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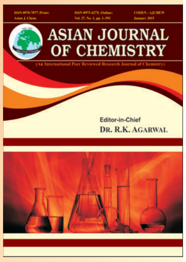

Electrochemical Studies of Protonation Reaction of Anion Radicals of Some Dinitroaromatics in Dichloromethane

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Protonation of anion radicals of 1,2-,1,3- and 1,4-dinitrobenzenes in dichloromethane in the temperature range 0, 5, 10 and 15 °C has been investigated by cyclic voltammetric method. 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.

Keywords: Anion radicals, Cyclic voltammetry, Protonation reactions, Dinitrobenzene, Dichloromethane.

INTRODUCTION

Integrated study of the dinitrobenzene electroreduction mechanism by electroanalytical and computational methods in DMF has already been done[1,2]. The electroreduction mechanism of aromatic nitroso compounds, particularly of nitrosobenzene, was the focus of a number of researches[3,4]. The eletroanalytical methods in combination with other experimental (*e. g.*, controlled potential electrolysis) and theoretical methods such as digital simulation have been employed for the studies on the mechanism of electrochemical processes and development of their theoretical models[5-14].

The objective of this research is to investigate the protonation of the first reduction product of dinitrobenzenes and to measure the heterogeneous electron transfer rate constants in dichloromethane solvent at different temperatures. The substrates are the three isomers of dinitrobenzenes and the protonating agents are benzoic acid and salicylic acid.

EXPERIMENTAL

Dinitroaromatic compounds such as 1,2-dinitrobenzene (mp found 116 °C: reported 116.5 °C) of BDH chemicals and 1,3-dinitrobenzene (mp found 90.5 °C: reported 90.5 °C) of Hopkin & Williams Ltd. were purified by crystallizing it from ethanol. Tetra *n*-butyl ammonium perchlorate (TBAP) used as supporting electrolyte throughout is prepared using tetra *n*-butyl ammonium bromide from BDH chemicals and magnesium perchlorate from Merck chemicals. The prepared salt is washed with deionized water and dried under vacuum in a desiccator for about 5 h and then used. The blank cyclic voltammetry run is used to determine impurity if any (mp found 212 °C: reported 212 °C). Protonating agents benzoic acid (Chemapol) and salicylic acid (Fluka) were purified by vacuum sublimation and melting points are determined (mp found 122 °C: reported 122 °C) and (mp found 159 °C: reported 159-160 °C), respectively. All of the above chemicals are purified as described by Perrin[15]. Dichloromethane (CH_2Cl_2) of Aldrich is purified by drying it over $CaCl_2$ and then distilled from CaH_2. It is then stored in a brown bottle with Linde type 4 Å molecular sieves[15].

Electrochemical cells, electrodes and instrumentation: For current-voltage measurements EG& G princeton applied research model 174A polarographic analyzer is used. This instrument offers complete flexibility in potential or current control for electrochemical applications[16].

A double walled electrochemical cell of EG & G princeton applied research is 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 are used in the present study.

The glassy carbon electrode (GCE) having an area of 0.485 cm^2 is used as a working or test electrode. This is a very hard vitreous carbon with good conductivity, very rugged and can usually be cleaned simply by wiping with tissue paper or a soft emery paper. The hanging mercury drop electrode (HMDE) is prepared by sealing a platinum wire of about 0.012 mm diameter. Then this electrode is electroplated with mercury using 0.1 M mercurous nitrate solution[17]. A platinum wire electrode is used as counter electrode. It is made by sealing a platinum wire about 1 mm diameter and 0.5 cm in length at the end of a capillary glass tube.

A silver wire is used as a Quasi Reference Electrode (QRE) and it is made by sealing a wire of about 0.069 mm diameter and about 1 cm in length at the end of the capillary glass tube. This electrode is cleaned every day by rubbing it with a soft emery paper to prevent it from being converted to AgS (surface layer)[18].

All the analyses are carried out under nitrogen atmosphere. 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 in the fourth trap (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 is bubbled through the solution for 15 min and after that the tip is drawn up to create the inert atmosphere.

A 0.1 M solution of tetra *n*-butyl ammonium perchlorate (TBAP) in solvent (CH_2Cl_2) is prepared in a 10 mL volumetric flask. The solution is transferred into the electrolytic cell and the cable connections are made to Ag wire as reference electrode, Pt wire as counter electrode and glassy carbon/HMDE as working electrode. The purified nitrogen gas is passed through the solution so as to deoxygenate the solution. 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 and 1,3- DNB) is added in the TBAP solution to make different concentrations ranging from 1×10^{-4} M to 1×10^{-3} M. Then after necessary deareation of this solution in the cell cyclic voltammograms are recorded at required scanning rates *i.e.*, 20, 50, 100 and 200 mv/sec. at 25 °C.

For protonation, the aliquots of 0.4, 0.6, 0.8, 1.0 and 1.4 mL of 0.1 M benzoic acid solution are added in succession. After each addition cyclic voltammograms are recorded at scan rates mentioned above.

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 used in this study, 5×10^{-4} M concentration showed the best reproducible results in CH_2Cl_2 at scan rate 50 mv/sec. 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. Scan rate higher than 50 mv/sec is not used because of IR (potential) drop problem.

RESULTS AND DISCUSSION

Electrochemical measurements (triangular wave cyclic voltammetry) are carried out at two different working electrodes *i.e.*, glassy carbon electrode and hanging mercury drop electrode. A platinum wire is used as counter electrode while a silver wire (Ag) as a reference electrode. All the measurements are carried out in aprotic solvent dichloromethane (CH_2Cl_2) at four different temperatures 0, 5, 10 and 15 °C. Tetra *n*-butyl ammonium per chlorate (TBAP) is used as supporting electrolyte.

The reduction process for a reversible reaction can be represented as

$$\mathrm{O} + n\bar{e} \rightleftharpoons \mathrm{R} \tag{1}$$

$$\mathrm{R} + [\mathrm{HA}] \xrightarrow{k_f} \mathrm{Z} \tag{2}$$

Thus the reduction of dinitrobenzene (DNB) could be expressed as

$$\mathrm{DNB} + \bar{e} \rightleftharpoons \mathrm{DNB}^{-\bullet} \tag{3}$$

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

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

The homogeneous pseudo first order rate constant (k_f) for the above process is calculated using the equation of Nicholson and Shain[19]

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

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) are recorded in two steps as in the absence of 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. Results are given in Tables 1 and 2.

Heterogeneous rate constant $k_{s,h}$ for the first reduction process is 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 given as input also 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

TABLE-1
(E_p-$E_{1/2}$) VALUES AND THE BIMOLECULAR RATE CONSTANT (k_2) FOR THE PROTONATION OF ANION RADICALS OF ISOMERS OF DINITROBENZENES IN CH_2Cl_2 (SCAN RATE: 50 mV sec^{-1} AND PROTONATING AGENT:BENZOIC ACID)

Compound	Concentration of benzoic acid (M)	Temperature (°C)	Glassy carbon electrode		Hanging mercury drop electrode	
			(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}	0	(-0.002 ± 0.012)	$(1.35 \pm 1.04) \times 10^3$	(-0.011 ± 0.005)	$(4.36 \pm 1.75) \times 10^2$
		5	(0.012 ± 0.011)	$(3.96 \pm 2.87) \times 10^3$	(0.013 ± 0.009)	$(3.84 \pm 2.44) \times 10^3$
		10	(0.019 ± 0.011)	$(6.70 \pm 4.81) \times 10^3$	(0.055 ± 0.008)	$(10.95 \pm 6.31) \times 10^4$
		15	(0.054 ± 0.009)	$(9.57 \pm 5.94) \times 10^4$	(0.066 ± 0.010)	$(26.53 \pm 17.71) \times 10^4$
1,3-DNB	1.0×10^{-2}	0	(-0.021 ± 0.007)	$(2.00 \pm 1.10) \times 10^2$	(0.022 ± 0.006)	$(7.49 \pm 3.52) \times 10^3$
		5	(0.015 ± 0.006)	$(3.95 \pm 1.83) \times 10^3$	(0.032 ± 0.008)	$(1.78 \pm 1.04) \times 10^4$
		10	(0.031 ± 0.007)	$(1.46 \pm 0.76) \times 10^4$	(0.034 ± 0.008)	$(1.96 \pm 1.13) \times 10^4$
		15	(0.053 ± 0.009)	$(8.80 \pm 5.50) \times 10^4$	(0.050 ± 0.006)	$(6.08 \pm 2.73) \times 10^4$
1,4-DNB	1.0×10^{-2}	0	(0.032 ± 0.010)	$(2.14 \pm 1.48) \times 10^4$	(0.029 ± 0.009)	$(1.57 \pm 1.04) \times 10^4$
		5	(0.045 ± 0.009)	$(5.56 \pm 3.53) \times 10^4$	(0.044 ± 0.006)	$(4.45 \pm 2.06) \times 10^4$
		10	(0.057 ± 0.006)	$(1.19 \pm 0.54) \times 10^5$	(0.061 ± 0.007)	$(1.71 \pm 0.88) \times 10^5$
		15	(0.068 ± 0.005)	$(2.51 \pm 0.96) \times 10^5$	(0.067 ± 0.010)	$(2.88 \pm 1.92) \times 10^5$

TABLE-2
(E_p-$E_{1/2}$) VALUES AND THE BIMOLECULAR RATE CONSTANT (k_2) FOR THE PROTONATION OF ANION RADICALS OF ISOMERS OF DINITROBENZENES IN CH_2Cl_2 (SCAN RATE: 50 mV sec^{-1} AND PROTONATING AGENT: SALICYLIC ACID)

Compound	Concentration of benzoic acid (M)	Temperature (°C)	Glassy carbon electrode		Hanging mercury drop electrode	
			(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}	0	(0.005 ± 0.009)	$(2.04 \pm 1.31) \times 10^3$	(-0.006 ± 0.006)	$(6.92 \pm 3.25) \times 10^2$
		5	(0.042 ± 0.006)	$(3.97 \pm 1.74) \times 10^4$	(0.035 ± 0.010)	$(2.55 \pm 1.74) \times 10^4$
		10	(0.048 ± 0.007)	$(5.89 \pm 3.06) \times 10^4$	(0.053 ± 0.006)	$(8.54 \pm 3.89) \times 10^4$
		15	(0.063 ± 0.006)	$(1.73 \pm 0.78) \times 10^5$	(0.067 ± 0.010)	$(2.88 \pm 1.92) \times 10^5$
1,3-DNB	1.0×10^{-2}	0	(-0.005 ± 0.009)	$(8.70 \pm 5.60) \times 10^2$	(-0.015 ± 0.011)	$(4.18 \pm 3.06) \times 10^2$
		5	(0.006 ± 0.006)	$(1.86 \pm 0.86) \times 10^3$	(0.018 ± 0.008)	$(5.54 \pm 3.23) \times 10^3$
		10	(0.042 ± 0.005)	$(3.35 \pm 1.30) \times 10^4$	(0.030 ± 0.005)	$(1.25 \pm 0.49) \times 10^4$
		15	(0.065 ± 0.009)	$(2.32 \pm 1.44) \times 10^5$	(0.045 ± 0.011)	$(5.16 \pm 3.66) \times 10^4$
1,4-DNB	1.0×10^{-2}	0	(-0.002 ± 0.007)	$(1.02 \pm 0.54) \times 10^3$	(-0.019 ± 0.006)	$(2.29 \pm 1.07) \times 10^2$
		5	(0.015 ± 0.010)	$(4.79 \pm 3.27) \times 10^3$	(0.004 ± 0.011)	$(2.03 \pm 1.47) \times 10^3$
		10	(0.024 ± 0.009)	$(9.04 \pm 5.68) \times 10^3$	(0.029 ± 0.009)	$(1.36 \pm 0.86) \times 10^4$
		15	(0.037 ± 0.010)	$(2.56 \pm 1.71) \times 10^4$	(0.052 ± 0.007)	$(7.43 \pm 3.80) \times 10^4$

changed until the simulated voltammogram exactly matches with the experimental voltammogram. The standard heterogeneous rate constant values are given in Tables 3 and 4.

Disproportionation constant (K_D) for the process is calculated by the following equation

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

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

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

Thermodynamic parameters ΔH°, ΔG°, ΔS° are calculated from the following relations

$$\Delta G^\circ = -RT \ln K_D \tag{7}$$

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

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{9}$$

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

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 and entropy of activation (ΔS^*) are calculated from the following relations

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

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

$$\Delta H^* = E_a - nRT \tag{11}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{12}$$

Activation parameters are given in Tables 7 and 8.

Voltammograms of dinitrobenzenes in aprotic solvent CH_2Cl_2 show typically two reversible waves. 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 CH_2Cl_2 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

TABLE-3
HETEROGENEOUS RATE CONSTANT FOR THE ISOMERS OF DINITROBENZENES FOR FIRST REDUCTION PROCESS IN CH_2CL_2 CALCULATED FROM DIGITAL SIMULATION METHOD (PROTONATING AGENT : BENZOIC ACID)

Compound	Temperature (°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})
1,2-DNB	0	-0.820	13.50	1.00	0.0105	-0.810	4.36	11.00	0.1159
	5	-0.850	39.60	-	-	-0.825	38.40	-	-
	10	-0.850	67.00	-	-	-0.850	119.5	-	-
	15	-0.860	957.0	-	-	-0.850	265.0	-	-
1,3-DNB	0	-0.835	2.00	30.00	0.3162	-0.800	74.90	-	-
	5	-0.830	39.50	-	-	-0.810	178.0	-	-
	10	-0.830	146.0	-	-	-0.810	196.0	-	-
	15	-0.850	880.0	-	-	-0.815	608.0	-	-
1,4-DNB	0	-0.635	241.0	-	-	-0.630	157.0	-	-
	5	-0.640	556.0	-	-	-0.640	445.0	-	-
	10	-0.640	1190.0	-	-	-0.650	1710.0	-	-
	15	-0.650	2510.0	-	-	-0.660	2880.0	-	-

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

TABLE-4
HETEROGENEOUS RATE CONSTANT FOR THE ISOMERS OF DINITROBENZENES FOR FIRST REDUCTION PROCESS IN CH_2Cl_2 CALCULATED FROM DIGITAL SIMULATION METHOD. (PROTONATING AGENT : SALICYLIC ACID)

Compound	Temperature (°C)	Glassy carbon electrode				Hanging mercury drop electrode			
		E_o (mv)	k_f (s^{-1})	RKS	HKO (cm s^{-1})	E_o (mv)	k_f (s^{-1})	RKS	HKO (cm s^{-1})
1,2-DNB	0	-0.820	20.40	1.00	0.0105	-0.825	6.92	15.00	0.1581
	5	-0.855	39.70	-	-	-0.840	255.0	-	-
	10	-0.855	589.0	-	-	-0.860	854.0	-	-
	15	-0.860	1730.0	-	-	-0.870	2880.0	-	-
1,3-DNB	0	-0.815	8.70	6.00	0.632	-0.825	4.18	24.00	0.2530
	5	-0.825	18.60	1.00	0.0105	-0.845	55.40	-	-
	10	-0.845	335.0	-	-	-0.845	125.0	-	-
	15	-0.855	2320.0	-	-	-0.855	516.0	-	-
1,4-DNB	0	-0.630	10.20	3.00	0.0316	-0.605	2.29	24.00	0.2530
	5	-0.655	47.90	-	-	-0.625	20.30	1.00	0.0105
	10	-0.660	90.40	-	-	-0.650	136.0	-	-
	15	-0.660	2560.0	-	-	-0.640	743.0	-	-

TABLE-5
THERMODYNAMIC PARAMETERS (ΔH°, ΔG°, ΔS°) CALCULATED FROM DISPROPORTIONATION CONSTANTS IN CH_2Cl_2 (PROTONATING AGENT = BENZOIC ACID)

Compound	Temperature (K)	Glassy carbon electrode				Hanging mercury drop electrode			
		-ln K_D	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1})	-ΔS° (JK^{-1} mol^{-1})	-ln K_D	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1})	-ΔS° (JK^{-1} mol^{-1})
1,2-DNB	273	4.91	11.14	213.1	40.04	5.63	12.78	669.0	44.35
	278	4.82	11.14		40.09	5.09	11.78		42.35
	283	4.77	11.23		39.67	4.81	11.31		39.97
	288	4.55	10.89		37.82	4.55	10.89		37.82
1,3-DNB	273	5.68	12.90	338.6	46.02	5.09	11.56	68.77	42.10
	278	5.84	13.49		48.52	4.77	11.02		39.63
	283	5.39	12.69		44.85	5.20	12.23		43.23
	288	5.23	12.53		43.49	5.07	12.15		42.18
1,4-DNB	273	3.41	7.75	160.1	27.80	2.92	6.62	5.03	24.23
	278	3.37	7.79		28.03	3.26	7.54		27.13
	283	3.12	7.33		25.91	3.09	7.29		25.76
	288	3.22	7.71		26.77	2.97	7.12		24.73

reversible at customary scan rates (50-100 mv/sec) *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 the solvent at glassy carbon electrode. The higher values of ΔE_p,s in the case of second reduction process at glassy carbon electrode may be due to the instability of the dianion at glassy carbon electrode 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 showed reversible peaks corresponding to the first and second reduction

TABLE-6
THERMODYNAMIC PARAMETERS (ΔH°, ΔG°, ΔS°) CALCULATED FROM DISPROPORTIONATION CONSTANTS IN CH_2Cl_2 (PROTONATING AGENT = SALICYLIC ACID)

Compound	Temperature (K)	Glassy carbon electrode				Hanging mercury drop electrode			
		-ln K_D	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1})	-ΔS° (JK^{-1} mol^{-1})	-ln K_D	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1})	-ΔS° (JK^{-1} mol^{-1})
1,2-DNB	273	4.76	10.81	61.23	39.37	5.39	12.23	530.2	42.87
	278	4.73	10.93		39.33	5.13	11.86		42.65
	283	4.63	10.89		38.49	4.90	11.52		40.71
	288	4.69	11.23		38.98	4.53	10.85		37.68
1,3-DNB	273	5.72	12.99	82.26	47.27	5.20	11.81	215.6	42.49
	278	5.55	12.82		46.11	4.91	11.35		40.84
	283	5.59	13.15		46.48	4.81	11.13		39.97
	288	5.56	13.32		46.26	4.86	11.64		40.44
1,4-DNB	273	3.32	7.54	149.1	27.08	2.62	5.95	251.7	20.87
	278	3.44	7.96		28.63	2.83	6.53		23.51
	283	3.17	7.46		26.35	3.19	7.50		26.49
	288	3.15	7.54		26.18	2.94	7.04		24.44

TABLE-7
ACTIVATION PARAMETERS (ΔG^*, ΔH^*, ΔS^*) CALCULATED FROM DISPROPORTIONATION CONSTANTS IN CH_2Cl_2 (PROTONATING AGENT = BENZOIC ACID)

Compound	Temperature (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})
1,2-DNB	273	93.93	50.30	91.66	151.5	161.3	52.86	159.0	388.8
	278		48.77	91.61	154.1		48.85	159.0	396.1
	283		48.46	91.57	152.2		47.30	159.0	394.4
	288		48.46	91.53	168.5		40.55	158.9	410.9
1,3-DNB	273	139.8	54.63	137.5	303.6	45.25	46.41	42.99	-12.54
	278		48.78	137.5	319.1		45.30	42.94	-8.48
	283		46.62	137.4	320.9		45.93	42.90	-10.70
	288		43.19	137.4	327.1		44.07	42.86	-4.21
1,4-DNB	273	58.06	44.03	55.79	43.09	71.91	44.73	69.64	91.26
	278		42.67	55.75	47.05		43.18	69.60	95.03
	283		41.69	55.71	49.54		40.83	69.56	101.5
	288		40.68	55.67	52.04		40.35	69.52	101.3

TABLE-8
ACTIVATION PARAMETERS (ΔG^*, ΔH^*, ΔS^*) CALCULATED FROM DISPROPORTIONATION CONSTANTS IN CH_2Cl_2 (PROTONATING AGENT = SALICYLIC ACID)

Compound	Temperature (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})
1,2-DNB	273	98.51	49.36	96.24	171.7	138.5	51.82	136.2	309.2
	278		43.45	96.20	189.7		44.47	136.2	329.9
	283		43.34	96.15	186.6		42.47	136.1	331.0
	288		41.57	96.11	189.4		40.35	136.1	333.1
1,3-DNB	273	139.2	51.30	136.9	313.7	109.1	52.96	106.9	197.5
	278		50.52	136.9	310.7		48.00	106.8	211.6
	283		44.67	136.8	325.7		47.00	106.8	211.3
	288		40.87	136.8	333.1		44.47	106.7	216.3
1,4-DNB	273	73.55	50.93	71.28	74.53	137.2	54.33	134.9	295.1
	278		48.33	71.24	82.39		50.32	134.8	304.1
	283		47.75	71.20	82.85		46.79	134.8	311.0
	288		46.14	71.16	86.85		43.59	134.8	316.6

processes and $\Delta E_p = \Delta E_{pc} - \Delta E_{pa}$ values for first reduction process were exactly 60 mv at hanging mercury drop electrode.

In the present study, the anion radical is generated by reducing 1,2-DNB, 1,3-DNB and 1,4-DNB.

$$\text{DNB} + \bar{e} \rightleftharpoons \text{DNB}^{-\bullet} \qquad (13)$$

on the surface of the working electrodes *i.e.*, glassy carbon electrode and hanging mercury drop electrode, respectively.

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 is observed and its broadening with increase in $\frac{k_f}{a}$ ratio occurred when protonating agent is 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).

In solvent CH_2Cl_2 at 0 °C, the k_2 (1,4) (2.14×10^4 L mol^{-1} s^{-1}) at the glassy carbon electrode and (1.57×10^4 L mol^{-1} s^{-1}) at hanging mercury drop electrode are higher than k_2 (1,2) and k_2 (1,3). At 5 °C temperature the k_2 (1,2) (3.96×10^2 L mol^{-1} s^{-1}) and k_2 (1,3) (3.95×10^2 L mol^{-1} s^{-1}) observed for glassy carbon electrode are comparable. The k_2 (1,4) values (5.56×10^2 L mol^{-1} s^{-1}) and (4.45×10^2 L mol^{-1} s^{-1}) observed for the glassy carbon electrode and hanging mercury drop electrode respectively were higher than for 1,2-DNB and 1,3-DNB. The bimolecular rate constant for the protonation of the anion radicals of dinitroberzenes follow the following pattern.

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

This behaviour can be explained if we consider the resonance structures of the dinitrobenzenes as shown in Fig. 1. Looking at the resonance structures 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. However, it should be noted that the rate constant for 1,2-DNB anion radical is comparable to 1,3-DNB in CH_2Cl_2 at 5 °C. 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.

Disproportionation for the dinitrobenzenes system may be depicted as follows:

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

Disproportionation constant (K_D) values for dinitrobenzenes are given in Tables 5 and 6. In the solvent CH_2Cl_2 disproportionation constant for the anion radical of 1,4-DNB at both electrodes is greater than $1,2\text{-DNB}^{-\bullet}$ and $1,3\text{-DNB}^{-\bullet}$ at all the temperatures selected for the present study. When the protonating agent is salicylic acid the similar trend is observed (Figs. 2 and 3).

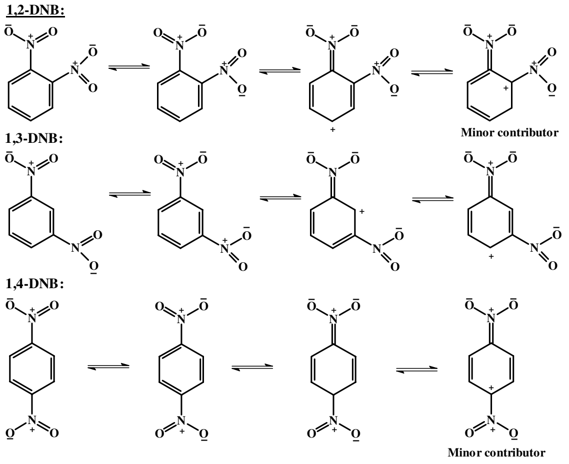
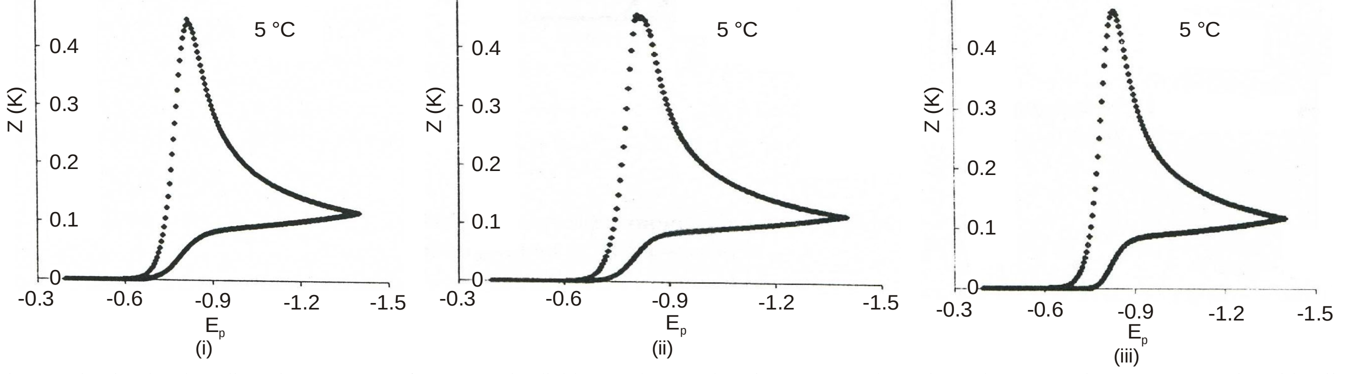


Fig. 1. Resonance structures of the dinitrobenzenes

In order to seek information regarding the stability of the electrochemical system and its kinetic behaviour, thermodynamic and activation parameters are calculated. In solvent CH_2Cl_2, the entropy and enthalpy of activation of $1,3\text{-DNB}^{-\bullet}$ is found higher than that of $1,2\text{-DNB}^{-\bullet}$ It seems that the lower ΔS^* value of $1,2\text{-DNB}^{-\bullet}$ is due to the activated complex of $1,2\text{-DNB}^{-\bullet}$ being as symmetrical and planer and more ordered. The observed decrease in ΔH^* values is expected as the two nitro groups are far apart.



(i) (ii) (iii)

Fig. 2. (i) Simulated cyclic voltammogram of 1,2-DNB in dichloromethane at hanging mercury drop electrode (protonating agent: Benzoic acid); (ii) Simulated cyclic voltammogram of 1,2-DNB in dichloromethane at glassy carbon electrode (protonating agent: benzoic acid); (iii) Simulated cyclic voltammogram of 1,3-DNB in dichloromethane at glassy carbon electrode (protonating agent: benzoic acid)

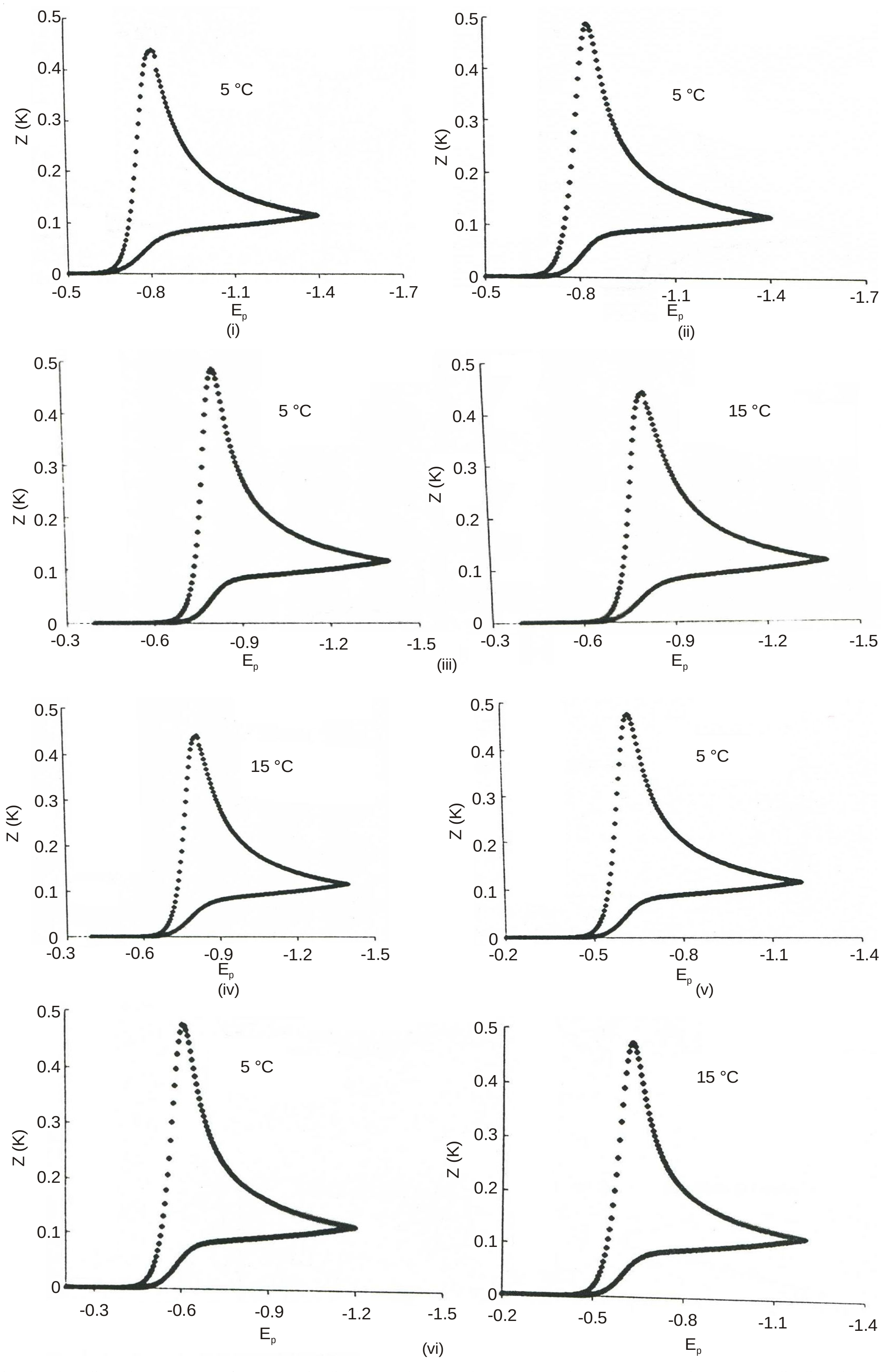


Fig. 3. (i) Simulated cyclic voltammogram of 1,2-DNB in dichloromethane at glassy carbon electrode (protonating agent: Salicylic acid); (ii) Simulated cyclic voltammogram of 1,2-DNB in dichloromethane at hanging mercury drop electrode (protonating agent: Salicylic acid); (iii) Simulated cyclic voltammogram of 1,3-DNB in dichloromethane at glassy carbon electrode (protonating agent: Salicylic acid); (iv) Simulated cyclic voltammogram of 1,3-DNB in dichloromethane at hanging mercury drop electrode (protonating agent: Salicylic acid); (v) Simulated cyclic voltammogram of 1,4-DNB in dichloromethane at glassy carbon electrode (protonating agent: Salicylic acid); (vi) Simulated cyclic voltammogram of 1,4-DNB in dichloromethane at hanging mercury drop electrode (protonating agent: Salicylic acid)

When salicylic acid is used as protonating agent in the CH_2Cl_2 the entropy and enthalpy of activation for the homogeneous chemical reaction of 1,2-DNB$^{-\bullet}$ is higher than 1,3-DNB$^{-\bullet}$ and 1,4-DNB$^{-\bullet}$. The higher values of 1,2-DNB$^{-\bullet}$ show that the two nitro groups are present close to each other and hence it is difficult for them to be in one plane. There is more disorderness in the activated complex of 1,2-DNB$^{-\bullet}$ than that of 1,3-DNB$^{-\bullet}$.

Solvent is known to play an important role in determining the rate of electron transfer in solution[20,21]. 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 pronounced effect on the kinetics of the electron transfer reactions[22]. On the other hand, substantial changes of electron transfer rate constants are solely observed for the dinitrobenzenes due to solvent polarity.

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. This will also minimize ohmic losses and diminish the problem of potential control error[23]. For solvents of dielectric constants much below 15, substantial ion association begins to take place.

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[20]. A high Z-value corresponds to high solvent polarity.

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 expanded 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

$$\lambda_o = \frac{1}{2}\left(\frac{1}{\varepsilon_o} - \frac{1}{\varepsilon}\right)\left(\frac{q_1^2}{a_1} + \frac{q_2^2}{a_2} + \frac{2q_1q_2}{R_{12}}\right) \qquad (15)$$

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[24]. 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.*, $a_1 = a_2 = 2.3$ Å while the value of $a_2 = 3.5$ Å. The charge densities are calculated from SCF-UHF and MNDO calculations. The multisphere model is adopted since a single sphere model had been shown to be inadequate[24].

The standard theoretical free energy is calculated by using the equation

$$\Delta G^o_{th} = w_r + \frac{[\lambda + w_p - w_r]^2}{4\lambda} \qquad (16)$$

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

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

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)[25]. 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[26,27]. In order to study the electrode reactions, Booth's expression is used after some modifications[28,29]. 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)[28,29]. Thus the value of ε for CH_2Cl_2 which have been considered as an effective dielectric constant in contrast to the values of 64.40 for the bulk dielectric constant. 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

$$k^{th}_{s,h} = Z_{el} \exp\left(-\frac{\Delta G^o_{th}}{kT}\right) \qquad (17)$$

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

Digital simulation method have played an important role in the analysis of the electrochemical data[30-32]. 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 9 and 10.

Conclusion

Kinetic study of protonating reactions of reactive intermediates by Nicholson and Shain polarographic method is simple and results are in good agreement with homogeneous electron transfer rate constant, which were previously reported

TABLE-9
THEORETICAL RESULTS FOR ELECTRODE REACTIONS INVOLVING ELECTRON TRANSFER IN CH_2Cl_2 at 25 °C (PROTONATING AGENT = BENZOIC ACID)

Compound	$\lambda_1^{SCF-UHF}$	q_1	q_2	w	Z_{het} (cm sec^{-1})	λ_o (e.v)	$\Delta G°_{th}$ (e.v)	$k^{th}_{s,h}$ (cm sec^{-1})
1,2-DNB $\varepsilon = 5.46$ $\varepsilon_o = 8.93$	0.076	-0.371	-0.258	0.119	4843	0.482	0.205	1.599
		-0.371	-0.258			0.593	0.232	0.566
1,3-DNB $\varepsilon = 5.46$ $\varepsilon_o = 8.93$	0.042	-0.312	-0.376	0.000	4843	0.492	0.134	26.34
		-0.312	-0.376			0.606	0.162	08.74
1,4-DNB $\varepsilon = 5.46$ $\varepsilon_o = 8.93$	0.062	-0.312	-0.338	0.129	4843	0.488	0.210	1.350
		-0.312	-0.338			0.601	0.236	0.477

TABLE-10
THEORETICAL RESULTS FOR ELECTRODE REACTIONS INVOLVING ELECTRON TRANSFER IN CH_2CL_2 AT 25 °C (PROTONATING AGENT = SALICYLIC ACID)

Compound	$\lambda_1^{SCF-UHF}$	q_1	q_2	w	Z_{het} (cm sec^{-1})	λ_o (e.v)	$\Delta G°_{th}$ (e.v)	$k^{th}_{s,h}$ (cm sec^{-1})
1,2-DNB $\varepsilon = 5.46$ $\varepsilon_o = 8.93$	0.076	-0.371	-0.258	0.119	4843	0.485	0.206	1.550
		-0.371	-0.258			0.596	0.233	0.544
1,3-DNB $\varepsilon = 5.46$ $\varepsilon_o = 8.93$	0.042	-0.370	-0.260	0.000	4843	0.482	0.131	29.09
		-0.370	-0.260			0.592	0.159	09.87
1,4-DNB $\varepsilon = 5.46$ $\varepsilon_o = 8.93$	0.062	-0.390	-0.221	0.129	4843	0.481	0.208	1.440
		-0.390	-0.221			0.591	0.234	0.514

in the literature. The digital simulation method based upon cyclic voltammograms is 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. Theoretical heterogeneous rate constant $k_{s,h}$ is also calculated using the Marcus theory with some modifications. Calculations of the theoretical heterogeneous rate constant requires the reorganization energy, λ_o, which in turn requires dielectric constant of the solvent. However, it is found that the use of λ_o calculated from effective dielectric constant (*i.e.* the dielectric constant in the interfacial region) produces theoretical values in good agreement with the experimental values obtained through simulations. This strengthens our assumption that the electron transfer takes place in the interfacial region. Thus the validity of the use of modified Marcus theory is established by agreement between theoretical and experimental $k_{s,h}$. The advantage of the theoretical calculations is that heterogeneous rate constant can be calculated for those compounds for which no experimental data is available.

REFERENCES

1. A.S. Mendkovich, M.A. Syroeshkin, L.V. Mikhalchenko, M.N. Mikhailov, A. Rusakov and V.P. Gultyai, *Int. J. Electrochem.*, 1 (2011).
2. A.S. Mendkovich, M.A. Syroeshkin, L.V. Mikhalchenko, A.I. Rusakov and V.P. Gultyai, *Russ. Chem. Bull.*, **57**, 1492 (2008).
3. E. Steudel, J. Posdorfer and R.N. Schindler, *Electrochim. Acta*, **40**, 1587 (1995).
4. M.A. Syroeshkin, A.S. Mendkovich, L.V. Mikhalchenko, A.I. Rusakov and V.P. Gul'tyai, *Mendeleev Commun.*, **19**, 258 (2009).
5. M.A. Syroeshkin, A.S. Mendkovich, L.V. Mikhal'chenko, A.I. Rusakov and V.P. Gul'tyai, Russ. Chem. Bull., **58**, 468 (2009).
6. V. Mikhalchenko, A.S. Mendkovich, M.A. Syroeshkin and V.P. Gul'tyai, *Mendeleev Commun.*, **19**, 96 (2009).
7. M.A. Syroeshkin, M.N. Mikhailov, A.S. Mendkovich and A.I. Rusakov, *Russ. Chem. Bull.*, **58**, 41 (2009).
8. A.S. Mendkovich, M.A. Syroeshkin, L.V. Mikhalchenko, A.I. Rusakov and V.P. Gultyai, *Russ. Chem. Bull.*, **57**, 1492 (2008).
9. L.J. Núñez-Vergara, J.A. Squella, C. Olea-Azar, S. Bollo, P.A. Navarrete-Encina and J.C. Sturm, *Electrochim. Acta*, **45**, 3555 (2000).
10. D.H. Evans, *Chem. Rev.*, **108**, 2113 (2008).
11. N.G. Tsierkezos, *J. Solution Chem.*, **36**, 289 (2007).
12. N.A. Macías-Ruvalcaba, J.P. Telo and D.H. Evans, *J. Electroanal. Chem.*, **600**, 294 (2007).
13. D.S. Silvester, A.J. Wain, L. Aldous, C. Hardacre and R.G. Compton, *J. Electroanal. Chem.*, **596**, 131 (2006).
14. M. Mohammad and M.J. Aslam, *J. Chem. Soc. Pak.*, **33**, 12 (2011).
15. D.D. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford/New York, edn 1 (1974).
16. Operating and Service Manual, Model 174A Polarographic Analyzer, EG & G Princeton Applied Research, New Jersey, USA.
17. J.W. Ross, R.D. DeMars and I. Shain, *Anal. Chem.*, **28**, 1768 (1956).
18. D.O. Wipf and R.M. Wightman, Anal. Chem., **62**, 98 (1990).
19. R.S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
20. D.T. Sawyer, Experimental Electrochemistry for Chemists, John Wiley & Sons, p. 170 (1974).
21. C. Reichardt, Solvents and Solvent Effect in Organic Chemistry, Ch. 7, VCH Publishers, Cambridge (1988).
22. N.E. Miller, M.C. Wander and R.J. Cave, *J. Phys. Chem.*, **103**, 1084 (1999).
23. D.H. Evans, *Chem. Rev.*, **108**, 2113 (2008).
24. Z.V. Todres, Ion-Radical Organic Chemistry: Principles and Applications, CRC Press, Taylor & Francis Group, Boca Raton, Fl., USA, edn 2 (2009).
25. M.J. Weaver, *J. Am. Chem. Soc.*, **106**, 6107 (1984).
26. F. Booth, *J. Chem. Phys.*, **19**, 391 (1951).
27. J.M. Hale, in ed.: N.S. Hush, Reactions of Molecules at Electrodes, Wiley Interscience, New York (1970).
28. D.R. Lide, Hand book of Organic Solvents, CRC Press Boca Roton, Ann Arbor, London, p. 142 (1995).
29. A.J. Bard and L.R. Faulkner, Electrochemical Methods, John Wiley & Sons, New York, edn 2 (2001).
30. D. Britz, Digital Simulation in Electrochemistry, Springer, Berlin (1981).
31. D.K. Gosser and P.H. Rieger, *Anal. Chem.*, **60**, 1159 (1988).
32. D.K. Gosser Jr., Cyclic Voltammetry, VCH, New York and Weinheim, Germany, p. 275 (1993).