Protonation Reaction of Anion Radicals of some Dinitroaromatics in Hexamethylphosphortriamide (HMPA)

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Summary: Cyclic voltammeric method has been employed to investigate the protonation of anion radicals of 1,2-, 1,3-, and 1,4- dinitrobenzenes in Hexamethylphosphortriamide (HMPA) in the temperature range 5°C, 15°C, 25°C and 35°C. Glassy carbon electrode and hanging mercury drop electrode are used as working electrodes. Benzoic acid and salicylic acid are used as protonating agents. Homogeneous rate constant is calculated by using Nicholson and Shain equation. The position of nucleophilic attack in dinitrobenzenes has been investigated by calculation of charge densities using MNDO and SCF-UHF molecular orbital methods. The heterogeneous rate constant $k_{s,h}$ for the first reduction process in dinitrobenzenes is determined by digital simulation of the cyclic voltammograms.

Key Words: Anion Radicals, Cyclic Voltammetry, Dinitrobenzenes, Glassy Carbon Electrode (GCE), Hanging Mercury Drop Electrode (HMDE), HMPA (hexamethylphosphortriamide), Protonation reactions.

Introduction

Investigations of physical and chemical properties of intermediates are being carried out since long [1-2]. However the main hurdle experienced in such studies are their instabilities. There is always the problem of generation of enough amounts of the reactive intermediates for sufficiently long period to permit study of their properties. Some familiar reactive intermediates are neutral free radicals, anion or cation radicals, dianions, dications. One of the several methods of generation of the reactive intermediates is the electrochemical method and other methods are being chemical [3-4], radiolosis [5-9] and photolysis [10-11]etc.

Nitroaromatics are interesting substrates and a number of workers have carried out various studies on them [12,13] including electron transfer kinetics. Voltammetric studies have also been carried out on viologens and pyridinium compounds which are an important class of compounds [14,15]. The main reason for investigations of nitroaromatics is the stability of their reduction products. They are stable enough on voltammetric time scale for further manipulations.

The objective of this research is to investigate the solvent and temperature dependence of first reduction process, to study the protonation of the first reduction products of dinitrobenzene and to measure the heterogeneous electron transfer rate constants in HMPA solvent at different temperatures. The substrates are the three isomers of dinitrobenzenes and the protonating agents are benzoic acid and salicylic acid.

Results and Discussion

Electrochemical measurements (triangular wave cyclic voltammetry) were carried out at two different working electrodes i.e., glassy carbon electrode (GCE) and hanging mercury drop electrode (HMDE). A platinum wire was used as counter electrode while a silver wire (Ag) electrode was used as a reference electrode. All the measurements were carried out in aprotic solvent Hexamethylphosphortriamide (HMPA) at four different temperatures 5°C, 15°C, 25°C and 35°C. Tetra n-butylammonium per chlorate (TBAP) was used as supporting electrolyte. The reduction process for a reversible reaction can be represented as

$$O + n\bar{e} \rightleftharpoons R \qquad (1)$$

$$R + [HA] \xrightarrow{k_f} Z \qquad (2)$$

Thus the reduction of DNB's could be expressed as

$$DNB + \bar{e} \rightleftharpoons DNB^{\cdot-} \qquad (3)$$

The reaction of the anion radical of dinitrobenzene with the protonating agent (HA) may be written as

$$\mathrm{DNB^{-\cdot}} + [\mathrm{HA}] \xrightarrow{k_f} \mathrm{Z} \tag{4}$$

The homogeneous pseudo first order rate constant (k_f) for the above process is calculated using the equation of Nicholson and Shain [16]

$$E_p = E_{1/2} - \frac{RT}{nF}[(0.78 - \ln\sqrt{\frac{k_f}{a}})] \tag{5}$$

Where $a = \frac{RT}{nF}v$

$E_{1/2}$ is the reversible half wave potential (potential corresponding to 85% of the peak current in above process), E_P is the peak potential after the addition of protonating agent and v is the scan rate (mv/sec.). Since large excess of A is used for pseudo first order conditions, [A] represents large excess of A.

Cyclic voltammograms of substrates (dinitrobenzenes) were recorded in two steps:

1) in the absence of the reactant (protonating agent) and
2) After addition of the protonating agent under pseudo first order conditions.

On addition of large excess of the protonating agent the anodic peak disappeared and the cathodic peak shifted anodically. The rate constant k_f could be calculated from this shift $(E_p - E_{1/2})$. The second order rate constant (k_2) is calculated from the relation $k_2 = \frac{k_f}{[HA]}$, [HA] being the concentration of the protonating agent which is present in large excess as given in tables (1-2).

Table-1: (E_p-$E_{1/2}$) values and the bimolecular rate constant (k_2) for the protonation of anion radicals of isomers of dinitrobenzene in HMPA. (scan rate: 50 mV sec^{-1} and protonating agent: benzoic acid)

Compound	Concentration of Benzoic Acid	Temperature	Working electrode Glassy carbon electrode		Working electrode Hanging mercury drop electrode	
	(M)	(°C)	(E_p-$E_{1/2}$) (V)	k_2 (L.mol^{-1} sec^{-1})	(E_p-$E_{1/2}$) (V)	k_2 (L.mol^{-1} sec^{-1})
1,2-DNB	1.0×10^{-2}	5	(-0.028±0.005)	(1.05±0.41)×10^{2}	(-0.022±0.009)	(2.11±1.34)×10^{2}
		15	(-0.014±0.011)	(4.30±3.10)×10^{2}	(0.007±0.008)	(2.06±1.17)×10^{3}
		25	(-0.008±0.007)	(5.60±2.81)×10^{2}	(0.021±0.006)	(5.40±2.49)×10^{3}
		35	(0.044±0.006)	(2.69±1.14)×10^{4}	(0.081±0.006)	(4.57±1.94)×10^{5}
1,3-DNB	1.0×10^{-2}	5	(-0.021±0.006)	(1.95±0.90)×10^{2}	(-0.015±0.007)	(3.36±1.77)×10^{2}
		15	(-0.0214±0.013)	(5.00±3.90)×10^{2}	(0.030±0.010)	(1.23±7.63)×10^{3}
		25	(-0.007±0.005)	(5.82±2.15)×10^{2}	(0.010±0.010)	(2.68±1.75)×10^{3}
		35	(0.020±0.009)	(5.05±2.98)×10^{3}	(0.017±0.011)	(4.34±3.01)×10^{3}
1,4-DNB	1.0×10^{-2}	5	(-0.016±0.005)	(2.86±1.13)×10^{2}	(-0.016±0.005)	(2.86±1.13)×10^{2}
		15	(-0.050±0.008)	(3.50±1.99)×10^{2}	(-0.004±0.005)	(7.56±2.89)×10^{2}
		25	(-0.010±0.005)	(4.61±1.71)×10^{2}	(0.000±0.005)	(1.00±0.37)×10^{3}
		35	(0.015±0.005)	(3.00±1.07)×10^{3}	(0.007±0.007)	(1.75±0.84)×10^{3}

Table-2: (E_p-$E_{1/2}$) values and the bimolecular rate constant (k_2) for the protonation of anion radicals of isomers of dinitrobenzene in HMPA (scan rate: 50 mVsec^{-1} and protonating agent: salicylic acid)

Compound	Concentration of Salicylic Acid	Temperature	Working electrode Glassy carbon electrode		Working electrode Hanging mercury drop electrode	
	(M)	(°C)	(E_p-$E_{1/2}$) (V)	k_2 (L.mol^{-1} sec^{-1})	(E_p-$E_{1/2}$) (V)	k_2 (L.mol^{-1} sec^{-1})
1,2-DNB	1.0×10^{-2}	5	(-0.003±0.011)	(1.13±0.82)×10^{3}	(0.027±0.007)	(11.21±5.90)×10^{3}
		15	(0.013±0.009)	(3.59±2.23)×10^{3}	(0.029±0.011)	(1.45±1.03)×10^{4}
		25	(0.017±0.006)	(3.90±1.70)×10^{3}	(0.032±0.012)	(1.62±1019)×10^{4}
		35	(0.047±0.009)	(3.87±2.28)×10^{4}	(0.037±0.009)	(2.22±1.41)×10^{4}
1,3-DNB	1.0×10^{-2}	5	(0.021±0.005)	(6.28±2.48)×10^{3}	(0.014±0.007)	(3.78±1.99)×10^{3}
		15	(0.026±0.005)	(8.50±3.23)×10^{3}	(0.030±0.007)	(1.26±0.64)×10^{4}
		25	(0.053±0.011)	(7.99±5.55)×10^{4}	(0.059±0.008)	(11.02±6.09)×10^{4}
		35	(0.064±0.006)	(12.42±5.26)×10^{4}	(0.074±0.008)	(2.84±1.53)×10^{5}
1,4-DNB	1.0×10^{-2}	5	(-0.010±0.006)	(4.72±1.86)×10^{2}	(-0.010±0.007)	(5.10±2.68)×10^{2}
		15	(-0.001±0.007)	(8.92±2.53)×10^{2}	(-0.006±0.007)	(6.90±3.50)×10^{2}
		25	(0.001±0.008)	(1.03±0.57)×10^{3}	(0.012±0.005)	(2.56±0.95)×10^{3}
		35	(0.003±0.006)	(1.25±0.53)×10^{3}	(0.018±0.005)	(3.76±1.35)×10^{3}

Heterogeneous rate constant $k_{s,h}$ for the first reduction process was calculated from digital simulation method. In this method experimental parameters (reduction potential, k_f, and scan rate) are given from the voltammetric studies as input for simulation. The dimensionless standard rate constant (RKS in the simulation program) is a variable parameter and its value is also given as input for simulation. The program calculates current and potential and draws the cyclic voltammogram for the first reduction process for the given RKS. The value of dimensionless standard rate constant RKS is continuously changed until the simulated voltammogram exactly matches with the experimental voltammogram. The standard heterogeneous rate constant $k_{s,h}$ thus obtained are given in tables (3, 4).

Disproportionation constant (K_D) for the process is calculated from relationship between log K_D and $\Delta E_{1/2}$

$$\log K_D = \frac{\Delta E_{1/2}}{2.303RT/nF} \qquad (6)$$

where $\Delta E_{1/2} = \mathbf{(E_{1/2})_2 - (E_{1/2})_1}$

$(E_{1/2})_1$ and $(E_{1/2})_2$ are the half wave potential of the first and second reduction processes respectively.

Thermodynamic parameters $\Delta H^o, \Delta G^o, \Delta S^o$ are calculated from the following relations

$$\Delta G^o = -RT \ln K_D \qquad (7)$$

$$\ln \frac{(K_D)_1}{(K_D)_2} = \frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (8)$$

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \qquad (9)$$

where $(K_D)_1$ and $(K_D)_2$ are the disproportionation constants corresponding to temperatures T_1 and T_2 respectively. These results are collected in tables (5, 6).

Table-3: Heterogeneous rate constant (k^o) for the isomers of dinitrobenzenefor first reduction process in HMPA calculated from digital simulation method. (protonating agent : benzoic acid)

Compound	**Temperature**	**Working electrode Glassy carbon electrode**				**Working electrode Hanging mercury drop electrode**			
	(^{o}C)	**E_0^a (mv)**	**k_f^b (s^{-1})**	**RKS^c**	**HKO^d (cms^{-1})**	**E_0^a (mv)**	**k_f^b (s^{-1})**	**RKS^c**	**HKO^d (cms^{-1})**
1,2-DNB	5	-0.640	1.05	35.00	0.3690	-0.635	2.11	38.00	0.4006
	15	-0.650	4.30	24.00	0.2529	-0.640	20.61	1.00	0.0105
	25	-0.660	5.60	24.00	0.2530	-0.645	54.00	-	-
	35	-0.665	269.0	-	-	-0.645	457.0	-	-
1,3-DNB	5	-0.800	1.95	35.00	0.3689	-0.790	3.36	65.00	0.6852
	15	-0.820	5.00	35.00	0.3700	-0.820	12.30	2.00	0.0211
	25	-0.820	5.82	35.00	0.3700	-0.820	26.80	-	-
	35	-0.820	50.50	-	-	-0.820	43.40	-	-
1,4-DNB	5	-0.565	2.86	28.00	0.2951	-0.550	2.86	28.00	0.2951
	15	-0.600	3.50	15.00	0.1581	-0.610	7.56	11.00	0.1159
	25	-0.600	4.61	22.00	0.2319	-0.610	10.00	3.00	0.0316
	35	-0.615	30.00	-	-	-0.610	17.50	1.00	0.0105

Table-4: Heterogeneous rate constant (k^o) for the isomers of dinitrobenzenefor first reduction process in HMPA calculated from digital simulation method. (protonating agent : salisylic acid)

Compound	**Temperature**	**Working electrode Glassy carbon electrode**				**Working electrode Hanging mercury drop electrode**			
	(^{o}C)	**E_0^a (mv)**	**k_f^b (s^{-1})**	**RKS^c**	**HKO^d (cms^{-1})**	**E_0^a (mv)**	**k_f^b (s^{-1})**	**RKS^c**	**HKO^d (cms^{-1})**
1,2-DNB	5	-0.680	5.92	29.00	0.3057	-0.665	7.00	12.00	0.1265
	15	-0.700	54.20	-	-	-0.670	78.60	-	-
	25	-0.680	64.50	-	-	-0.670	95.30	-	-
	35	-0.695	307.0	-	-	-0.675	111.0	-	-
1,3-DNB	5	-0.815	53.20	-	-	-0.800	79.10	-	-
	15	-0.820	72.40	-	-	-0.800	104.0	-	-
	25	-0.830	851.0	-	-	-0.800	265.0	-	-
	35	-0.840	1335.0	-	-	-0.815	432.0	-	-
1,4-DNB	5	-0.570	2.32	40.00	0.4216	-0.560	5.78	35.00	0.3689
	15	-0.580	6.44	14.00	0.1476	-0.560	9.96	3.00	0.0316
	25	-0.580	16.50	1.00	0.0105	-0.565	17.10	1.00	0.0105
	35	-0.585	20.30	1.00	0.0105	-0.585	38.60	-	-

a. Reduction potential of dinitrobenzenes b. Pseudo first order rate constant. c. Continuously changing rate constant

d. Standard heterogeneous rate constant

Table-5: Thermodynamic parameters (ΔH°, ΔG°, ΔS°) calculated from disproportionation constants in HMPA (Protonating agent = Benzoic acid)

Compound	**Temperature**	**Working Electrode Glassy carbon electrode**				**Working Electrode Hanging mercury drop electrode**			
	/K	**-ln K_D**	**ΔG^{o} /kJmol^{-1}**	**ΔH^{o} /Jmol^{-1}**	**$-\Delta S^{o}$ /JK^{-1} mol^{-1}**	**-ln K_D**	**ΔG^{o} /kJmol^{-1}**	**ΔH^{o} /Jmol^{-1}**	**$-\Delta S^{o}$ /JK^{-1} mol^{-1}**
1,2-DNB	278	5.80	13.41		47.59	5.63	12.78		44.35
	288	5.62	13.45	177.1	46.69	5.09	11.78	669.0	42.35
	298	5.44	13.49		45.27	4.81	11.31		39.97
	308	5.28	13.53		43.93	4.55	10.89		37.82
1,3-DNB	278	7.50	17.34		61.86	5.09	11.56		42.10
	288	7.89	18.89	147.4	65.61	4.77	11.02	68.77	39.63
	298	7.20	17.85		59.89	5.20	12.23		43.23
	308	7.26	18.56		60.26	5.07	12.15		42.18
1,4-DNB	278	7.21	16.67		59.02	2.92	6.62		24.23
	288	6.86	16.42	267.6	57.02	3.26	7.54	5.03	27.13
	298	6.58	16.30		54.69	3.09	7.29		25.76
	308	6.45	16.51		53.59	2.97	7.12		24.73

Table-6: Thermodynamic parameters (ΔH°, ΔG°, ΔS°) calculated from disproportionation constants in HMPA (Protonating agent = Salicylic acid)

Compound	**Temperature**	**Working Electrode Glassy carbon electrode**				**Working Electrode Hanging mercury drop electrode**			
	/K	**-ln K_D**	**ΔG^{o} /kJmol^{-1}**	**ΔH^{o} /Jmol^{-1}**	**$-\Delta S^{o}$ /JK^{-1} mol^{-1}**	**-ln K_D**	**ΔG^{o} /kJmol^{-1}**	**ΔH^{o} /Jmol^{-1}**	**$-\Delta S^{o}$ /JK^{-1} mol^{-1}**
1,2-DNB	278	5.60	12.94		46.45	6.76	15.63		55.79
	288	5.37	12.86	32.59	44.66	6.65	15.92	117.9	55.28
	298	5.61	13.91		46.67	6.61	16.38		54.97
	308	5.41	13.87		45.02	6.20	15.88		51.55
1,3-DNB	278	8.08	18.68		66.45	8.28	19.14		67.82
	288	7.79	18.64	211.2	64.73	8.01	19.19	291.6	66.62
	298	7.66	18.98		63.68	7.61	18.85		63.26
	308	7.44	19.06		61.89	7.48	19.14		62.16
1,4-DNB	278	6.67	15.42		54.85	7.12	16.46		58.33
	288	6.56	15.71	167.4	54.55	6.75	16.17	249.9	56.15
	298	6.48	16.04		53.84	6.61	16.38		54.97
	308	6.15	15.75		51.14	6.36	16.30		52.91

Activation energy, E_a, of protonating step is obtained by plotting $\ln k_2$ vs $\frac{1}{T}$ in accordance with Arrhenius equation for the reaction rate. Other activation parameters such as free energy of activation (ΔG^{*}), enthalpy of activation (ΔH^{*}), and entropy of activation (ΔS^{*}) are calculated from the following relations

$$k_2 = \frac{kT}{h} e^{-\Delta G^{*}/RT} \qquad (10)$$

where k is Boltzmann constant, R is gas constant, h is Planck's constant

$$\Delta H^{*} = E_a - nRT \qquad (11)$$

$$\Delta G^{*} = \Delta H^{*} - T\Delta S^{*} \qquad (12)$$

Activation parameters are given in tables (7-8).

In aprotic solvent HMPA cyclic voltammograms of dinitrobenzenes show typically two reversible waves [Fig. 1-2]. The first and the second waves correspond to the formation of radical anion and dianion respectively. The three dinitrobenzenes i.e., 1,2-DNB, 1,3-DNB and 1,4-DNB exhibit completely reversible first reduction wave in HMPA at glassy carbon electrode. The $\Delta E_P = E_{Pc} - E_{Pa}$ values range between 65mv to 75mv and E_p -$E_{p/2}$ values are nearly 65mv. The second reduction process is quasi reversible at customary scan rates (50–100mv/sec) i.e., E_p -$E_{p/2}$ values are greater than 100mv and $\Delta E_P = E_{Pc} - E_{Pa}$ values range between 100mv to 200mv at GCE. The higher vales of ΔE_p ,s in the case of second reduction process at GCE may be due to the instability of the dianion at GCE which may be due to the catalytic decomposition of slow electron transfer or this may be due to the large surface area of working electrode. All the three dinitrobenzenes show reversible peaks corresponding to the first and second reduction processes and $\Delta E_P = E_{Pc} - E_{Pa}$

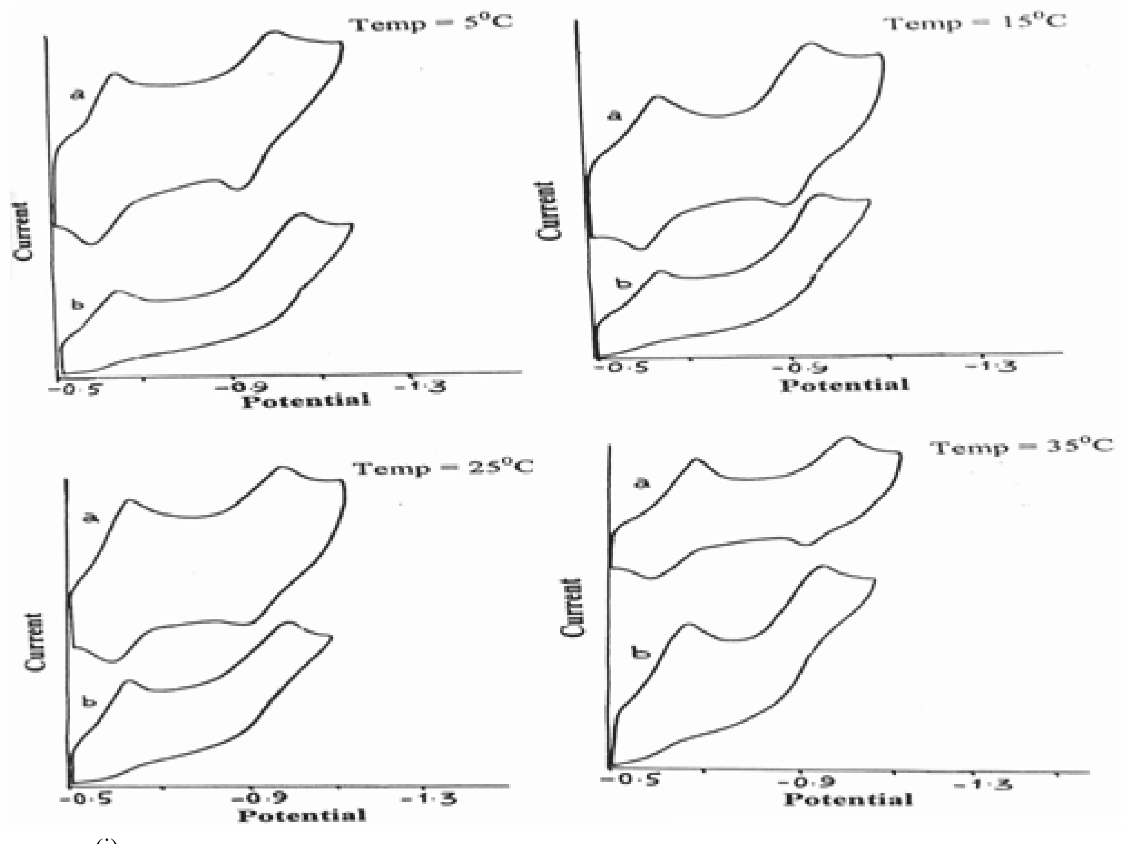
values for first reduction process are exactly 60mv at hanging mercury drop electrode.

In the present study the anion radical is generated by reducing dinitrobenzenes (1,2-, 1,3-, 1,4-) on the surface of the working electrodes i.e., GCE and HMDE respectively.

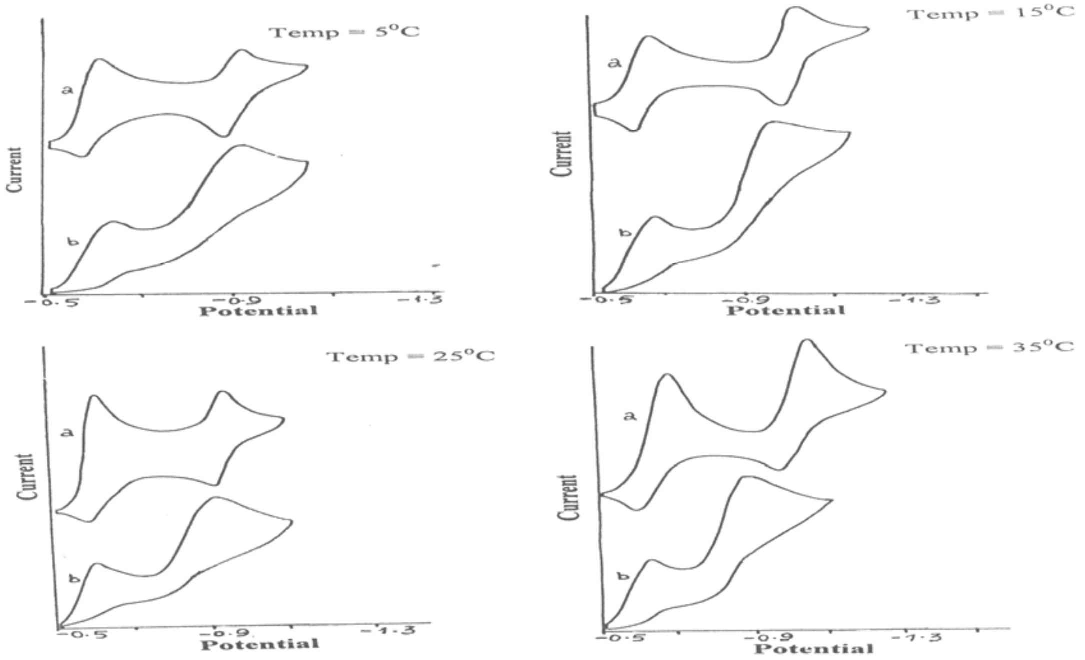
$$\mathrm{DNB} + \bar{e} \rightleftharpoons \mathrm{DNB}^{-\cdot} \qquad (13)$$

When the protonating agent is added, the cathodic peak shifted anodically and the anodic peak completely disappeared. The pseudo first order rate constant is calculated from the voltammograms recorded after the addition of protonating agent.

In this case it is observed that on addition of protonating agent the first peak increased in height at the expense of the second peak. It is thought initially that the increase in the peak height is due to the presence of water as impurity in the solvent. But addition of more water produced no effect on the observed peak height. The possibility of catalytic and kinetic reactions is also ruled out as no cathodic shift in the peak position was observed and its broadening with increase in $\frac{k_f}{a}$ ratio occurred when protonating agent was added. From the shift in the peak potential (E_p-$E_{1/2}$) the pseudo first order rate constant k_f is obtained from Nicholson and Shain equation. The electron transfer reaction between these anion radicals and the protonating agent could be ruled out on the basis of the shape of the cyclic voltammogram. The homogeneous reaction of dinitrobenzenes and a protonating agent involves electron transfer reaction. The second order rate constant (k_2) is obtained by dividing the k_f by the concentration of the protonating agent (benzoic acid / salicylic acid).



(i)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a
b
Current
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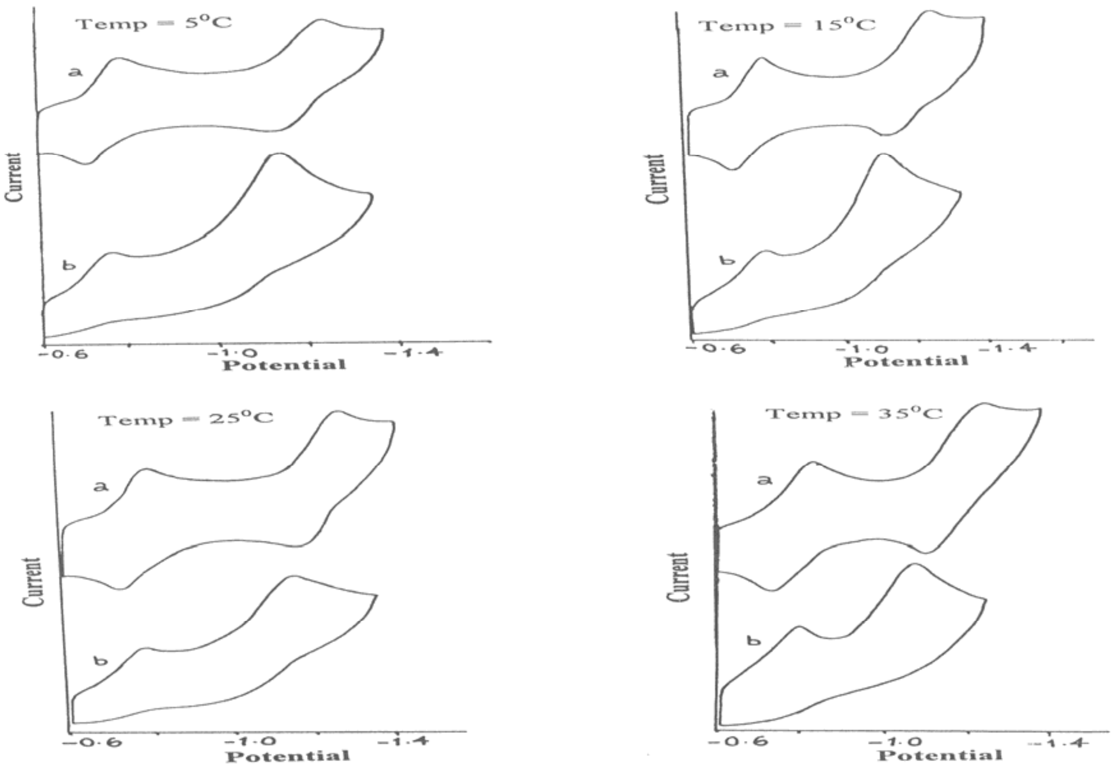
-0.9
-1.3
Potential
Temp = 15°C
a
b
Current
-0.5
-0.9
-1.3
Potential
Temp = 25°C
a
b
Current
-0.5
-0.9
-1.3
Potential
Temp = 35°C
a
b
Current
-0.5
-0.9
-1.3
Potential

(ii)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b
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-1.0
-1.4
Potential
Temp = 15°C
a
b
Current
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-1.0
-1.4
Potential
Temp = 25°C
a
b
Current
-0.6
-1.0
-1.4
Potential
Temp = 35°C
a
b
Current
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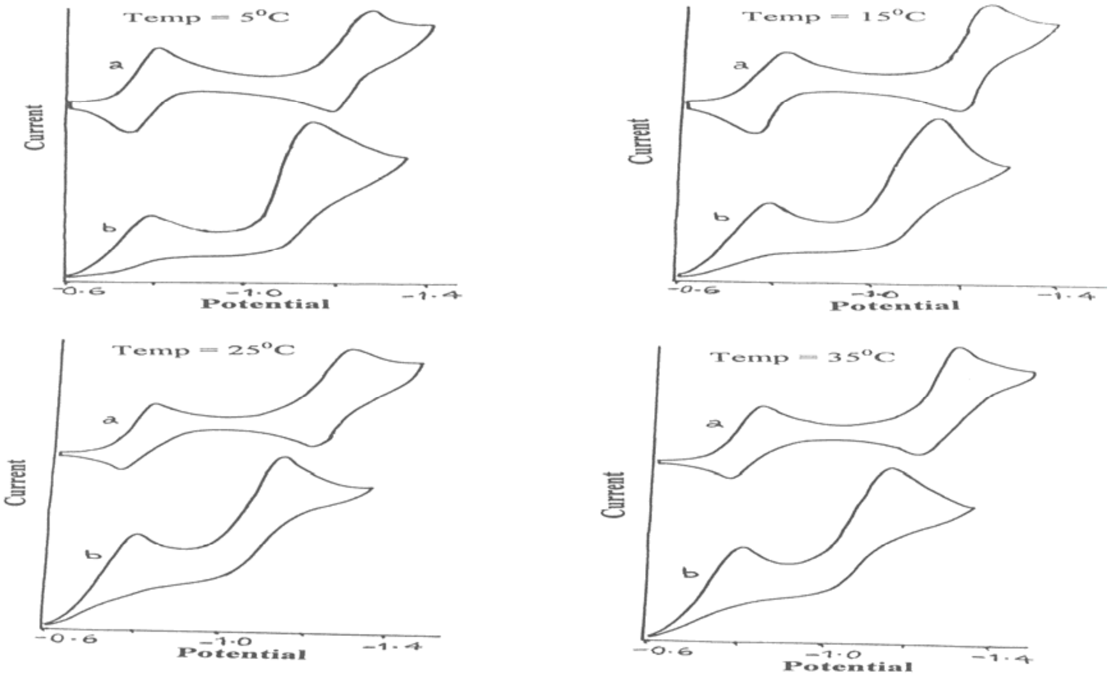
-1.4
Potential

(iii)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Temp = 15°C
Temp = 25°C
Temp = 35°C
a
b
Current
Potential
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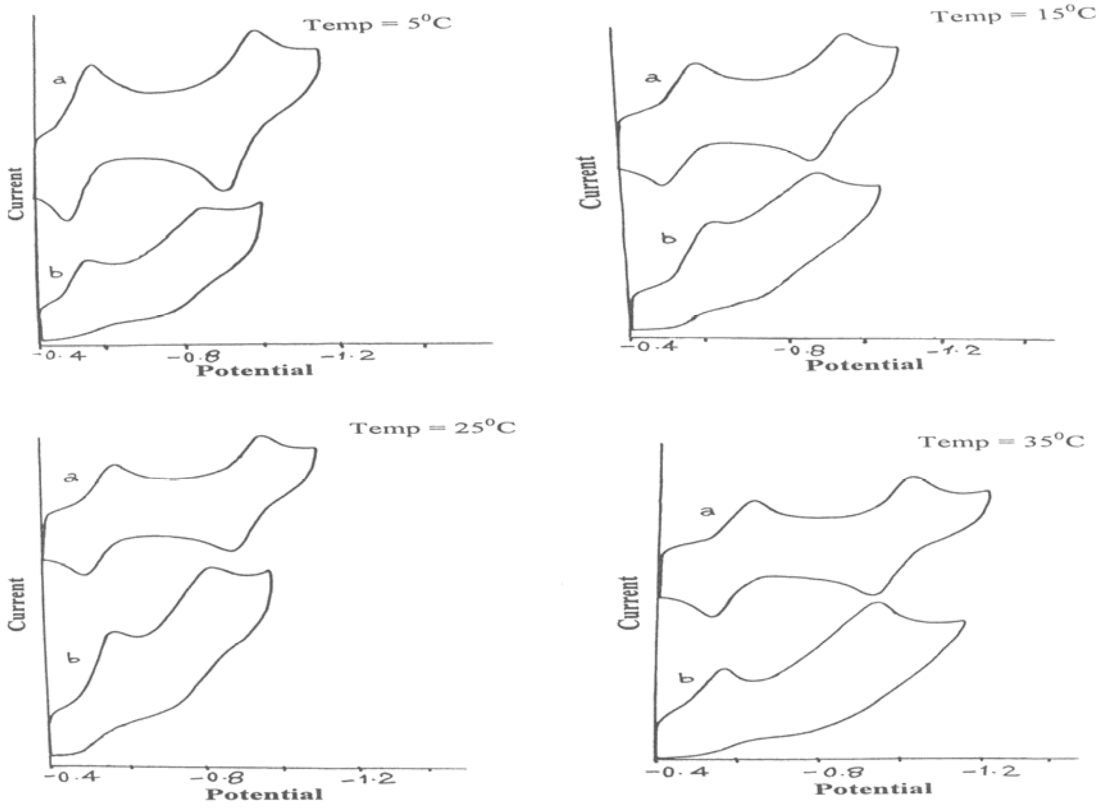
-1.0
-1.4

(iv)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a
b
Current
Potential
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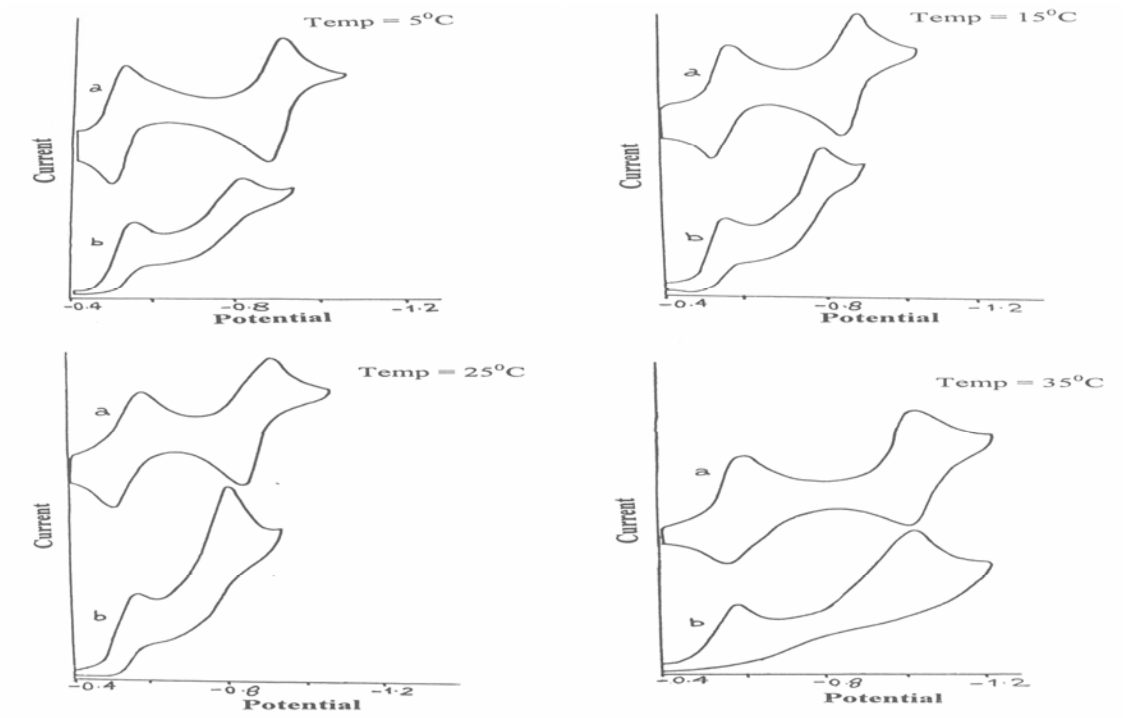
-0.8
-1.2

(v)



(vi)

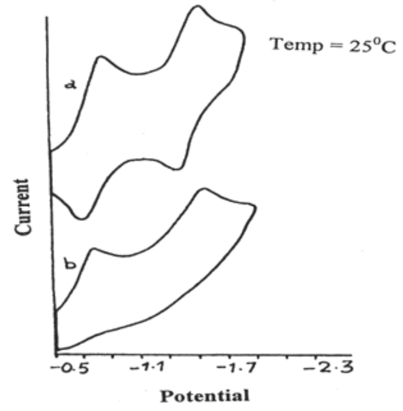
Fig.1: (i) a-Reversible voltammogram of 1,2-DNB in HMPA at GCE
b-voltammogram after the addition of protonating agent Benzoic acid.
(ii) a-Reversible voltammogram of 1,2-DNB in HMPA at HMDE
b-voltammogram after the addition of protonating agent Benzoic acid.
(iii) a-Reversible voltammogram of 1,3-DNB in HMPA at GCE
b-voltammogram after the addition of protonating agent Benzoic acid.
(iv) a-Reversible voltammogram of 1,3-DNB in HMPA at HMDE
b-voltammogram after the addition of protonating agent Benzoic acid.
(v) a-Reversible voltammogram of 1,4-DNB in HMPA at GCE
b-voltammogram after the addition of protonating agent Benzoic acid.
(vi) a-Reversible voltammogram of 1,4-DNB in HMPA at HMDE
b-voltammogram after the addition of protonating agent Benzoic acid.

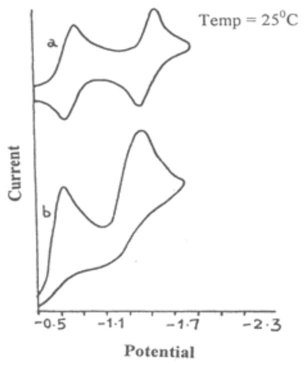
Table-7: Activation parameters (ΔG^*, ΔH^*, ΔS^*) calculated from disproportionation constants in HMPA (Protonating agent = Benzoic acid)

Compound	**Temperature**	**Working Electrode Glassy carbon electrode**				**Working Electrode Hanging mercury drop electrode**			
	/K	**E_a /kJmol^{-1}**	**ΔG^* /kJmol^{-1}**	**ΔH^* /kJmol^{-1}**	**$-\Delta S^*$ /JK^{-1} mol^{-1}**	**E_a /kJmol^{-1}**	**ΔG^* /kJmol^{-1}**	**ΔH^* /kJmol^{-1}**	**$-\Delta S^*$ /JK^{-1} mol^{-1}**
1,2-DNB	278		57.16	116.7	214.3		55.55	167.4	402.5
	288	119.1	55.92	116.7	210.9	169.7	52.36	167.3	399.3
	298		57.30	116.6	198.9		51.69	167.3	387.9
	308		49.39	116.5	217.9		42.14	167.2	406.0
1,3-DNB	278		55.73	67.64	42.83		54.48	58.23	13.50
	288	69.95	55.57	67.56	41.63	60.54	53.41	58.15	41.63
	298		57.21	67.47	34.45		53.42	58.06	34.45
	308		53.68	67.39	44.52		54.07	57.98	44.52
1,4-DNB	278		54.85	49.01	-21.02		54.85	38.54	-58.66
	288	51.32	56.42	48.92	-26.04	40.85	54.58	38.46	-55.97
	298		57.78	48.84	-30.02		55.87	38.38	-58.69
	308		55.01	48.76	-21.31		56.39	38.29	-58.76

Table-8: Activation parameters (ΔG^*, ΔH^*, ΔS^*) calculated from disproportionation constants in HMPA (Protonating agent = Salicylic acid)

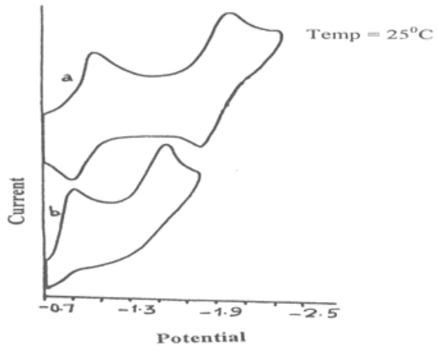
Compound	Temperature	Working Electrode Glassy carbon electrode				Working Electrode Hanging mercury drop electrode			
	/K	E_a /kJmol^{-1}	ΔG^* /kJmol^{-1}	ΔH^* /kJmol^{-1}	$-\Delta S^*$ /JK^{-1} mol^{-1}	E_a /kJmol^{-1}	ΔG^* /kJmol^{-1}	ΔH^* /kJmol^{-1}	$-\Delta S^*$ /JK^{-1} mol^{-1}
1,2-DNB	278		53.17	83.53	109.2		52.78	59.15	22.92
	288		49.86	83.45	116.6		48.97	59.07	35.06
	298	85.84	51.25	83.36	107.8	61.46	50.28	58.99	29.21
	308		49.06	83.28	111.1		51.66	58.90	23.51
1,3-DNB	278		48.09	83.91	128.8		47.18	40.46	-24.14
	288		49.17	83.82	120.3		48.30	40.38	-27.50
	298	86.22	44.86	83.74	130.5	42.78	47.75	40.30	-24.99
	308		45.29	83.66	124.6		48.18	40.22	-25.86
1,4-DNB	278		55.33	51.07	-15.35		53.22	41.93	-40.62
	288		54.96	50.98	-13.82		53.92	41.85	-41.92
	298	53.38	54.62	50.90	-12.50	44.24	54.54	41.76	-42.86
	308		56.01	50.82	-16.87		54.37	41.68	-41.19

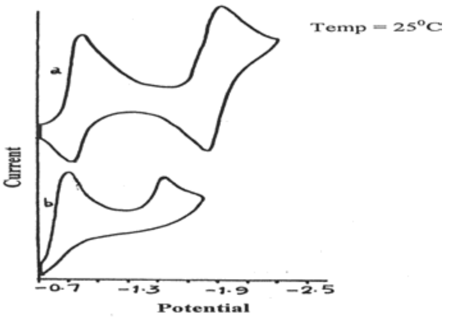




(i)

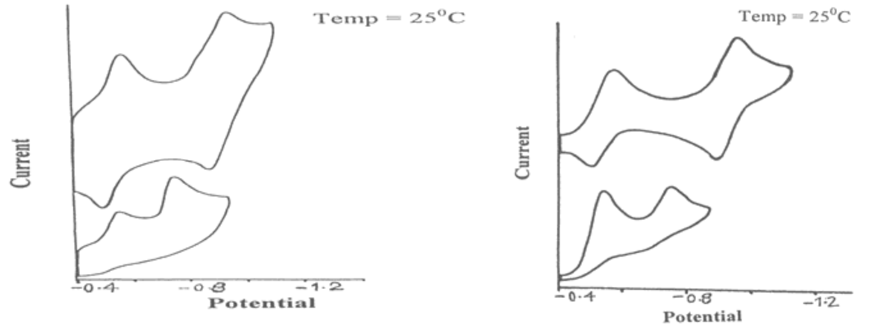
(ii)





(iii)

(iv)



(v) (vi)

Fig. 2: (i) a-Reversible voltammogram of 1,2-DNB in HMPA at GCE
b-voltammogram after the addition of protonating agent Salicylic acid.
(ii). a-Reversible voltammogram of 1,2-DNB in HMPA at HMDE
b-voltammogram after the addition of protonating agent Salicylic acid.
(iii) a-Reversible voltammogram of 1,3-DNB in HMPA at GCE
b-voltammogram after the addition of protonating agent Salicylic acid.
(iv) a-Reversible voltammogram of 1,3-DNB in HMPA at HMDE
b-voltammogram after the addition of protonating agent Salicylic acid.
(v) a-Reversible voltammogram of 1,4-DNB in HMPA at GCE
b-voltammogram after the addition of protonating agent Salicylic acid.
(vi) a-Reversible voltammogram of 1,4-DNB in HMPA at HMDE
b-voltammogram after the addition of protonating agent Salicylic acid.

At 5°C, in solvent HMPA with GCE, the observed second order rate constant k_2 for 1,2–DNB (1.05×10^2 Lmol^{-1}s^{-1}) and 1,3-DNB (1.95×10^2 Lmol^{-1}s^{-1}) are comparable but that of 1,4-DNB (2.86×10^2 Lmol^{-1}s^{-1}) is higher. At HMDE the rate constant for 1,3-DNB is found relatively higher (3.36×10^2 Lmol^{-1}s^{-1}) while for 1,2-DNB (2.11×10^2 Lmol^{-1}s^{-1}) and 1,4–DNB (2.86×10^2Lmol^{-1}s^{-1}) the values are comparable. An increase in temperature to 15°C increased the rate constant substantially for 1,2-DNB and 1,3-DNB both at HMDE and GCE while for 1,4-DNB the increment is comparatively less. When the temperature was raised further to 25°C, the rate constants increased and the values for 1,2-DNB (5.60×10^2 Lmol^{-1}s^{-1}) and 1,3-DNB (5.82×10^2 Lmol^{-1}s^{-1}) became comparable at GCE. The rate constant for 1,4-DNB (4.61×10^2 Lmol^{-1}s^{-1}) also increased and approached the observed values for 1,2-DNB and 1,3-DNB. For HMDE the trend of increasing rate constants with temperature persists for all the three isomers of dinitrobenzene. However, the values are higher than those observed at the GCE. At 35°C the second order rate constant for 1,2-DNB ($2.69 \mathrm{x} 10^4$Lmol^{-1}s^{-1}) increased greatly at GCE in comparison to 1,3-DNB (5.05×10^3Lmol^{-1}s^{-1}) and 1,4-DNB (3.00×10^3Lmol^{-1}s^{-1}). Similar trend is observed at the HMDE though the values for the rate constants are higher.

When the protonating agent is salicylic acid, the k_2 value for 1,3-DNB for the GCE as well as the HMDE is higher than that observed for 1,2-DNB and 1,4-DNB in solvent HMPA. However, it should be noted that the rate constant for 1,2-DNB anion radical is comparable to 1,3-DNB at 5°C and 25°C in solvent HMPA and it may be due to the closely placed nitro groups which hinder the attack of bulky protonating agent (benzoic acid). For 1,4-DNB the nitro groups are farthest apart and hence the rate constant is higher. At 35°C the rate constant for 1,2-DNB anion radical in solvent HMPA is much higher than 1,3-DNB and 1,4-DNB. This behavior may be explained by considering that the two nitro groups are present in close proximity. Due to higher temperature these groups would undergo some rotational motion. Hence the repulsion of nitro groups would make 1,2-DNB even less stable. Consequently the second order homogeneous rate constant has become higher in value.

The trend observed in the values of the rate constants in resonance contributing digital simulation method has played an important role in the analysis of the electrochemical data [17-20]. In the present study heterogeneous electron transfer rate constant $k_{s,h}$ is calculated by simulation method. The results of these $k_{s,h}$ are collected in tables (3, 4) and simulated voltammograms are shown in [Fig. 3,4]. The

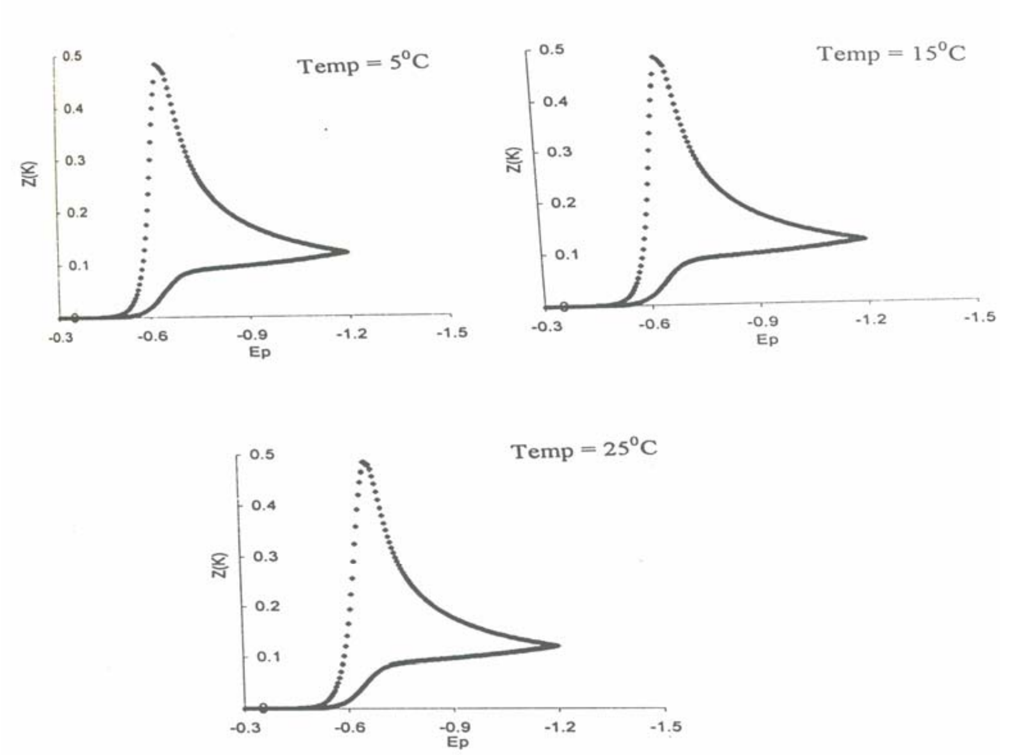
Disproportionation for the dinitroaromatic system may be depicted as follows:

$$2\text{DNB}^{-} \rightleftharpoons \text{DNB} + \text{DNB}^{2-} \qquad (14)$$

Disproportionation constant (K_D) values for dinitroaromatics are given in Tables (5, 6). In solvent HMPA the disproportionation constant for 1,2-DNB$^{-\cdot}$ at both GCE and HMDE is greater than 1,3-DNB$^{-\cdot}$ and 1,4-DNB$^{-\cdot}$ for all the temperature range 5°C to 35°C.

In order to seek information regarding the stability of the electrochemical system and its kinetic behavior, thermodynamic and activation parameters are calculated. For the case of homogeneous reaction of 1,2-DNB anion radical, E_a, ΔH^* and ΔS^* values are higher than for 1,3-DNB$^{-\cdot}$ and 1,4-DNB$^{-\cdot}$ irrespective of the electrode system in solvent HMPA when benzoic acid is used as protonating agent. The observed decrease in ΔH^* values for the 1,4-DNB is expected as the two nitro groups are far apart.

When salicylic acid is used as protonating agent in HMPA the entropy and enthalpy of activation for the homogeneous chemical reaction of 1,2-DNB$^{-\cdot}$ is higher than 1,3-DNB$^{-\cdot}$ and 1,4-DNB$^{-\cdot}$, while at GCE the entropy and enthalpy values for 1,3-DNB$^{-\cdot}$ are found higher than 1,2-DNB$^{-\cdot}$ and 1,4-DNB. The higher values of 1,2-DNB$^{-\cdot}$ show that in the 1,2-DNB$^{-\cdot}$ two nitro groups are present close to each other and hence it is difficult for them to be in one plane. There is more disorderliness in the activated complex of 1,2-DNB$^{-\cdot}$ than that of 1,3-DNB$^{-\cdot}$ and 1,4-DNB$^{-\cdot}$.



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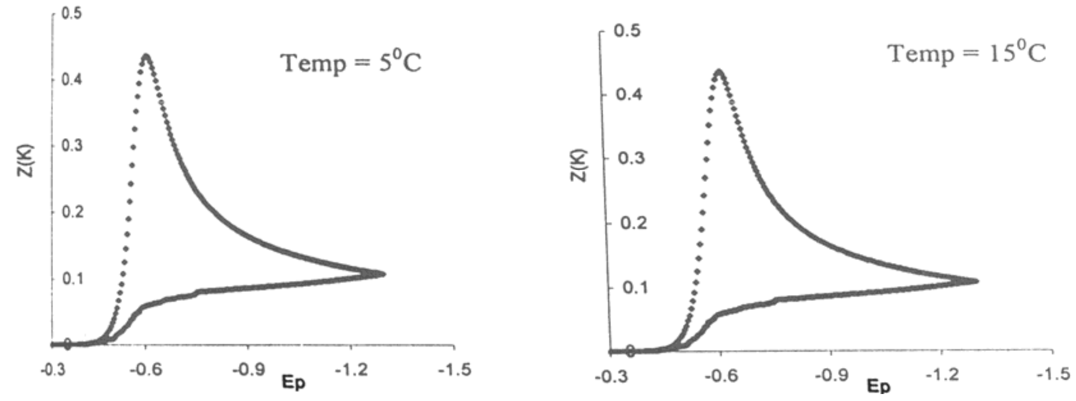
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-1.5
Ep
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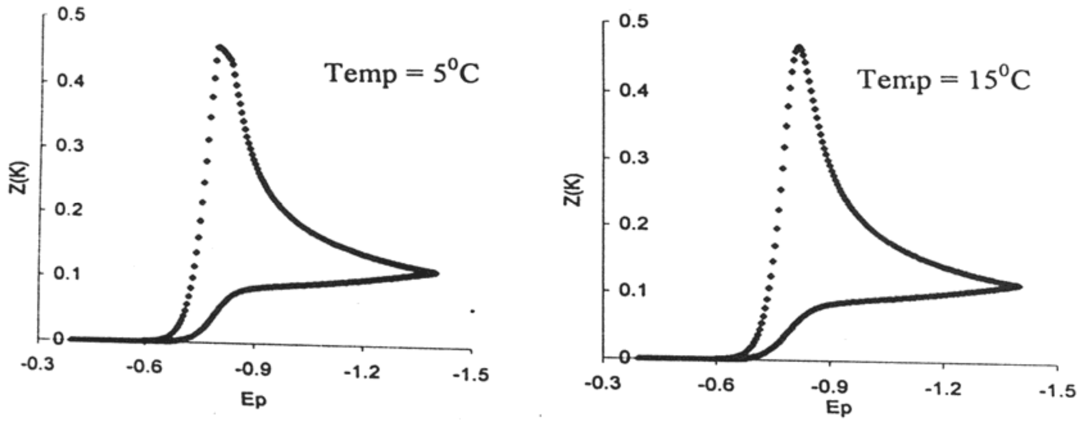
Z(K)
Ep

(ii)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-1.5
Ep
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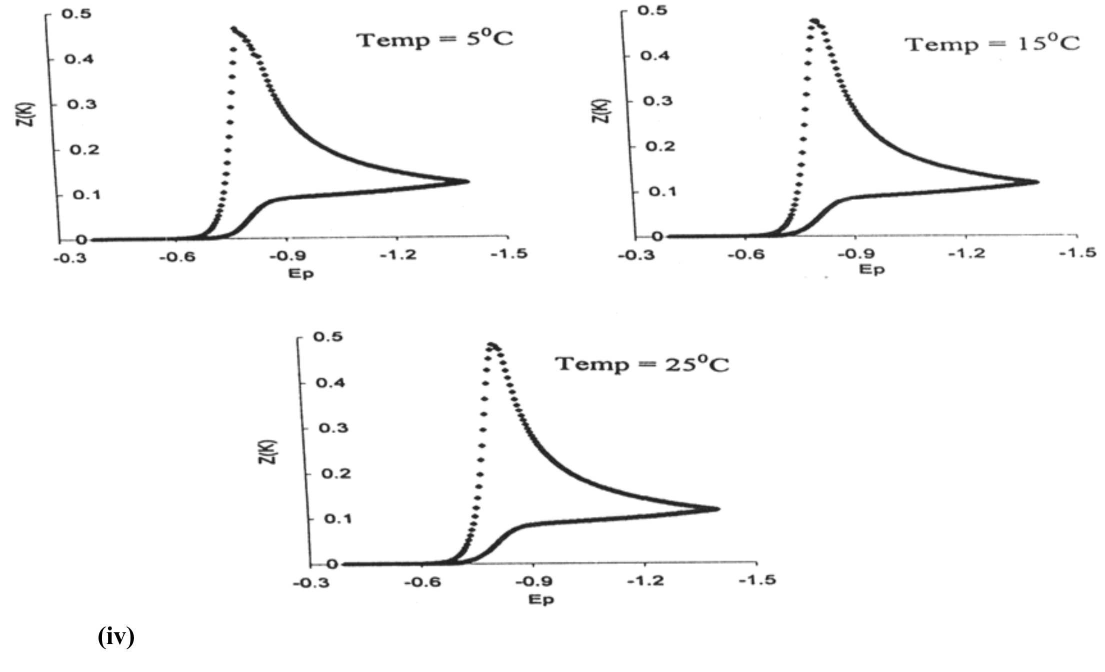
Z(K)
Ep

(iii)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0
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-1.5
Ep
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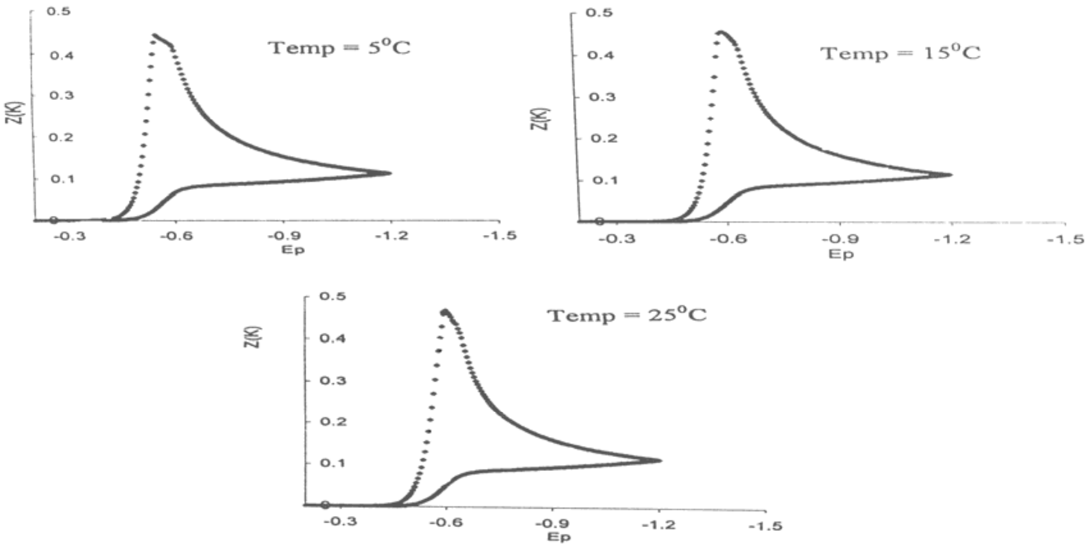
Z(K)
Ep
Temp = 25⁰C
Z(K)
Ep

(iv)



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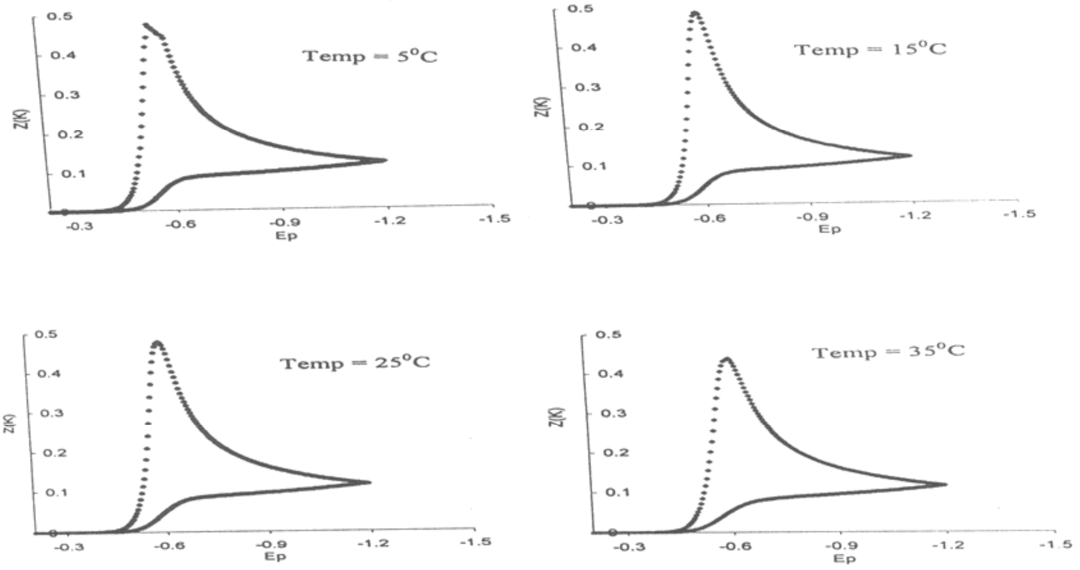
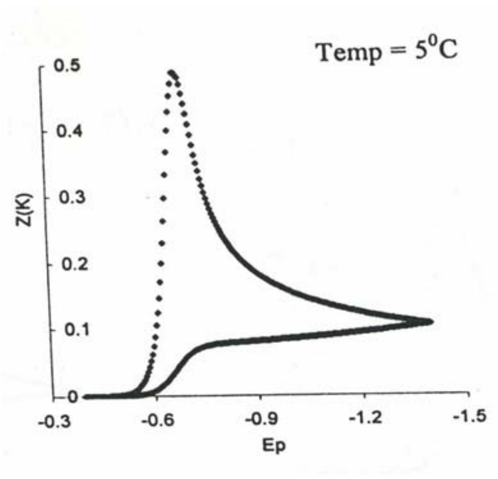


(vi)

Fig.3: (i) Simulated cyclic voltammogram of 1,2-DNB in solvent HMPA at HMDE (protonating agent: Benzoic acid).
(ii) Simulated cyclic voltammogram of 1,2-DNB in solvent HMPA at GCE (protonating agent: Benzoic acid).
(iii) Simulated cyclic voltammogram of 1,3-DNB in solvent HMPA at HMDE (protonating agent: Benzoic acid).
(iv) Simulated cyclic voltammogram of 1,3-DNB in solvent HMPA at GCE (protonating agent: Benzoic acid).
(v) Simulated cyclic voltammogram of 1,4-DNB in solvent HMPA at HMDE (protonating agent: Benzoic acid).
(vi) Simulated cyclic voltammogram of 1,4-DNB in solvent HMPA at GCE (protonating agent: Benzoic acid).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-0.6
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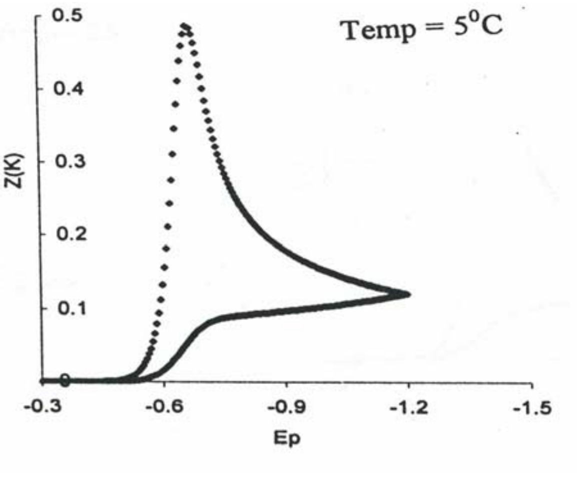
-1.2
-1.5
Ep

(i)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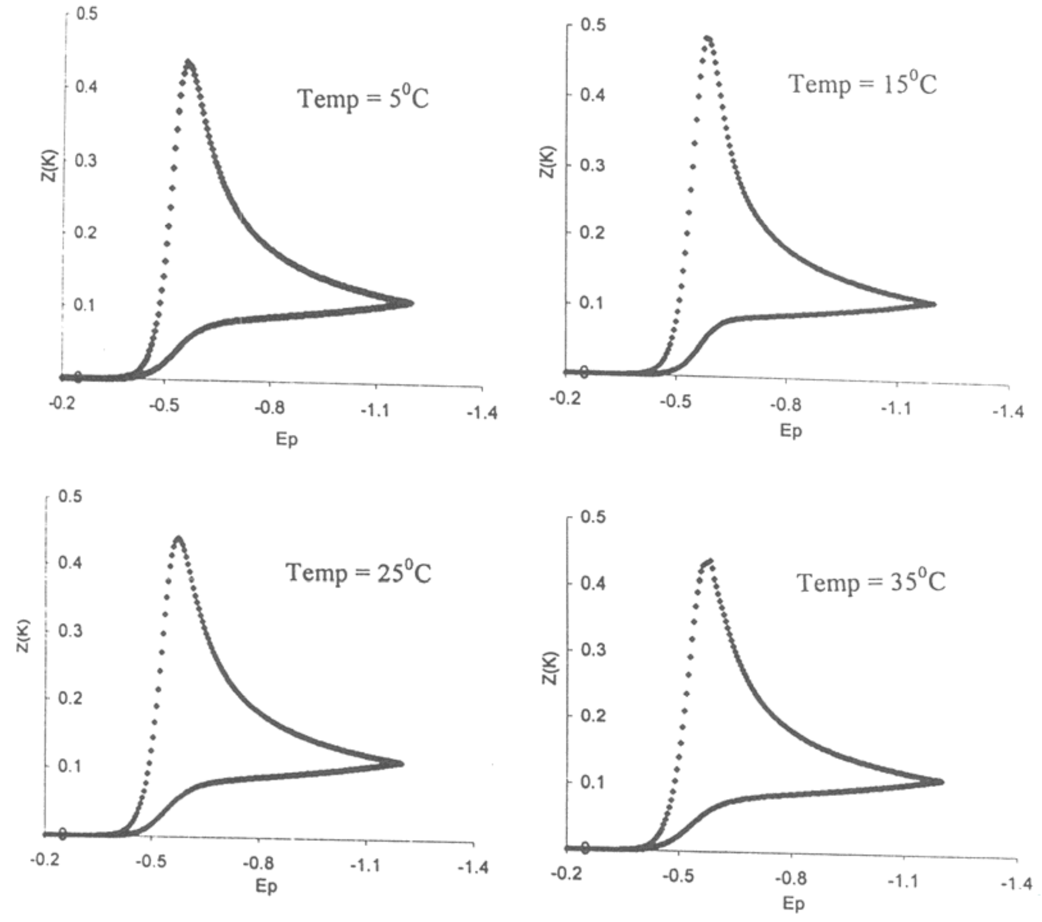
-1.5
Ep

(ii)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Temp = 25⁰C
Temp = 35⁰C
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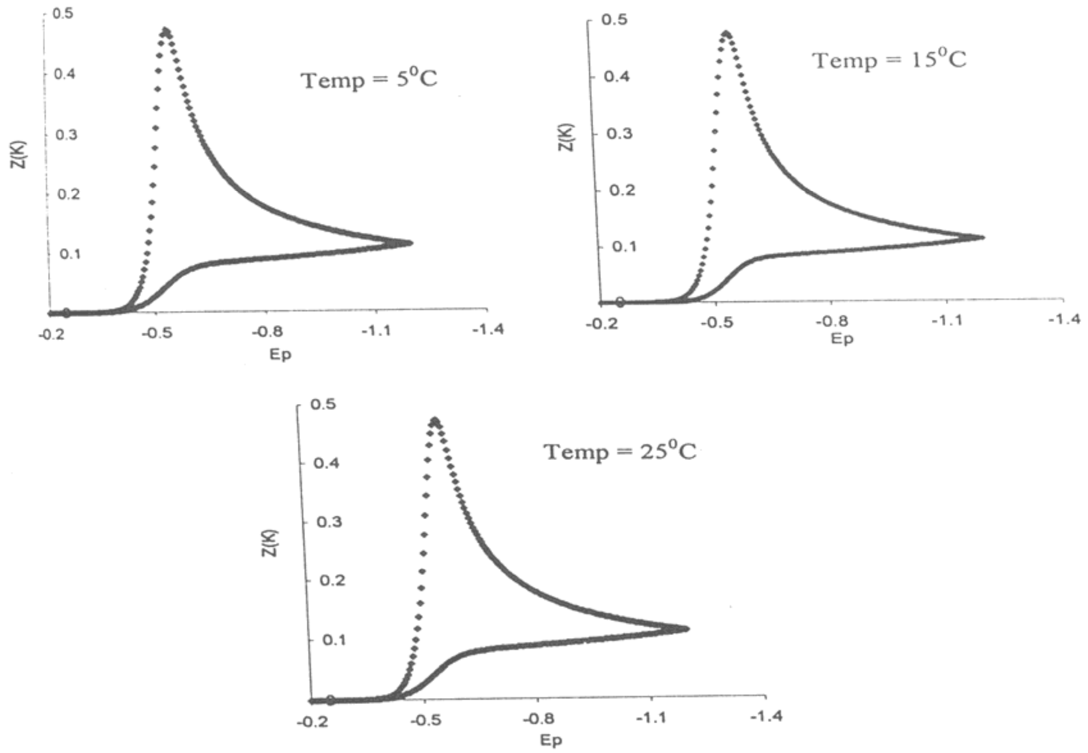
-0.5
-0.8
-1.1
-1.4
Ep

(iii)



(iv)

Fig. 4: (i) Simulated cyclic voltammogram of 1,2-DNB in solvent HMPA at GCE (protonatin`g agent: Salicylic acid).
(i) Simulated cyclic voltammogram of 1,2-DNB in solvent HMPA at HMDE (protonating agent: Salicylic acid).
iii) Simulated cyclic voltammogram of 1,4-DNB in solvent HMPA at GCE (protonating agent: Salicylic acid).
(iv) Simulated cyclic voltammogram of 1,4-DNB in solvent HMPA at HMDE (protonating agent: Salicylic acid).

Experimental

Chemicals and Reagents

Dinitroaromatics compounds such as 1, 2-dinitrobenzene (1, 2-DNB) of BDH chemicals was purified by crystallizing it from ethanol (m.p found 116°C: reported 116.5°C) and 1, 3- dinitrobenzene (1, 3-DNB) of HOPKIN & WILLIAMS Ltd. was purified by crystallizing it from ethanol (m.p found 90.5°C: reported 90.5°C). 1, 4- dinitrobenzene (1, 4-DNB) of MERCK chemicals was purified by drying it under vacuum over P_2O_5 (m.p found 172.5°C: reported 173°C). Tetra n-butyl ammonium perchlorate (TBAP) which was used as supporting electrolyte throughout prepared from tetra n-butyl ammonium bromide from BDH chemicals and magnesium perchlorate from MERCK chemicals. The prepared salt was washed with deionized water and dried under vacuum in a desiccator for about five hours and then used. The blank CV run was used to determine impurity if any (m.p found 212°C: reported 212°C). Protonating agents Benzoic acid (CHEMAPOL chemicals) and salicylic acid (FLUKA) were purified by vacuum sublimation and melting point was determined (m.p found 122°C: reported 122°C) and (m.p found 159°C: reported 159-160°C) respectively. Hexamethylphosphorictriamide (HMPA) of FLUKA chemicals was refluxed over calcium hydride for about 10 hours in an atmosphere of pure nitrogen. It was then distilled under vacuum, only the middle fraction (88°C/4mm Hg) was collected and used [21].

Electrochemical Cells, Electrodes and Instrumentation

A double walled electrochemical cell of EG&G Princeton Applied Research was used for all electrochemical studies. The cell cap contains five

14/20 standard taper holes in which working electrode, counter electrode, reference electrode, and nitrogen inlet etc. are embedded. The electrochemical cell is connected to a circulating thermostat LAUDA Model K-4R for maintaining constant temperature during measurements.

Two working electrodes were used in the present study.

The Glassy Carbon electrode having area 0.485 cm^2 was used as working or test electrode. The Glassy carbon electrode is a very hard vitreous carbon with good conductivity. This electrode is very rugged and can usually be cleaned simply by wiping with tissue paper or a very soft emery paper. The hanging mercury drop electrode (HMDE) was prepared by the method given in literature [22]. It was prepared by sealing a platinum wire about 0.012 mm diameter and then electroplating it with mercury using 0.1M mercurous nitrate solution.

A platinum wire electrode was used as counter electrode. It was made by sealing a platinum wire about 1mm diameter and 0.5 cm in length at the end of a capillary glass tube.

A silver wire was used as a quasi reference electrode [23] (QRE) and it was made by sealing a wire of about 0.069 mm diameter and about 1cm in length at the end of the capillary glass tube. This electrode was cleaned every day by rubbing it with a soft emery paper to prevent it from being converted to AgS (surface layer) [23].

All analysis was carried out under nitrogen atmosphere because solutions exposed to air contain dissolved oxygen. It causes interference in the voltammetric determinations because of oxygen reduction waves that occurs in aqueous solution at approximately -0.05 V and -0.9 V vs Ag/Ag^+ electrode. Nitrogen drying apparatus consists of six traps or bubblers. Nitrogen from the cylinder is first passed through two traps filled with chromous chloride solution (over Zinc amalgam and HCl) to remove the traces of oxygen. The third bottle is kept empty to avoid mixing of chromous chloride solution and concentrated sulphuric acid present in the fourth trap (sulphuric acid is used to absorb water from the nitrogen gas). The nitrogen gas leaving the fourth trap is then passed through fifth bottle containing silica gel for complete drying. The gas is then passed through the sixth trap containing the purified (pertinent) solvent. Finally the gas was bubbled through the solution for 15 minutes and after that the tip was drawn up to create the inert atmosphere.

For Current-Voltage measurements, EG& G PRINCETON APPLIED RESEARCH MODEL 174A POLAROGRAPHIC ANALYZER was used. The Model 174A Polarographic Analyzer is an electronic Polarographic instrument capable of performing normal and sampled dc polarography, pulse polarography, differential pulse polarography, linear sweep voltammetry at a stationary electrode and anodic stripping analysis. This instrument offers complete flexibility in potential or current control for electrochemical applications.

Experimental Procedure

A 0.1M solution of tetra n- butyl ammonium perchlorate (TBAP) in solvent (HMPA) was prepared in a 10ml volumetric flask. The solution was transferred into the electrolytic cell and the cable connections were made to Ag wire as reference electrode, Pt wire as counter electrode and Glassy Carbon/ hanging mercury drop electrode as working electrode. The purified nitrogen gas was passed through the solution so as to deoxygenate the solution. After 10- 15 minutes deareation of the solution it was subjected to current- voltage scanning to check any impurity in the blank solution. The blank run showed that the solution was free of impurities. After running the blank an appropriate amount of compound (1,2- DNB, 1,3- DNB and 1,4- DNB) was added in the TBAP solution to make (dinitrobenzene) solution in the concentrations range from 1×10^{-4}M - 1×10^{-3}M. Then after necessary deareation of this solution (in the cell) cyclic voltammograms were recorded at required scanning rates i.e., 20mv/sec., 50mv/sec., 100mv/sec. and 200mv/sec at 25°C temperature.

For protonation, 0.1M Benzoic acid solution was added aliquots of 0.4, 0.6, 0.8, 1.0 and 1.4ml in succession. After each addition cyclic voltammograms were recorded at scan rates of 20mv/sec., 50mv/sec., 100mv/sec. and 200mv/sec. From cyclic voltammograms of nitroaromatic compounds (1,2- DNB, 1,3- DNB, 1,4- DNB) before and after the addition of protonating agent and by using equation 5, homogeneous pseudo first order rate constant (k_f) was calculated as

$$k_2 = \frac{k_f}{[HA]}$$

where [HA] is concentration of protonating agent. In order to optimize the experimental conditions, it was observed from the rate constant values that out of five concentrations (1×10^{-3} M, 8×10^{-4} M, 5×10^{-4} M,

2.5×10^{-4} M, 1×10^{-4}M) of dinitrobenzenes used in this study, 5×10^{-4} M concentration show the best reproducible results in HMPA at scan rate 50mv/ sec. Concentration of the protonating agent was kept at 1×10^{-2} M for the protonation studies to maintain pseudo first order conditions for the reaction. Higher concentrations of protonating agent were avoided due to its dimerization. Scan rate higher than 50mv/sec was also not used because of IR drop problem.

The heterogeneous electron transfer rate constant ($k_{s,h}$) was calculated from the digital simulation method.

Conclusion

Nicholson and Shain polarographic method is a valid, elegent and simple method for studying the kinetics of protonating reactions of reactive intermediates. The present results are in good agreement with homogeneous electron transfer rate constant, which were previously reported in the literature. The Digital simulation method based upon cyclic voltammograms was used for the evaluation of heterogeneous rate constant $k_{s,h}$. This method is found useful in the determination of heterogeneous rate constant in the present study since measurements are made at one scan rate only.

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