Asian Journal of Chemistry; Vol. 27, No. 12 (2015), 4327-4336

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.19105

Study of Protonation Reaction of Anion Radicals of Some Dinitroaromatics in N,N-Dimethylformamide Using Cyclic Voltammetry

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Received: 15 February 2015; *Accepted*: 12 May 2015; *Published online*: 29 August 2015; AJC-17467

In the present work, cyclic voltammetric method has been used to investigate the protonation of anion radicals of 1,2-, 1,3- and 1,4-dinitrobenzenes in N,N-dimethylformamide in the temperature range 5, 15, 25 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 modified neglect of diatomic overlap (MNDO) and self consistent field-unrestricted Hartree Fock (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.

Keywords: Anion radicals, Cyclic voltammetry, Dinitrobenzenes, Glassy carbon electrode, Protonation reactions.

INTRODUCTION

The investigation of electrochemical reduction of dinitrobenzenes in different solvents has remained the focus of various studies; one of the reasons being the simple structure of their anion[1-3]. The electron transfer rate and the effect of solvent on the potential energy surface (PES) of the electro-chemical reactions play an important role during the electron transfer process. This is due to the migrating charge which can actively interact with the solvent molecules of the medium, especially in the case of dinitrobenzene molecules[4]. Considering the case of aprotic media, the two nitro groups attached to an aromatic system will cause the transfer of one or two electrons during the electrochemical process which may result in the formation of an anion or dianion[5]. Mendkovich *et al.*[6] used this technique for the study of mechanism of electroreduction of dinitrobenzenes in DMF as a solvent and investigated the formation of radical anions and dianions in the presence of proton donors.

The investigation of electrochemical nature of dinitroaromatics can provide useful data for exploring their applications. These compounds are commonly being employed in industry as solvents for colognes, drugs, *etc*. as well as chemical intermediates for the synthesis of various dyes and pesticides[7].

Among different analytical techniques being employed for their study, the cyclic voltammetry has proven itself as a foremost technique to investigate the anion radical formations of various nitroaromatic compounds[8,9]. Moreover, it has been useful for the study of kinetics of different redox reactions, as well as identification of side and final products[10].

The focus of our work was to study the effect of temperature on the protonation of anion radicals of 1,2-, 1,3- and 1,4-dinitrobenzenes in N,N-dimethylformamide (DMF) as a solvent using cyclic voltammetry in the presence of benzoic acid and salicylic acid as proton donors.

EXPERIMENTAL

Spectroscopic grade N,N-dimethylformamide of BDH chemicals was used after drying (on 4 Å molecular sieves) and distilling it under reduce pressure. All other chemicals are same as described in our earlier research articles[11,12].

Experimental procedure: Electrochemical cells, electrodes and instrumentation are same as described in our research articles earlier[11,12].

A 0.1 M solution of tetra *n*-butyl ammonium perchlorate (TBAP) in solvent N,N-dimethylformamide is prepared in a 10 mL volumetric flask. The solution is transferred into the electrolytic cell and the cable connections are made of Ag wire as reference electrode, Pt wire as counter electrode and glassy carbon/hanging mercury drop electrode as working electrode. The solution is deoxygenated by passing purified nitrogen gas through it. After 10-15 min deareation of the solution it is subjected to current-voltage scanning to check any impurity in the blank solution. The blank run showed that the solution is free of impurities. After running the blank an appropriate amount of compound (1,2-DNB, 1,3-DNB and 1,4-DNB) is added in the tetra *n*-butyl ammonium perchlorate solution to make (dinitrobenzene) solution in the concentrations range from 1×10^{-4} to 1×10^{-3} M (five different concentrations). After necessary deareation of this solution (in the cell) cyclic voltammogrms are recorded at required scanning rates *i.e.*, 20, 50, 100 and 200 mV/s at 25 °C temperature.

For protonation, 0.1 M benzoic acid solution is added aliquots of 0.4, 0.6, 0.8, 1.0 and 1.4 mL in succession. After each addition cyclic voltammograms are recorded at scan rates of 20, 50, 100 and 200 mV/s.

In order to optimize the experimental conditions, it is 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, 5×10^{-4} M concentration shows the best reproducible results in DMF at scan rate 50 mV/s. Concentration of the protonating agent is kept at 1×10^{-2} M for the protonation studies to maintain pseudo first order conditions for the reaction. Higher concentrations of protonating agent are avoided due to its dimerization. The heterogeneous electron transfer rate constant ($k_{s,h}$) was calculated from the digital simulation method.

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 electrode as a reference electrode. All the measurements were carried out in aprotic solvent N,N-dimethylformamide at four different temperatures 5, 15, 25 and 35 °C. Tetra *n*-butylammonium perchlorate was used as supporting electrolyte. The reduction process for a reversible reaction has been shown previously[1,11].

Thus the reduction of dinitrobenzenes (DNBs) could be expressed as

$$\text{DNB} + ne \rightleftharpoons \text{DNB}^{\cdot-} \qquad (1)$$

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

$$\text{DNB}^{\cdot-} + [\text{HA}] \xrightarrow{k_f} \text{Z} \qquad (2)$$

The homogeneous pseudo first order rate constant (k_f) for the above process is calculated using the equation of Nicholson and Shain[12]

$$E_p = E_{1/2} - \frac{RT}{nF}[(0.78 - \ln\sqrt{\frac{k_f}{a}})] \qquad (3)$$

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/s). 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 the absence of the reactant (protonating agent) and 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 Table-1.

Heterogeneous rate constant $k_{s,h}$ for the first reduction process was calculated from digital simulation method. Simulated cyclic voltammograms are given in Figs. 3 and 4. 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 Table-2.

Disproportionation constant (K_D), thermodynamic parameters ΔH°, ΔG°, ΔS° and activation energy (E_a), free energy of activation (ΔG^*), enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) are calculated as described earlier[1,11]. These results are collected in Tables 3 and 4.

In aprotic solvent DMF, cyclic voltammograms of dinitrobenzenes show typically two reversible waves Figs. 1 and 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 DMF at glassy carbon electrode. The $\Delta E_P = E_{Pc} - E_{Pa}$ values range between 65 to 75 mV and $E_p - E_{p/2}$ values are nearly 65 mV. The second reduction process is quasi reversible at customary scan rates (50-100 mV/s) *i.e.*, E_p -$E_{p/2}$ values are greater than 100 mV and $\Delta E_P = E_{Pc} - E_{Pa}$ values range between 100 to 200 mV for all the solvents at GCE. The higher values 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 dinitrobenzene showed reversible peaks corresponding to the first and second reduction processes and $\Delta E_P = E_{Pc} - E_{Pa}$ values for first reduction process were exactly 60 mV at hanging mercury drop electrode.

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

When the protonating agent was added, the cathodic peak shifted anodically and the anodic peak completely disappeared.

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 DMF (SCAN RATE: 50 mV s^{-1})

Compound	Concentration (M)	Temp. (°C)	Glassy carbon electrode		Hanging mercury drop electrode	
			(E_p-$E_{1/2}$) (V)	k_2 (L mol^{-1} s^{-1})	(E_p-$E_{1/2}$) (V)	k_2 (L mol^{-1} s^{-1})
Protonating agent:Benzoic acid						
1,2-DNB	1.0×10^{-2}	5	(-0.003 ± 0.011)	$(1.13 \pm 0.82) \times 10^3$	(0.027 ± 0.007)	$(11.21 \pm 5.90) \times 10^3$
		15	(0.013 ± 0.009)	$(3.59 \pm 2.23) \times 10^3$	(0.029 ± 0.011)	$(1.45 \pm 1.03) \times 10^4$
		25	(0.017 ± 0.006)	$(3.90 \pm 1.70) \times 10^3$	(0.032 ± 0.012)	$(1.62 \pm 1019) \times 10^4$
		35	(0.047 ± 0.009)	$(3.87 \pm 2.28) \times 10^4$	(0.037 ± 0.009)	$(2.22 \pm 1.41) \times 10^4$
1,3-DNB	1.0×10^{-2}	5	(0.021 ± 0.005)	$(6.28 \pm 2.48) \times 10^3$	(0.014 ± 0.007)	$(3.78 \pm 1.99) \times 10^3$
		15	(0.026 ± 0.005)	$(8.50 \pm 3.23) \times 10^3$	(0.030 ± 0.007)	$(1.26 \pm 0.64) \times 10^4$
		25	(0.053 ± 0.011)	$(7.99 \pm 5.55) \times 10^4$	(0.059 ± 0.008)	$(11.02 \pm 6.09) \times 10^4$
		35	(0.064 ± 0.006)	$(12.42 \pm 5.26) \times 10^4$	(0.074 ± 0.008)	$(2.84 \pm 1.53) \times 10^5$
1,4-DNB	1.0×10^{-2}	5	(-0.010 ± 0.006)	$(4.72 \pm 1.86) \times 10^2$	(-0.010 ± 0.007)	$(5.10 \pm 2.68) \times 10^2$
		15	(-0.001 ± 0.007)	$(8.92 \pm 2.53) \times 10^2$	(-0.006 ± 0.007)	$(6.90 \pm 3.50) \times 10^2$
		25	(0.001 ± 0.008)	$(1.03 \pm 0.57) \times 10^3$	(0.012 ± 0.005)	$(2.56 \pm 0.95) \times 10^3$
		35	(0.003 ± 0.006)	$(1.25 \pm 0.53) \times 10^3$	(0.018 ± 0.005)	$(3.76 \pm 1.35) \times 10^3$
Protonating agent:Salicylic acid						
1,2-DNB	1.0×10^{-2}	5	(0.019 ± 0.007)	$(5.75 \pm 3.02) \times 10^3$	(0.010 ± 0.011)	$(3.35 \pm 2.43) \times 10^3$
		15	(0.025 ± 0.006)	$(8.11 \pm 3.64) \times 10^3$	(0.025 ± 0.006)	$(8.11 \pm 3.64) \times 10^3$
		25	(0.032 ± 0.007)	$(1.30 \pm 0.64) \times 10^4$	(0.057 ± 0.011)	$(11.01 \pm 7.59) \times 10^4$
		35	(0.052 ± 0.009)	$(5.64 \pm 3.33) \times 10^4$	(0.062 ± 0.012)	$(13.91 \pm 9.99) \times 10^4$
1,3-DNB	1.0×10^{-2}	5	(0.039 ± 0.009)	$(3.37 \pm 2.14) \times 10^4$	(0.042 ± 0.006)	$(3.77 \pm 1.74) \times 10^4$
		15	(0.040 ± 0.008)	$(4.27 \pm 1.97) \times 10^4$	(0.055 ± 0.005)	$(10.16 \pm 3.37) \times 10^4$
		25	(0.051 ± 0.008)	$(5.96 \pm 3.29) \times 10^4$	(0.065 ± 0.007)	$(17.02 \pm 8.46) \times 10^4$
		35	(0.060 ± 0.005)	$(8.92 \pm 3.21) \times 10^4$	(0.068 ± 0.005)	$(4.03 \pm 1.45) \times 10^5$
1,4-DNB	1.0×10^{-2}	5	(-0.019 ± 0.005)	$(2.22 \pm 0.88) \times 10^2$	(-0.026 ± 0.005)	$(1.57 \pm 1.01) \times 10^2$
		15	(-0.011 ± 0.006)	$(4.45 \pm 1.99) \times 10^2$	(-0.019 ± 0.007)	$(2.42 \pm 1.24) \times 10^2$
		25	(-0.004 ± 0.005)	$(7.35 \pm 2.73) \times 10^2$	(-0.004 ± 0.005)	$(7.35 \pm 2.73) \times 10^2$
		35	(0.005 ± 0.005)	$(14.10 \pm 5.08) \times 10^2$	(-0.001 ± 0.007)	$(9.56 \pm 4.62) \times 10^2$

TABLE-2
HETEROGENEOUS RATE CONSTANT (k^o) FOR THE ISOMERS OF DINITROBENZENE FOR FIRST REDUCTION PROCESS IN HMPA CALCULATED FROM DIGITAL SIMULATION METHOD

Compound	Temp. (°C)	Glassy carbon electrode				Hanging mercury drop electrode			
		E_o[a] (mV)	k_f[b] (s^{-1})	RKS[c]	HKO[d] (cm s^{-1})	E_o[a] (mV)	k_f[b] (s^{-1})	RKS[c]	HKO[d] (cm s^{-1})
Protonating agent:Benzoic acid									
1,2-DNB	5	-0.805	11.35	20.00	0.2110	-0.820	112.1	-	-
	15	-0.820	35.95	-	-	-0.825	145.0	-	-
	25	-0.820	39.00	-	-	-0.825	162.0	-	-
	35	-0.825	387.0	-	-	-0.825	222.0	-	-
1,3-DNB	5	-0.865	62.85	-	-	-0.860	37.8	-	-
	15	-0.870	85.00	-	-	-0.864	126.0	-	-
	25	-0.900	799.0	-	-	-0.895	1102.0	-	-
	35	-0.910	1242.0	-	-	-0.910	2840.0	-	-
1,4-DNB	5	-0.640	4.72	22.00	0.2319	-0.630	5.10	18.00	0.1897
	15	-0.645	8.79	6.00	0.0632	-0.640	6.90	16.00	0.1686
	25	-0.650	10.30	3.00	0.0316	-0.650	25.60	-	-
	35	-0.670	12.50	2.00	0.0211	-0.660	37.60	-	-
Protonating agent:Salicylic acid									
1,2-DNB	5	-0.805	57.50	-	-	-0.820	33.50	-	-
	15	-0.820	81.10	-	-	-0.825	81.10	-	-
	25	-0.820	130.0	-	-	-0.825	1101.0	-	-
	35	-0.825	564.0	-	-	-0.825	1391.0	-	-
1,3-DNB	5	-0.865	377.0	-	-	-0.860	337.0	-	-
	15	-0.870	1016.0	-	-	-0.864	427.0	-	-
	25	-0.900	1702.0	-	-	-0.895	596.0	-	-
	35	-0.910	4030.0	-	-	-0.910	892.0	-	-
1,4-DNB	5	-0.640	2.22	30.00	0.3162	-0.620	1.57	55.00	0.5797
	15	-0.640	4.45	27.00	0.2846	-0.625	2.42	35.00	0.3689
	25	-0.640	7.35	16.00	0.1686	-0.625	7.35	16.00	0.1686
	35	-0.645	14.10	1.00	0.0105	-0.625	9.56	3.00	0.0316

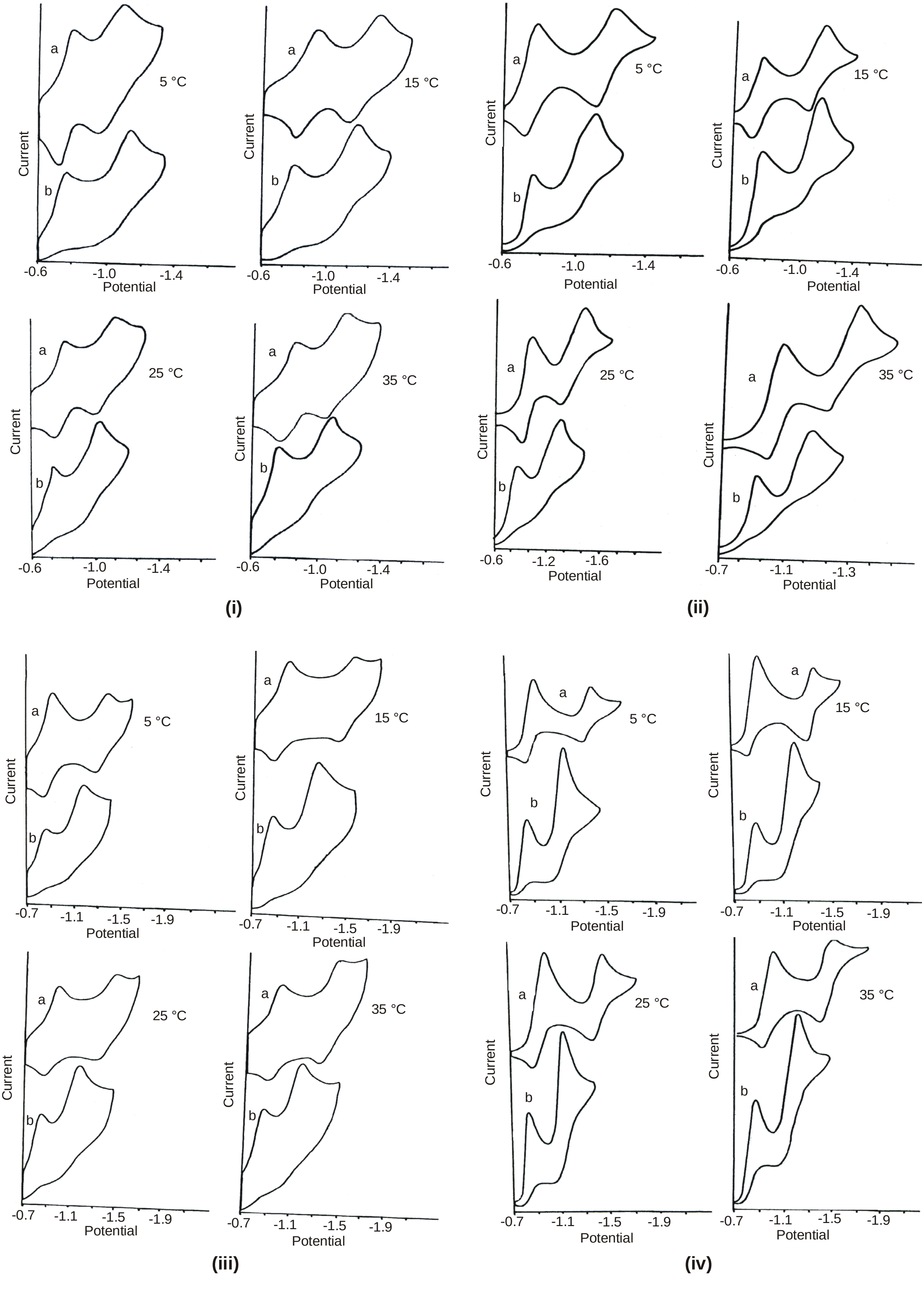
[a]Reduction potential of dinitrobenzenes; [b]Pseudo first order rate constant; [c]Continuously changing rate constant; [d]Standard heterogeneous rate constant

TABLE-3
THERMODYNAMIC PARAMETERS ($\Delta H°$, $\Delta G°$, $\Delta S°$) CALCULATED FROM DISPROPORTIONATION CONSTANTS IN DMF

Compound	Temp. (K)	Glassy carbon electrode				Hanging mercury drop electrode			
		-ln K_D	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (J mol^{-1})	- $\Delta S°$ (JK^{-1} mol^{-1})	-ln K_D	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (J mol^{-1})	- $\Delta S°$ (JK^{-1} mol^{-1})
Protonating agent:Benzoic acid									
1,2-DNB	278	5.06	11.69	213.1	41.28	5.13	11.86	188.6	44.35
	288	4.69	11.23		38.98	4.85	11.60		42.35
	298	4.46	11.06		37.11	4.72	11.69		39.97
	308	4.45	11.39		36.99	4.56	11.69		37.82
1,3-DNB	278	5.78	13.36	54.02	47.88	6.07	14.03	162.8	42.10
	288	5.62	13.45		46.69	5.81	13.91		39.63
	298	6.00	14.79		49.63	5.71	14.16		43.23
	308	5.84	15.00		48.56	5.58	14.29		42.18
1,4-DNB	278	4.22	9.76	183.0	34.45	4.04	9.34	130.0	24.23
	288	3.92	9.38		32.58	3.80	9.09		27.13
	298	3.74	9.26		31.07	3.77	9.34		25.76
	308	3.70	9.47		30.74	3.63	9.30		24.73
Protonating agent:Salicylic acid									
1,2-DNB	278	4.71	10.89	183.6	38.52	4.93	11.39	221.1	40.19
	288	4.43	10.60		36.80	4.46	10.68		37.09
	298	4.01	9.93		33.32	4.28	10.60		35.57
	308	4.27	10.93		35.50	4.29	11.00		35.64
1,3-DNB	278	5.55	12.82	39.34	45.98	6.07	14.03	144.5	49.96
	288	5.72	13.70		47.57	5.67	13.57		47.13
	298	5.70	14.12		47.38	5.85	14.50		48.64
	308	5.68	14.54		47.20	5.55	14.20		46.11
1,4-DNB	278	4.24	9.80	98.61	34.91	4.22	9.76	159.9	34.54
	288	3.85	9.22		32.00	3.88	9.30		32.29
	298	4.09	10.14		34.02	3.87	9.59		32.19
	308	3.84	9.84		31.95	3.71	9.51		30.88

TABLE-4
ACTIVATION PARAMETERS (ΔG^*, ΔH^*, ΔS^*) CALCULATED FROM DISPROPORTIONATION CONSTANTS IN DMF

Compound	Temp. (K)	Glassy carbon electrode				Hanging mercury drop electrode			
		E_a (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})	E_a (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})
Protonating agent:Benzoic acid									
1,2-DNB	278	75.45	51.67	73.16	77.27	15.34	46.37	13.03	-119.9
	288		50.85	73.07	77.16		47.51	12.95	-120.0
	298		52.49	72.99	68.78		49.00	12.87	-121.1
	308		48.46	72.91	79.36		49.89	12.78	-120.5
1,3-DNB	278	79.55	47.71	77.24	106.2	107.7	48.88	10.54	203.3
	288		48.78	77.16	98.50		47.84	10.53	199.6
	298		45.01	77.07	107.6		44.22	10.52	204.8
	308		45.48	76.99	102.3		43.36	10.52	200.6
1,4-DNB	278	22.03	53.69	19.71	-122.2	519.1	53.51	49.60	-14.06
	288		54.18	19.63	-120.0		54.80	49.52	-18.33
	298		55.79	19.55	-121.6		53.54	49.44	-13.76
	308		57.25	19.47	-122.7		54.43	49.35	-16.50
Protonating agent:Salicylic acid									
1,2-DNB	278	51.54	47.91	49.23	4.75	98.38	49.16	96.06	168.7
	288		48.90	49.15	0.88		48.90	95.98	163.5
	298		49.51	49.07	-1.49		44.22	95.90	173.4
	308		47.50	48.98	4.82		45.19	95.82	164.4
1,3-DNB	278	23.06	43.83	20.75	-82.99	54.30	43.57	52.00	30.33
	288		44.92	20.67	-84.20		42.84	51.91	31.47
	298		45.74	20.59	-84.40		43.14	51.82	29.15
	308		46.32	20.50	-83.83		42.46	51.74	30.12
1,4-DNB	278	43.05	55.43	40.74	-52.87	51.68	56.78	49.37	-26.65
	288		55.85	40.65	-52.76		57.31	49.29	-27.84
	298		56.63	40.57	-53.89		56.63	49.21	-24.90
	308		56.94	40.49	-53.44		57.94	49.12	-28.62

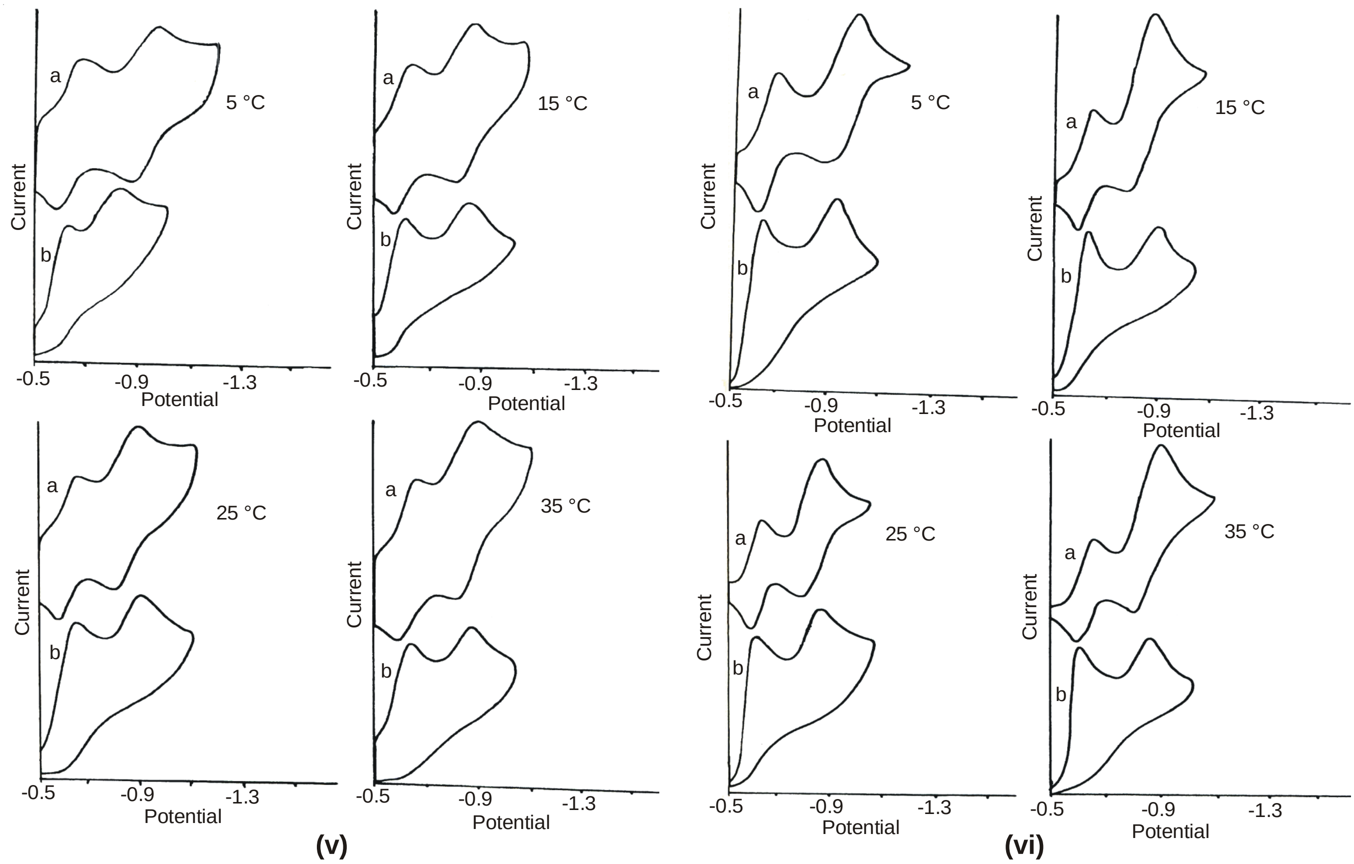


(i)

(ii)

(iii)

(iv)



(v) (vi)

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

The pseudo first order rate constant was calculated from the voltammograms recorded after the addition of protonating agent.

It was observed that on addition of protonating agent the first peak increased in height at the expense of the second peak. It was thought initially that the increase in the peak height was 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 was 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 was 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) was obtained by dividing the k_f by the concentration of the protonating agent (benzoic acid/salicylic acid).

In solvent DMF, generally at the GCE the bimolecular rate constant for the protonation of anion radicals of dinitrobenzenes shows the following pattern

$$k_2(1,3) > k_2(1,2) > k_2(1,4)$$

where, $k_2(1,3)$, $k_2(1,2)$ and $k_2(1,4)$ represent bimolecular rate constant for the 1,2-, 1,3- and 1,4-dinitrobenzene respectively.

For HMDE, $k_2(1,2)$ and $k_2(1,3)$ are found larger than $k_2(1,4)$. However $k_2(1,2)$ has lower values than $k_2(1,3)$ at 25 and 35 °C. The results of the present study of the three isomeric dinitrobenzenes in DMF may be compared with the previous work[13]. Though the trend is similar, slight variation in the rate constant values is revealed which may arise from the effect of the reference electrode. In earlier work, the reference electrode used was a saturated calomel electrode (SCE), while in the present study quasi reference electrode (Ag wire) has been used. The nature of the reference electrode may affect the electrochemical reaction. For example water leakage from the SCE may bring about a change in the environment near the electrode and stabilize the anion radical.

This behaviour can be explained if we consider the resonance structures of the dinitrobenzenes as reported earlier[11], it may be seen that when an electron reacts with dinitrobenzene it would react with greater ease with 1,3-DNB as the positive charge is delocalized over the entire ring giving it greater stability than 1,2-DNB and 1,4-DNB. For the later two isomers the two resonance structures are minor contributors. On adding the protonating agent it is expected that 1,2-DNB and 1,4-DNB would be more reactive towards the protonating agent than 1,3-DNB as the later species is more stable.

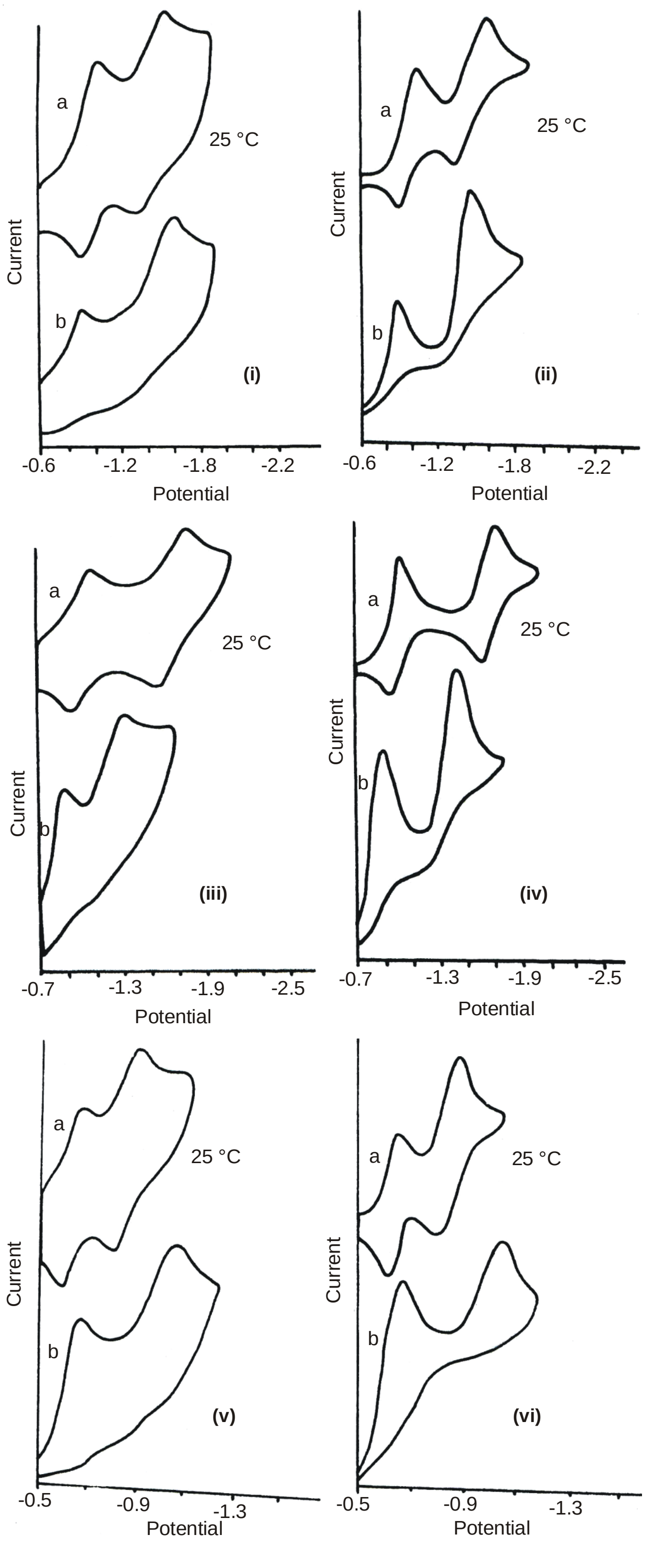


Fig. 2. (i) a-Reversible voltammogram of 1,2-DNB in DMF at GCE; b-voltammogram after the addition of protonating agent salicylic acid; (ii) a-Reversible voltammogram of 1,2-DNB in DMF at HMDE; b-voltammogram after the addition of protonating agent salicylic acid; (iii) a-Reversible voltammogram of 1,3-DNB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

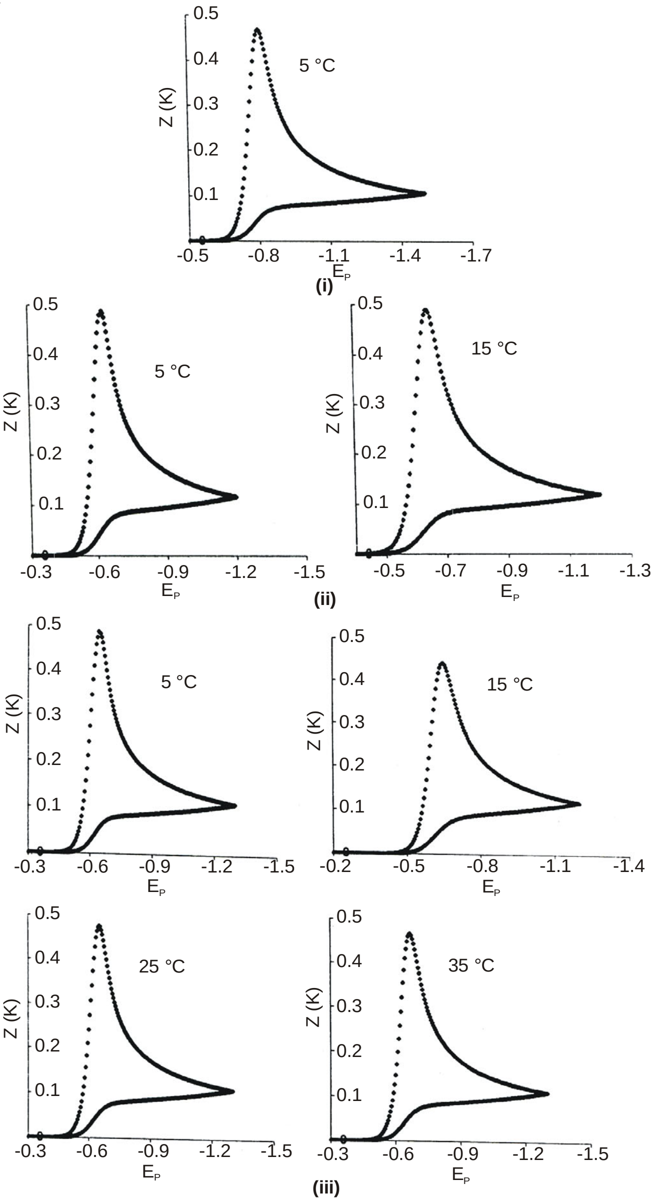


Fig. 3. (i) Simulated cyclic voltammogram of 1,2-DNB in solvent DMF at GCE (protonating agent: benzoic acid); (ii) Simulated cyclic voltammogram of 1,4-DNB in solvent DMF at HMDE (protonating agent: benzoic acid); (iii) Simulated cyclic voltammogram of 1,4-DNB in solvent DMF at GCE (protonating agent: benzoic acid).

Disproportionation for the dinitroaromatic system may be shown as follows:

$$2\text{DNB}^{\cdot-} \rightleftharpoons \text{DNB} + \text{DNB}^{2-} \qquad (4)$$

Disproportionation constant (K_D) values for dinitrobenzenes are given in Table-3. The disproportionation constant for the anion radical of 1,4-DNB in solvent DMF atboth the electrodes (GCE and HMDE) in the presence of protonating agent benzoic acid is greater than 1,3-$\text{DNB}^{\cdot-}$ and 1,2-$\text{DNB}^{\cdot-}$ for all the temperature range 5 to 35 °C. When the protonating agent was salicylic acid the similar trend was observed.

To check the stability of the electrochemical system and its kinetic behaviour, thermodynamic and activation parameters were calculated. For solvent DMF, the ΔH^* and ΔS^* values for 1,3-$\text{DNB}^{\cdot-}$ exceeded from that of 1,2-$\text{DNB}^{\cdot-}$.

When salicylic acid was used as protonating agent in DMF at GCE, the entropy and enthalpy values for 1,3-$\text{DNB}^{\cdot-}$ were

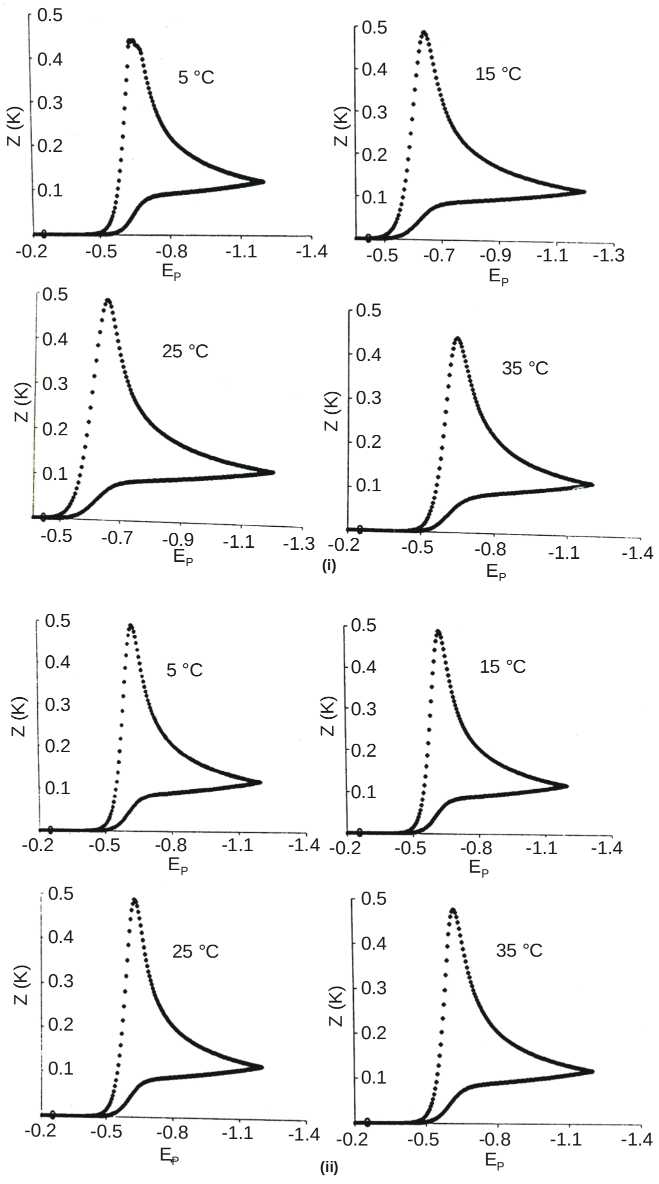


Fig. 4. (i) Simulated cyclic voltammogram of 1,4-DNB in solvent DMF at GCE (protonating agent: salicylic acid); (ii) Simulated cyclic voltammogram of 1,4-DNB in solvent DMF at HMDE (protonating agent: salicylic acid)

found higher than 1,2-DNB$^{\cdot-}$ and 1,4-DNB. The higher values of 1,2-DNB$^{\cdot-}$ showed that in 1,2-DNB$^{\cdot-}$ the two nitro groups were present close to each other and hence it was 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$^{\cdot-}$.

The well known Marcus–Hush outer sphere reorganization energy arises from dielectric polarization effects in response to the transferring electrons and can lead to decrease in the rate of electron transfer in highly polar solvents. The solvent dynamics has a pronounced effect on the kinetics of the electron transfer reactions[14].

Digital simulation methods have played an important role in the analysis of the electrochemical data[15,16]. In the present study, the heterogeneous electron transfer rate constant $k_{s,h}$ was calculated by simulation method. The results of these $k_{s,h}$ are collected in Table-5.

The dipole moment (μ) of a molecule is the vector sum of bond moments and is a function of charge separation and geometry of the molecule. Because of the geometry factor and possibility of the bond moments, dipole moment is probably a less useful measure of the ability of a solvent to promote dissociation of an ionic solute than is the dielectric constant "ε". Solvents with substantially higher dielectric constants should be used preferably in electrochemical work in order to minimize the solution resistance. For solvents of dielectric constants much below 15, substantial ion association begins to take place. In the protonating agent salicylic acid the plot between rate constants values of 1,4-DNB *vs.* dielectric constant showed that the rate constant decreases linearly with increase in dielectric constant. The dipole moment of salicylic acid, 1,2-DNB, 1,3-DNB and 1,4-DNB are 1.513D, 4.00D, 5.00D and 0.00D respectively. This effect may be explained by considering the position of the nitro groups in 1,4-DNB as the nitro groups in 1,4-DNB are far apart so they have weaker or non existence of dipole-dipole and dipole induced dipole interactions in 1,4-DNB.

The Z-parameter is a measure of the ability of the medium to stabilize an ion-pair to a less polar electronically excited state produced by charge transfer[17]. A high Z-value corresponds to high solvent polarity.

TABLE-5
THEORETICAL RESULTS FOR ELECTRODE REACTIONS INVOLVING ELECTRON TRANSFER IN DMF AT 25 °C

Compound		λ_i^{SCF-UH}	q_1	q_2	w	Z_{het} (cm s^{-1})	λ_o (eV)	$\Delta G°_{th}$ (eV)	$k^{th}_{s.h}$ (cm s^{-1})	$K^{exp}_{s.h}$ (cm s^{-1})
PA:BA										
1,2-DNB	$\varepsilon = 6.42$ $\varepsilon_o = 36.71$	0.076	-0.371 -0.371	-0.258 -0.258	0.119	4843	0.517 0.717	0.214 0.262	1.16 0.175	0.042
1,3-DNB	$\varepsilon = 6.42$ $\varepsilon_o = 36.71$	0.042	-0.312 -0.312	-0.376 -0.376	0.000	4843	0.528 0.732	0.142 0.193	18.70 02.55	2.700
1,4-DNB	$\varepsilon = 6.42$ $\varepsilon_o = 36.71$	0.062	-0.331 -0.331	-0.338 -0.338	0.129	4843	0.523 0.726	0.218 0.267	0.982 0.146	0.930
PA:SA										
1,2-DNB	$\varepsilon = 6.42$ $\varepsilon_o = 36.71$	0.076	-0.340 -0.340	-0.319 -0.319	0.119	4843	0.519 0.720	0.214 0.263	1.120 0.167	0.042
1,3-DNB	$\varepsilon = 6.42$ $\varepsilon_o = 36.71$	0.042	-0.370 -0.370	-0.260 -0.260	0.000	4843	0.516 0.716	0.139 0.189	20.80 02.96	2.700
1,4-DNB	$\varepsilon = 6.42$ $\varepsilon_o = 36.71$	0.062	-0.390 -0.390	-0.221 -0.221	0.129	4843	0.515 0.715	0.216 0.264	1.050 0.160	0.930

The solvent reorganization energy λ_o measures the energy required to reorganize the atoms and molecules of the environments of the reactants from their position at equilibrium to the position around the product species. This reorganization energy comprises of two parts: internal reorganization energy λ_i and solvent reorganization energy, λ_o. The internal reorganization energy λ_i measures the work expended in changing the bond length and bond angles within the molecules whereas λ_o measures the work expended in changing the external environment. The solvent reorganization energy is calculated using a multisphere model. Charges on the sphere (that of nitro groups and benzene ring) is estimated using SCF-UHF and MNDO methods and equation is

$$\lambda_o = \frac{1}{2}\left(\frac{1}{\varepsilon_o} - \frac{1}{\varepsilon}\right)\left(\frac{q_1^2}{a_1} + \frac{q_2^2}{a_2} + \frac{2q_1q_2}{R_{12}}\right) \tag{5}$$

where, ε_o and ε are optical and effective dielectric constants respectively; q_1 and q_2 are charges on the nitro group and benzene ring in radical; a_1 and a_2 are radii of nitro group and benzene ring respectively.

The internal reorganization energy λ_i measures the work expended in changing the bond length and bond angles within the molecules. However, the contribution of these energies is small as compared to the solvent reorganization energy as $\lambda_o >> \lambda_i$ the major contribution to λ arises from λ_o *i.e.*,

$$\lambda = \lambda_i + \lambda_o$$

inspite of that energy λ_i is not neglected. The λ_i's are calculated by applying SCF-UHF method for bond orders. The contribution of λ_i to λ is about 8 % when the bulk dielectric constant is taken and 10 % when the effective dielectric constant is taken.

The radius of the nitro groups is taken as 2.3 Å *i.e.*, $a_1 = a_3 = 2.3$ Å while the value of $a_2 = 3.5$ Å. The charge densities q_i's are calculated from SCF-UHF and MNDO calculations. The multisphere model is adopted since a single sphere model had been shown to be inadequate.

The standard theoretical free energy is calculated by using the equation:

$$\Delta G^o_{th} = w_r + \frac{[\lambda + w_p - w_r]^2}{4\lambda} \tag{6}$$

where w_r and w_p are work terms for the reactant and product respectively.

For the first reduction process w_r is zero, so the above equation becomes:

$$\Delta G^o_{th} = \frac{[\lambda + w_p]^2}{4\lambda} \tag{7}$$

The dielectric constant for an interfacial phase, however, is entirely different from the bulk phase and it is the interfacial dielectric constant which may be relevant in the present study because we are working in the vicinity of the electrode. As far as heterogeneous rate constant is concerned, the most important thing is the local environment created by the solvent molecules around the initial and transition state. So instead of taking the bulk dielectric constant, it is more appropriate to take an effective dielectric constant (for the evaluation of λ_o)[18]. The expression for the variation of dielectric constant as a function of distance from the centers of the charged ion is given by Booth and it has been adopted for the present study. In order to study the electrode reactions, Booth's expression is used after some modifications[19]. The charge of the ion (Z) is replaced by the effective charge of the electrode. This effective charge assumed to be 7 reproduced the dielectric constant of 4.1 at a distance of 6 Å (which is the thickness of the inner layer IHP adjacent to the electrode)[20]. The rate constants calculations are carried out by using these values of effective dielectric constants. The theoretical heterogeneous rate constant $k^{th}_{s,h}$ is calculated from the equation:

$$k^{th}_{s,h} = Z_{el} \exp\left(-\frac{\Delta G^o_{th}}{kT}\right) \tag{8}$$

where collision frequency $Z_{el} = \left(\frac{kT}{2\pi m}\right)^{1/2}$

The theoretical rate constant values were compared with experimental values for the three isomers of dinitrobenzenes in DMF. Results was found in good agreement with the experimental values of 1,3-DNB and 1,4-DNB with the exception of 1,2-DNB. The reason for this deviation in the case of 1,2-DNB may be due to the fact that in the reduction process the electron density on the nitro groups increases thus increasing the electronic repulsion. This would lead to the destabilization of the molecule which may be responsible for the lower value of the rate constant.

Conclusion

The mechanism of electrochemical reduction of dinitrobenzenes in DMF in the presence of controlled amounts of proton donors was studied by cyclic voltammetry. The Nicholson and Shain polarographic method for studying the kinetics of protonation reactions of dinitrobenzenes in DMF, proved to be simple and valid. The use of cyclic voltammetry employing digital simulation method was found favourable for determining heterogenous rate constants. Moreover, the theoretical calculations of these rate constants using modified Marcus theory were also in agreement with the experimental results.

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