of $KMnO_4$.

Direct oxidation of 1,5-diphenylcarbazide with $KMnO_4$ was found to generate two cathodic peaks, first peak of DPCI was obtained at the reduction potential of -1.33V vs S.C.E, Whereas, the second peak was obtained at the potential range of –0.38V to –0.39V vs S.C.E, which shows reduction of 1,5-diphenylcarbazone (one of the oxidation product of 1,5-diphenylcarbazide) to 1,5-diphenylcarbazide. Table 1 shows the effect of increasing concentration of $KMnO_4$ on the peak potential (Ep) and peak current (ip) of DPCI with increasing concentration of $KMnO_4$.

Table 1. Electrochemical data for voltammetric reduction of 0.05 mol L^{-1} of 1,5-diphenylcarbazide with 0.005 mol L^{-1} of $KMnO_4$.

Volume of 0.005 mol L^{-1} $KMnO_4$ added	ip in µamp DPCO	Ep in Volts DPCO	ip in µamp DPCI	Ep in Volts DPCI
0.1	-0.076	-0.386	-17.28	-1.33
0.2	-0.155	-0.393	-18.57	-1.34
0.3	-0.205	-0.395	-19.14	-1.34
0.4	-0.235	-0.395	-19.57	-1.34
0.5	-0.267	-0.393	-20.28	-1.35
0.6	-0.244	-0.395	-18.14	-1.35

The voltammograms of DPCI obtained by using $KMnO_4$ as an oxidizing agent were recorded in Fig.1 and Fig.2.

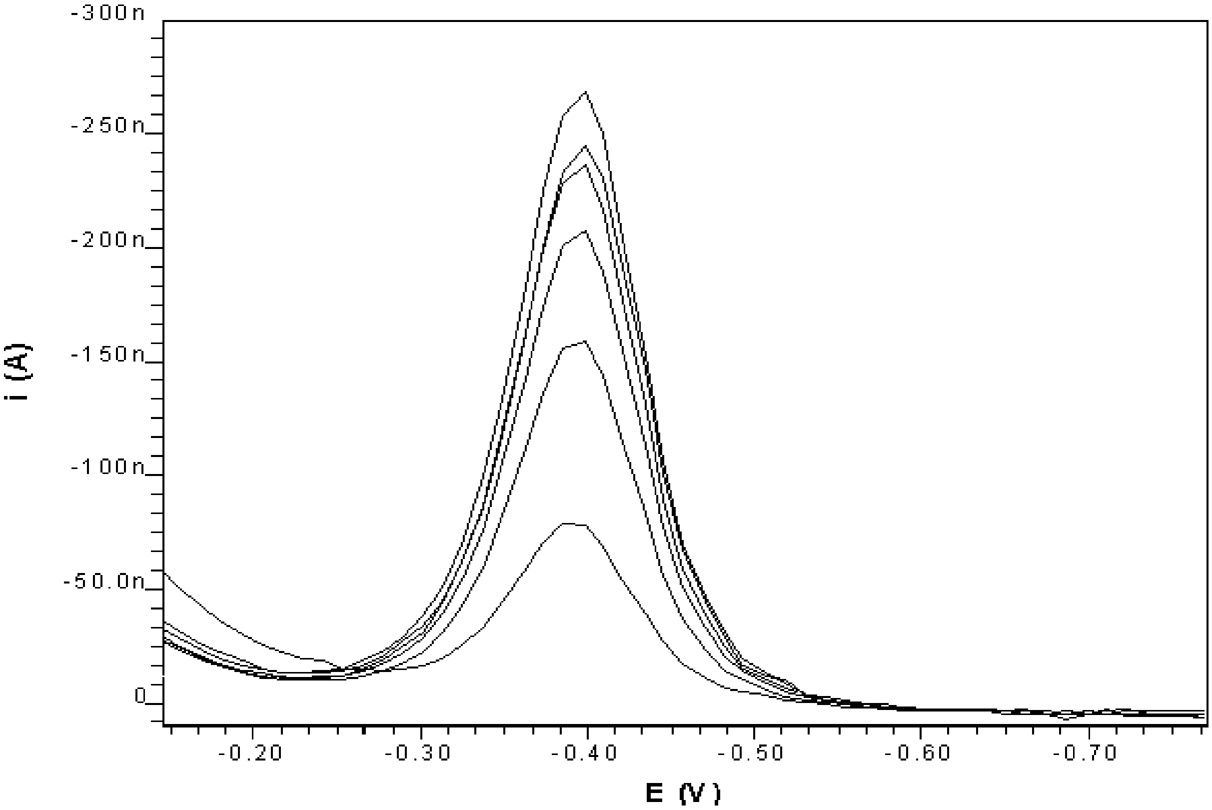


Fig.1. Typical differential pulse voltammograms of DPCO formed during the addition of increasing concentration of 0.005 mol L^{-1} of $KMnO_4$ as an oxidizing agent, in buffer solution of pH 2.07.

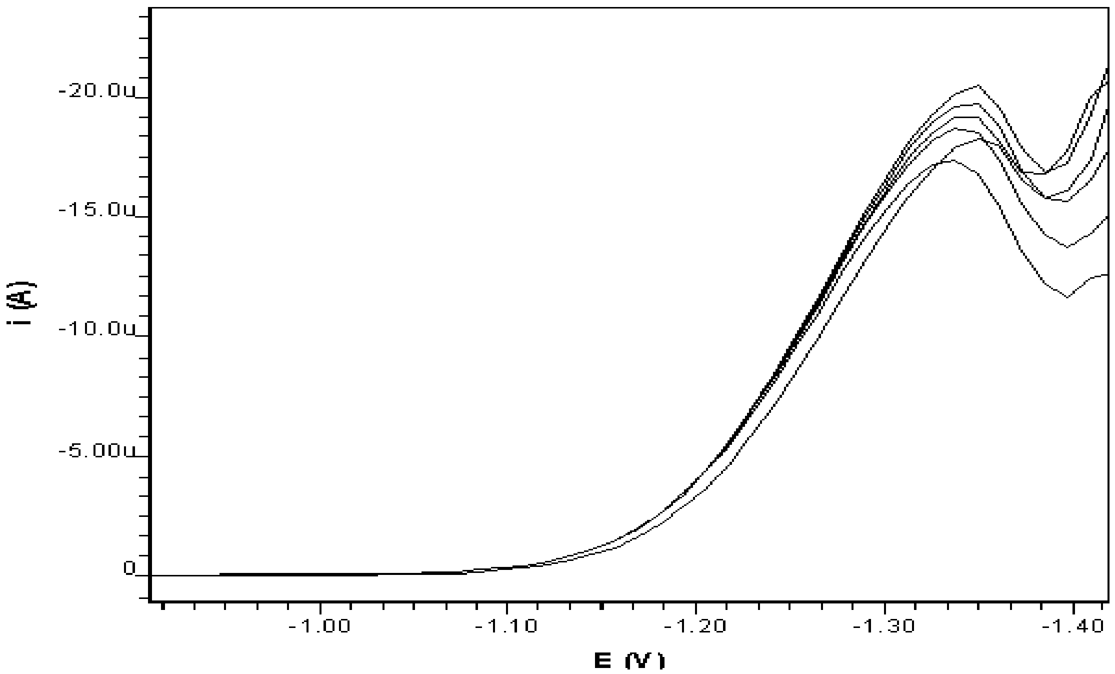


Fig.2. Typical differential pulse voltammograms of 5 cm^3 of 0.05 mol L^{-1} of DPCI present during the addition of increasing concentration of 0.005 mol L^{-1} of $KMnO_4$ as an oxidizing agent in buffer solution of pH 2.07.

2.5. Direct Oxidation of 1,5-diphenylcarbazide in presence of $K_2Cr_2O_7$.

The impact of direct oxidation of 1,5-diphenylcarbazide with $K_2Cr_2O_7$ revealed the presence of three cathodic peaks in the voltammogram. The DPCI peak was obtained at the potential of –1.3V. The second peak obtained at the reduction potential of –0.3V vs S.C.E could be due to reduction of 1,5-diphenylcarbazone to 1,5-diphenylcarbadiazone. Whereas, the third peak obtained at the reduction potential of -0.6V vs S.C.E may be due to reduction of 1,5-diphenylcarbadiazone to 1,5-diphenylcarbazide. Table 2 shows the effect on the peak potential (Ep) and peak current (ip) of DPCI with increasing concentration of $K_2Cr_2O_7$. The polarograms of DPCI obtained with $K_2Cr_2O_7$ as an oxidizing agent are shown in Fig.3 and Fig.4.

Table 2. Electrochemical data for voltammetric reduction of 0.05 mol L^{-1} of 1, 5-diphenylcarbazide with 0.005 mol L^{-1} of $K_2Cr_2O_7$.

Volume of 0.005 mol L^{-1} $K_2Cr_2O_7$ added	ip in µamp DPCO	Ep in Volts DPCO	ip in µamp DPCZ	Ep in Volts DPCZ	ip in µamp DPCI	Ep in Volts DPCI
0.1	-0.0005	-0.364	-0.0017	-0.624	-18.25	-1.341
0.2	-0.003	-0.371	-0.0085	-0.635	-18.25	-1.341
0.3	-0.005	-0.375	-0.0159	-0.641	-17.90	-1.334
0.4	-0.009	-0.379	-0.0231	-0.645	-16.74	-1.318
0.5	-0.010	-0.385	-0.0291	-0.647	-14.99	-1.298
0.6	-0.012	-0.389	-0.0331	-0.657	-12.79	-1.279
0.7	-0.014	-0.375	-0.0391	-0.641	-12.55	-1.274

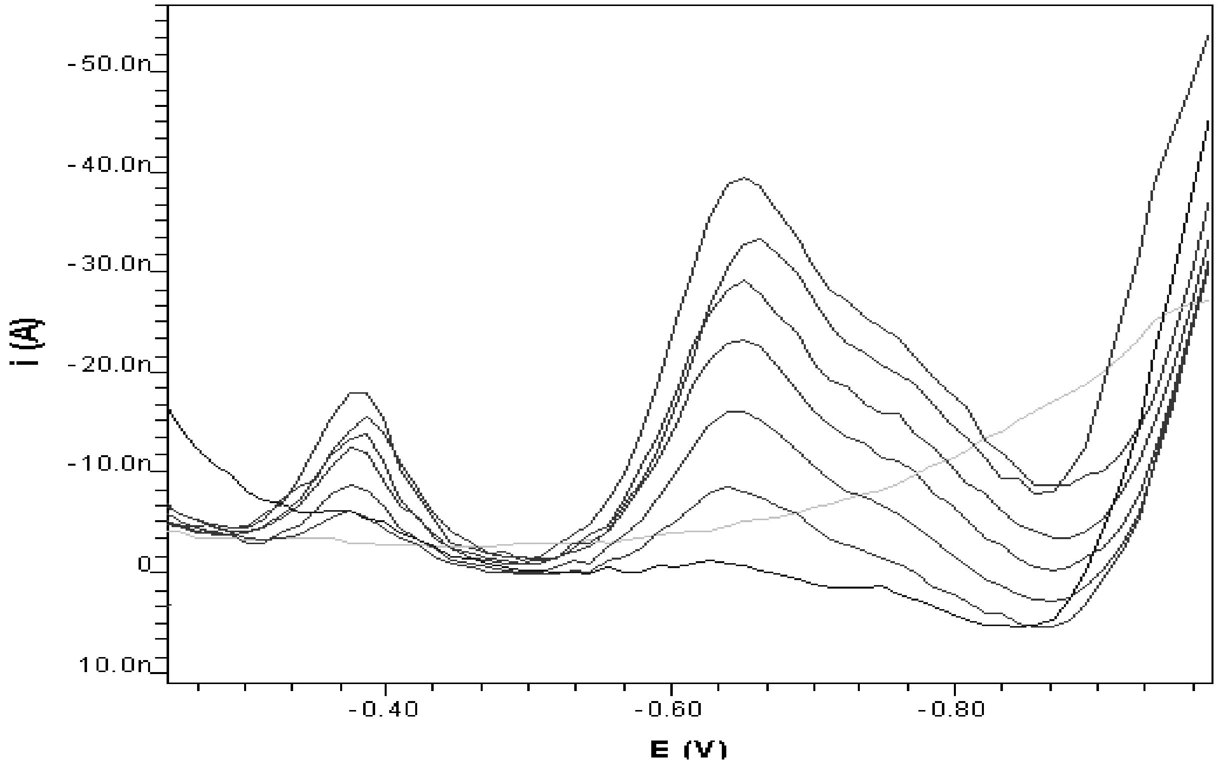


Fig.3. Typical differential pulse voltammograms of DPCO and DPCZ formed during the addition of increasing concentration of 0.005 mol L^{-1} of $K_2Cr_2O_7$ as an oxidizing agent in buffer solution of pH 2.07.

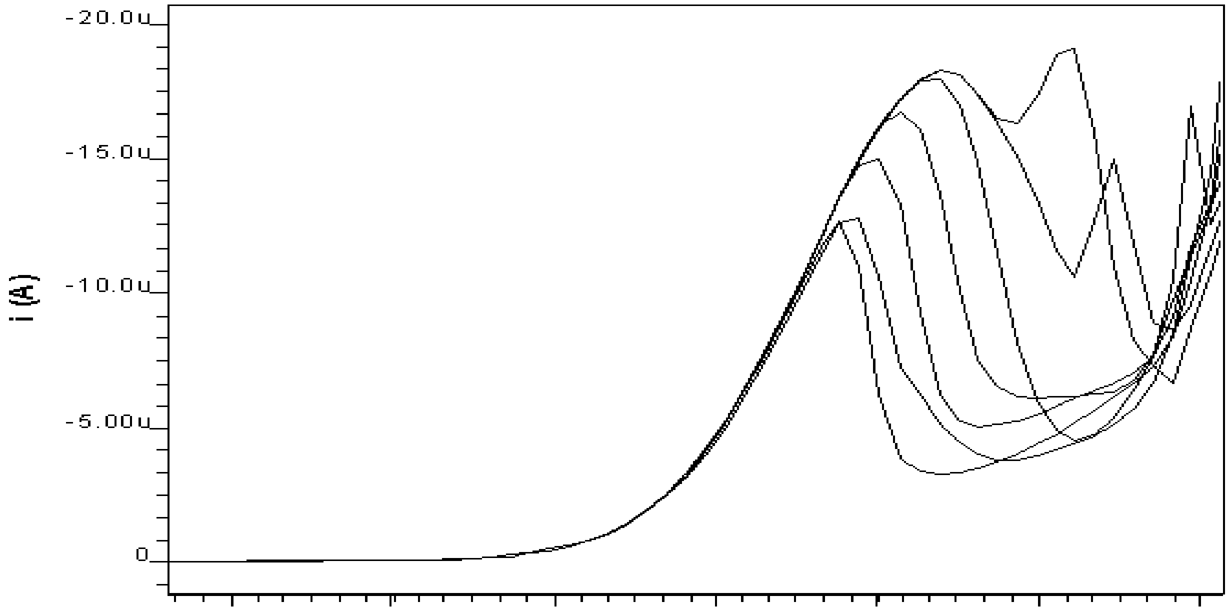


Fig.4. Typical differential pulse voltammograms of 5 cm^3 of 0.05 mol L^{-1} of DPCI present during the addition of increasing concentration of 0.005 mol L^{-1} of $K_2Cr_2O_7$ as an oxidizing agent in buffer solution of pH 2.07.

3. Results and Discussion.

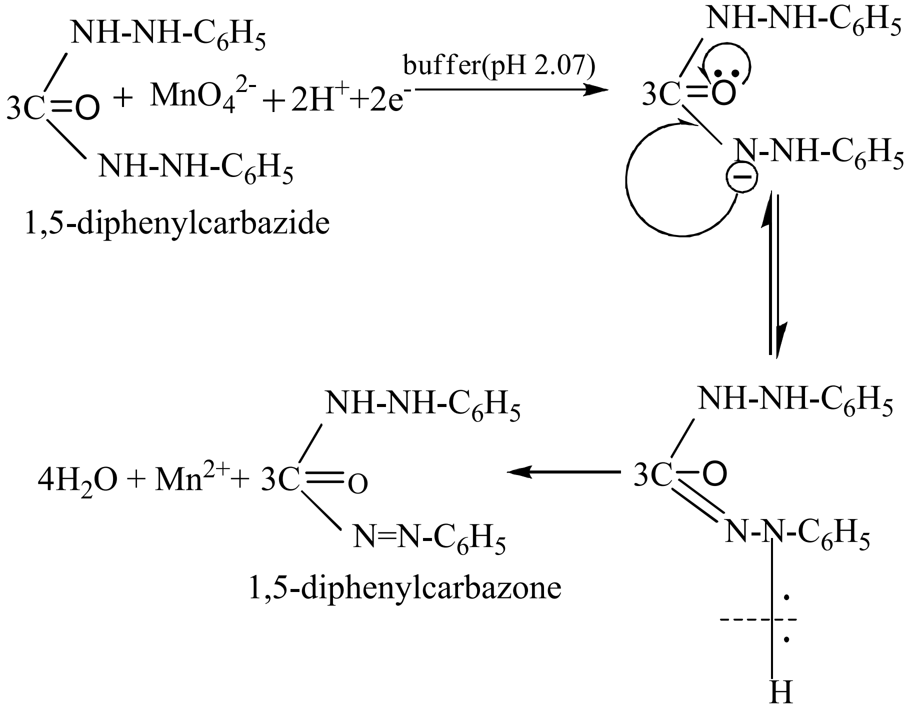
The cathodic peak obtained at the potentials of –1.30V vs. S.C.E, could be due to cathodic reduction of carbonyl group(C=O) present in 1,5-diphenylcarbazide. Whereas, the peaks obtained at the reduction potential of –0.3V vs. S.C.E shows addition of oxidizing agents to 1,5-diphenylcarbazide leads to the formation of 1,5-diphenylcarbazone which is the first stage oxidation product of 1,5-diphenylcarbazide. Peak obtained at the reduction potential of –0.6V in presence of oxidizing agent could be due to the formation of 1,5-diphenylcarbadiazone. Differential pulse voltammetric study of DPCI in the presence of oxidizing agents revealed one common cathodic peak. The reduction potential of this peak was similar to reduction potential of DPCO, whereas, additional peak obtained with $K_2Cr_2O_7$ revealed presence of two stages of oxidation of DPCI, as compared to single step oxidation with $KMnO_4$. Thus it can be concluded that $KMnO_4$ can be utilized for controlled step oxidation of DPCI, whereas, $K_2Cr_2O_7$ can be utilized for obtaining both the oxidation products of DPCI.

The mechanism of oxidation of DPCI to DPCO with direct oxidation with $KMnO_4$ is proposed in scheme A.

4. Indirect oxidation study of 1,5-diphenylcarbazide in water mixed solvent system by differential pulse voltammetric technique.

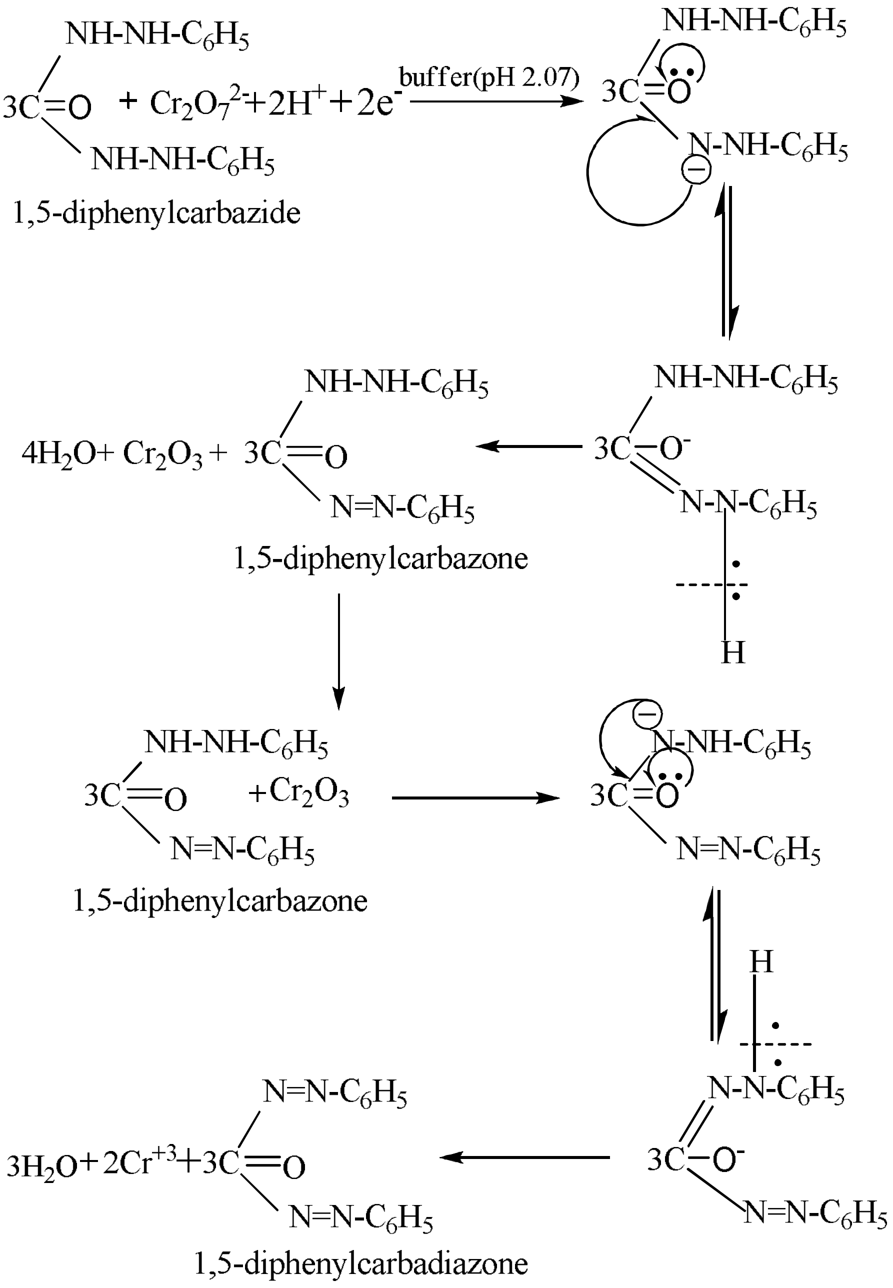
4.1. Mixed solvent systems

Study of Oxidative behaviour of DPCI was carried out separately in two different mixed solvent systems of ethanol-water and glacial acetic acid-water, the proportions in which these solvents were mixed are (75:25 v/v).



Scheme A

Mechanism of oxidation of DPCI to DPCO and then to DPCZ with direct oxidation with $K_2Cr_2O_7$ is proposed in scheme B.



Scheme B
Part II

4.2. Procedure

Study of Indirect oxidative behavior of DPCI was carried out with 0.05 mol L^{-1} of DPCI stock solution in ethanol-water solvent system and 0.05mol L^{-1} of DPCI in glacial acetic acid-water solvent system. The analyses in both the solvent system were carried out in buffer solution of pH 2.07. The blank solution compositions were kept similar as mentioned earlier. Differential pulse voltammograms of 0.8cm^3 of the stock solutions were recorded at different time spans of 0, 24, 48, 72, 96, 120 hrs with a suitable scan rate of 30mV s^{-1}.In this study, the stock solutions of DPCI prepared in both the mixed solvent systems were tested for its stability under normal conditions of room temperature and moisture. The electrochemical data illustrated in Table 3 and Table 4 show the impact of aerial oxidation on peak potential (Ep) and peak current (ip) of DPCI with progression in time duration.

Table3. Electrochemical data of 0.05 mol L^{-1} of DPCI in ethanol-water (75:25 v/v) mixed solvent system.

Time in Hours	ip(ηA) DPCO	Ep (V) DPCO	$E_{1/2}$ DPCO	ip(μA) DPCI	Ep(V) DPCI	$E_{1/2}$ DPCI
0	-------	--------	-	-17.84	-1.265	-1.290
24	-0.42	-0.263	-0.288	-16.11	-1.246	-1.271
48	-0.85	-0.331	-0.356	-24.99	-1.259	-1.284
72	-1.01	-0.352	-0.377	-12.10	-1.249	-1.274
96	-2.17	-0.338	-0.363	-22.36	-1.345	-1.370
120	-3.16	-0.372	-0.397	-15.00	-1.249	-1.274

Table4. Electrochemical data of 0.05 mol L^{-1} of DPCI in glacial acetic acid-water (75:25 v/v) mixed solvent system.

Time in Hours	ip(ηA) DPCO	Ep (V) DPCO	$E_{1/2}$ DPCO	ip(μA) DPCI	Ep(V) DPCI	$E_{1/2}$ DPCI
0	------	------	-	-5.22	-1.301	-1.326
24	-0.27	-0.376	-0.401	-5.99	-1.293	-1.318
48	-1.99	-0.384	-0.409	-4.61	-1.272	-1.297
72	-4.58	-0.400	-0.425	-4.63	-1.275	-1.300
96	-7.14	-0.357	-0.382	-4.89	-1.235	-1.260
120	-12.26	-0.348	-0.373	-5.00	-1.250	-1.299

5. Results and discussion (Indirect oxidation study of DPCI).

Aerial oxidation study of DPCI in both solvent system revealed the generation of peak at the reduction potential of –0.3V to-0.4V after a time span of 24 hrs. Progression in time revealed increment in the peak current. Considerable peak heights were observed after a span of 120 hrs as shown in Fig.5 and Fig.6. Fig.7 shows the variation of half wave potential with respect to time.

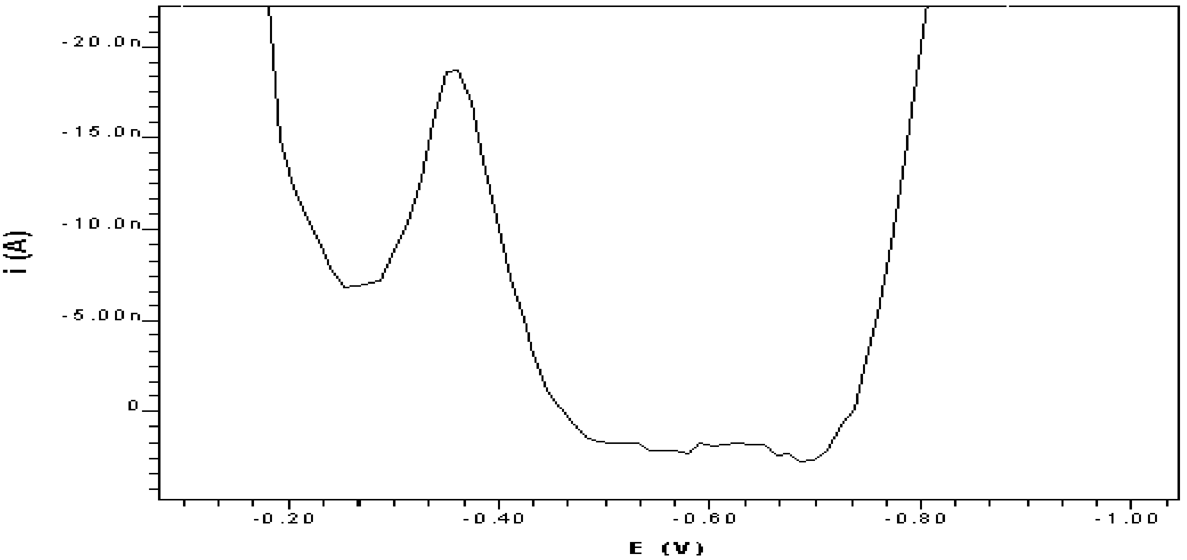


Fig.5. Typical differential pulse voltammograms of DPCO obtained due to aerial oxidation of DPCI in ethanol and water solvent system in buffer solution of pH 2.07, at 120 hrs.

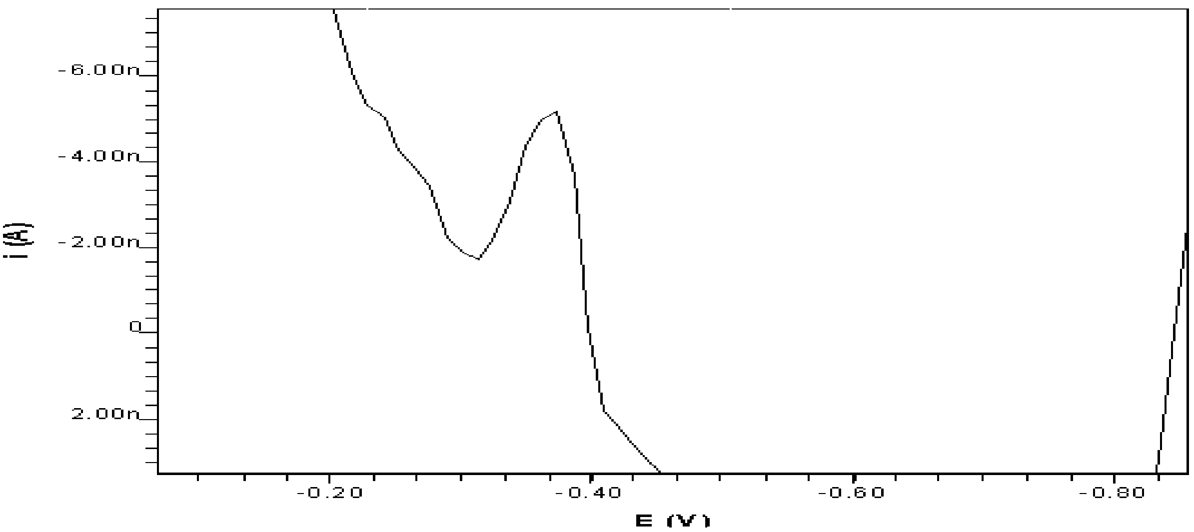


Fig.6. Typical differential pulse voltammograms of DPCO obtained due to aerial oxidation of DPCI in glacial acetic acid and water solvent system in buffer solution of pH 2.07, at 120 hrs.

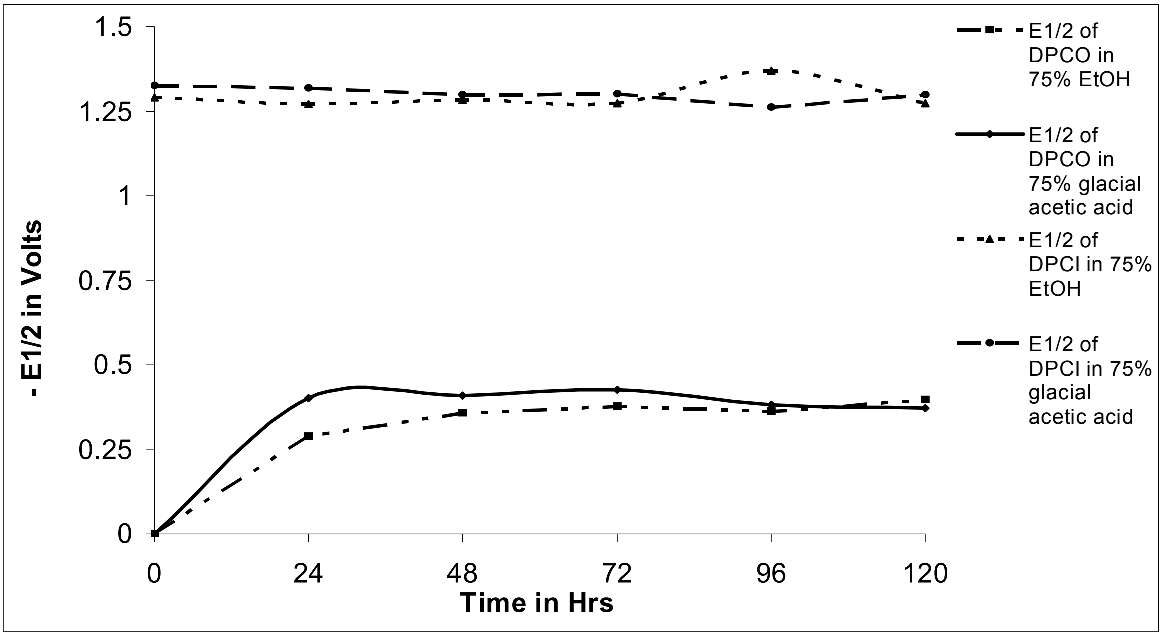
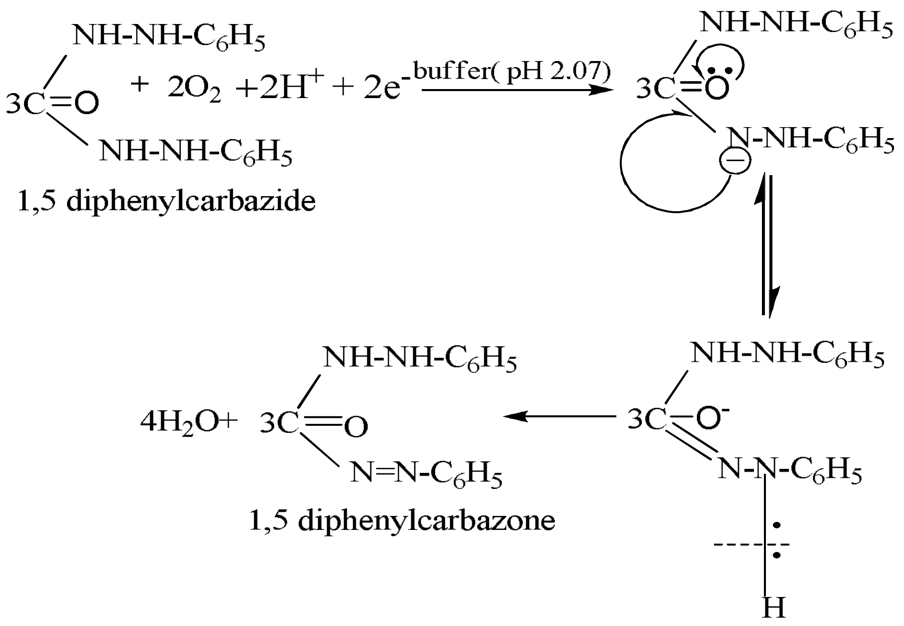


Fig.7. Plot of -$E_{1/2}$ vs time of DPCI and DPCO peaks obtained of during aerial oxidation study of DPCI in buffer solution of pH 2.07.

The proposed mechanism for the electrochemical behaviour of DPCI during aerial oxidation process is shown as Scheme C.



Scheme C

Thus the aerial oxidation process in both the mixed solvent systems resulted in the oxidation of DPCI to DPCO, and the time taken for this oxidation process reveals that the rate of conversion in presence of acidic medium was observed to be slow.

References

1. Willems G J, Balton N M, Peters O M, Ranter D (1977) The Interaction of Chromium(VI), Chromum(III) and Chromium(II) with Diphenylcarbazide, Diphenylcarbazone and Diphenylcarbadiazone. Anal Chim Acta 88: 345.
2. Bryson W G, Goodball C M (1981) Improved Spectrophotometric Determination of Chromium in Animal Tissue Digests with Diphenylcarbazide. Anal Chim Acta 124: 391.
3. Paniagua A R, Vazque M D, Tascon M L, Batanero P S (1993) Determination of Chromium (VI) and Chromium (III) by Using a Diphenylcarbazide -Modified Carbon Paste Electrode. Electroanalysis 5: 155.
4. Kemula W, Najdekar E (1970) Polarographic and Chronovoltammetric Investigation of Reactions of Diphenylcarbazone with Chromium(III) and Diphenylcarbazide with Chromium(VI). Rocz Chem 44(12): 2289.
5. Malakhova N A, Chemysheva A V, Brainina K Z (1991) Adsorptive Stripping Voltammetry of Chromium 1,5-diphenylcarbazonate. Electroanalysis 3: 803.
6. Labuda J, Palaskon V (1990) Determination of Mercury Ions on a Diphenyl carbazone Bulk Modified Graphite Electrode. Anal Chim Acta 228: 259.
7. Navratilova Z (1991) Hg (II) Voltammetry on a 1, 5-diphenylcarbazide Containing Carbon Paste Electrode. Electroanalysis 3: 799.
8. Goldstein G, Manning D L, Menis O,.Dean J A (1961) Spectrophotometric Methods for the Determination of Osmium-I: Extraction and Ultraviolet Spectrophotometric Determination of Osmium Tetroxide. Talanta 7: 296.

9. Jaya S, Ramakrishna T (1982) Spectrophotometric determination of osmium with 1, 5-diphenylcarbazide. Talanta 29: 619.
10. Dean R, Pocock T (2004) Diphenylcarbazide Restores Electron Transport in Isolated, Illuminated Chloroplasts After Electron Transport from Water has been Eliminated by Mild Heat Treatment. Biochem Molecular Biol Educ 6(32): 381.
11. Herrmann M (1994) Chromium in Water. J Chem Educ 4(71): 323.
12. Kemula W, Najdekar E (1970) Polarographic and Chronovoltammetric Investigation of Diphenylcarbazide, Diphenylcarbazone and Diphenylcarbadiazone Rocz Chem 44(11): 2243.
13. Kemula W, Kublik Z, Najdeker E (1962) Polarographic and Voltammetric Investigation of Diphenylcarbazone and Diphenylcarbazide solutions. Rocz Chem 36: 937.
14. Paniagua A R, Vazquez M D, Tascon M L, Sanchez P (2005) Determination of Chromium(VI) and Chromium(III) by Using a Diphenylcarbazide-Modified Carbon Paste Electrode, Electroanalysis 5(2): 155.
15. Malakhova N A, Chernysheva A V, Brainina K Z (1991) Adsorptive Stripping Voltammetry of Chromium 1,5-Diphenylcarbazonate. Electroanalysis 3(8): 799.
16. Ramirez M , Perez A, Hernandez A (1996), Electrochemical Study of 1,5Diphenyl Carbazide and 1,5-Diphenylcarbazone in 0.3 M $HClO_4$. J Electroanal Chem 410: 203.