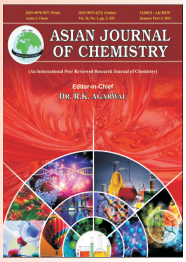
Asian Journal of Chemistry;   Vol. 26, No. 16 (2014), 5063-5072

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16319



Thermodynamic and Kinetic Study for Protonation Reaction of Anion Radicals of Some Dinitroaromatics in Acetonitrile

FARZANA HANIF[1], GHAZALA YASMEEN[2,*], RASHIDA PERVEEN[3] and MUHAMMAD AAMIR[2]

[1]Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan
[2]Institute of Chemical Sciences, Bahauddin Zakariya University, Multan, Pakistan
[3]Department of Plant Pathology, University College of Agriculture, Bahauddin Zakariya University, Multan, Pakistan

*Corresponding author: Tel: +92 300 6345628; E-mail: ghazala31pk@yahoo.com

Received: 10 September 2013;   *Accepted*: 12 December 2013;   *Published online*: 28 July 2014;   AJC-15632

Cyclic voltammeric method has been employed to investigate the protonation of anion radicals of 1,2-, 1,3-, and 1,4-dinitrobenzenes in acetonitrile 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. Thermodynamic parameters are calculated by disproportionation constant. 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 ks, h for the first reduction process in dinitrobenzenes is determined by digital simulation of the cyclic voltammograms.

Keywords: Anion radicals, Dinitrobenzene, Acetonitrile, Glassy carbon electrode, Hanging mercury drop electrode, Protonation reactions.

INTRODUCTION

Physical and chemical properties of intermediates are being studied since long[1,2]. However the main problem was in such studies is their instabilities. Electrochemical methods such as controlled potential electrolysis has been used in the generation of some reactive intermediates[3], while electrolysis at microelectrodes, optical transparent electrode and minigrid electrode have been used to obtain ESR and optical spectra of some reactive intermediates[4-7]. For the study of the kinetics of reactions involving reactive intermediates such as protonation, electron transfer, atom abstraction, *etc*. several methods have been developed and employed in recent decades[8-10]. Among the transient techniques in electrochemistry, the triangular wave cyclic voltammetry (CV) has found extensive applications in electron transfer studies[11-15].

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 acetonitrile solvent at different temperatures. The substrates are the three isomers of dinitrobenzenes and the protonating agents were benzoic acid and salicylic acid.

EXPERIMENTAL

Dinitroaromatics compounds such as 1,2-dinitrobenzene (1,2-DNB) of BDH chemicals is 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. is 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 is 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 is used as supporting electrolyte throughout prepared from 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 desicator for about 5 h and then used. The blank CV run is used to determine impurity if any (m.p. found 212 °C: reported 212 °C). Protonating agents benzoic acid (Chemapol chemicals) and salicylic acid (Fluka) are purified by vacuum sublimation and melting point is determined (m.p. found 122 °C: reported 122 °C) and (m.p. found 159 °C: reported 159-160 °C), respectively. Acetonitrile (CH_3CN) of Aldrich (A.C.S. reagent) is used after drying on 4°A molecular sieves and then fractionally distilling at high reflux. A small amount of P_2O_5 was added in the distillation flask to remove traces of the remaining water[16].

Electrochemical cells, electrodes and instrumentation: 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 were used in the present study: The glassy carbon electrode having area 0.485 cm^2 is 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[17]. It was prepared by sealing a platinum wire about 0.012 mm diameter. Then electroplating it with mercury using 0.1 M mercurous nitrate solution.

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[17] (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 analysis is 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 is bubbled through the solution for 15 min and after that the tip is drawn up to create the inert atmosphere.

For current-voltage measurements, EG & G Princeton Applied Research Model 174a Polarographic Analyzer is 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 0.1 M solution of tetra *n*-butyl ammonium perchlorate (TBAP) in solvent acetonitrile CH_3CN 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 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, 1,3-DNB and 1,4-DNB) is added in the TBAP solution to make (dinitrobenzene) solution in the concentrations range from 1×10^{-4} M to 1×10^{-3} M (five different concentrations). Then 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 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 used in this study, 5×10^{-4} M concentration show the best reproducible results in acetonitrile solvent 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. Scan rate higher than 50 mV/s is not used because of IR drop problem.

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

RESULTS AND DISCUSSION

Electrochemical measurements such as triangular wave cyclic voltammetry are carried out at two different working electrodes *i.e*., glassy carbon electrode (GCE) and hanging mercury drop electrode (HMDE). A platinum wire is used as counter electrode while a silver wire electrode is used as a reference electrode. All the measurements are carried out in aprotic solvent acetonitrile at four different temperatures 5, 15, 25 and 35 °C. Tetra *n*-butylammonium per chlorate (TBAP) is 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

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

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

$$DNB^{\bullet-} + [HA] \xrightarrow{k_f} Z \qquad (4)$$

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

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

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/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 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 and 2.

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 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 as shown in Figs. 1 and 2. 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 and 4.

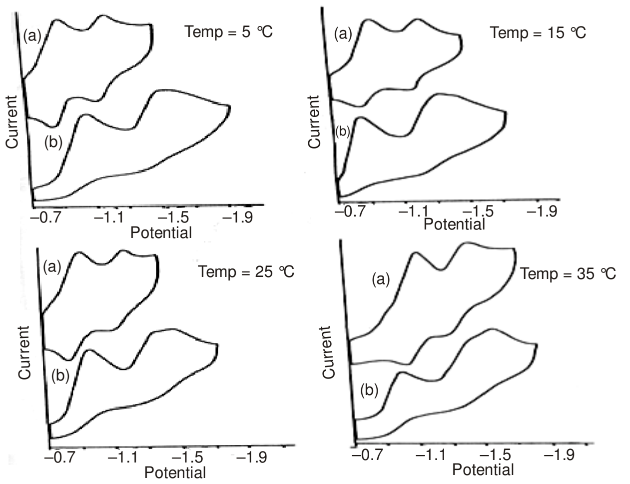


Fig. 1(i) (a) Reversible voltammogram of 1,2-DNB in acetonitrile at GCE (b) voltammogram after the addition of protonating agent Benzoic acid

TABLE –1
$(E_P\text{-}E_{1/2})$ VALUES AND THE BIMOLECULAR RATE CONSTANT (k_2) FOR THE PROTONATION OF ANION RADICALS OF ISOMERS OF DINITROBENZENE IN CH_3CN (SCAN RATE: 50 mV SEC^{-1})

Compound	Concentration of benzoic acid (M)	Temperature (°C)	Working electrode glassy carbon electrode		Working electrode hanging mercury drop electrode	
			$(E_p\text{-}E_{1/2})$ (V)	k_2 (L mol^{-1} s^{-1})	$(E_p\text{-}E_{1/2})$ (V)	k_2 (L mol^{-1} s^{-1})
1,2-DNB	1.0×10^{-2}	5	(0.001 ± 0.006)	$(12.26 \pm 5.68)\times10^{2}$	(-0.004 ± 0.011)	$(10.40\pm7.54)\times10^{2}$
		15	(0.026 ± 0.007)	$(9.16 \pm 4.67)\times10^{3}$	(0.013 ± 0.008)	$(3.34 \pm 1.90)\times 10^{3}$
		25	(0.043 ± 0.008)	$(3.19 \pm 1.77)\times10^{4}$	(0.044 ± 0.010)	$(3.79 \pm 2.47)\times 10^{4}$
		35	(0.058 ± 0.008)	$(8.50 \pm 4.60)\times10^{4}$	(0.050 ± 0.009)	$(4.85 \pm 2.86)\times 10^{4}$
1,3-DNB	1.0×10^{-2}	5	(-0.001 ± 0.007)	$(5.09 \pm 2.68)\times10^{2}$	(-0.007 ± 0.010)	$(7.63 \pm 5.21)\times 10^{2}$
		15	(0.006 ± 0.005)	$(1.69 \pm 0.65)\times10^{3}$	(0.001 ± 0.007)	$(1.22 \pm 0.62)\times 10^{3}$
		25	(0.010 ± 0.006)	$(2.26 \pm 0.98)\times10^{3}$	(0.010 ± 0.010)	$(2.19 \pm 0.81)\times 10^{3}$
		35	(0.013 ± 0.011)	$(3.28 \pm 2.23)\times10^{3}$	(0.013 ± 0.012)	$(3.46 \pm 2.48)\times 10^{3}$
1,4-DNB	1.0×10^{-2}	5	(0.005 ± 0.007)	$(1.78 \pm 0.94)\times10^{3}$	(0.025 ± 0.006)	$(9.10 \pm 4.21)\times 10^{3}$
		15	(0.026 ± 0.007)	$(9.14 \pm 4.67)\times10^{3}$	(0.043 ± 0.008)	$(3.76 \pm 2.13)\times 10^{4}$
		25	(0.028 ± 0.009)	$(10.38 \pm 6.28)\times10^{3}$	(0.054 ± 0.009)	$(7.87 \pm 4.76)\times 10^{4}$
		35	(0.001 ± 0.007)	$(4.82 \pm 2.33)\times10^{4}$	(0.059 ± 0.008)	$(9.16\pm4.94)\times10^{4}$

TABLE-2
$(E_P\text{-}E_{1/2})$ VALUES AND THE BIMOLECULAR RATE CONSTANT (k_2) FOR THE PROTONATION OF ANION RADICALS OF ISOMERS OF DINITROBENZENE IN CH_3CN (SCAN RATE: 50 mV SEC^{-1})

Compound	Concentration of salicylic acid (M)	Temperature (°C)	Working electrode Glassy carbon electrode		Working electrode Hanging mercury drop electrode	
			$(E_p\text{-}E_{1/2})$ (V)	k_2(L mol^{-1} s^{-1})	$(E_p\text{-}E_{1/2})$ (V)	k_2 (L mol^{-1} s^{-1})
1,2-DNB	1.0×10^{-2}	5	(-0.015 ± 0.016)	$(5.80 \pm 5.05)\times 10^{2}$	(-0.007 ± 0.007)	$(6.55 \pm 3.44)\times 10^{2}$
		15	(0.007 ± 0.005)	$(1.84 \pm 0.70)\times 10^{3}$	(0.003 ± 0.007)	$(1.43 \pm 0.73)\times 10^{3}$
		25	(0.049 ± 0.006)	$(4.71 \pm 2.06)\times 10^{4}$	(0.047 ± 0.009)	$(4.56 \pm 2.76)\times 10^{4}$
		35	(0.068 ± 0.007)	$(17.36 \pm 8.40)\times 10^{4}$	(0.058 ± 0.008)	$(8.47 \pm 4.58)\times 10^{4}$
1,3-DNB	1.0×10^{-2}	5	(-0.005 ± 0.012)	$(1.02 \pm 0.78)\times 10^{3}$	(-0.012 ± 0.008)	$(4.52 \pm 2.64)\times 10^{2}$
		15	(0.004 ± 0.012)	$(2.01 \pm 1.50)\times 10^{3}$	(-0.009 ± 0.007)	$(5.43 \pm 2.78)\times 10^{2}$
		25	(0.020 ± 0.009)	$(4.77 \pm 1.77)\times 10^{3}$	(0.025 ± 0.007)	$(7.54 \pm 3.75)\times 10^{3}$
		35	(0.024 ± 0.008)	$(6.54 \pm 3.53)\times 10^{3}$	(0.039 ± 0.010)	$(22.16 \pm 14.13)\times 10^{3}$
1,4-DNB	1.0×10^{-2}	5	(0.028 ± 0.007)	$(1.22 \pm 0.64)\times 10^{4}$	(0.023 ± 0.007)	$(8.02 \pm 4.22)\times 10^{3}$
		15	(0.038 ± 0.007)	$(2.40 \pm 1.23)\times 10^{4}$	(0.025 ± 0.007)	$(8.43 \pm 4.31)\times 10^{3}$
		25	(0.059 ± 0.008)	$(11.11 \pm 6.15)\times 10^{4}$	(0.046 ± 0.007)	$(3.87 \pm 1.93)\times 10^{4}$
		35	(0.063 ± 0.008)	$(12.38 \pm 6.68)\times 10^{4}$	(0.058 ± 0.007)	$(8.17 \pm 3.95)\times 10^{4}$

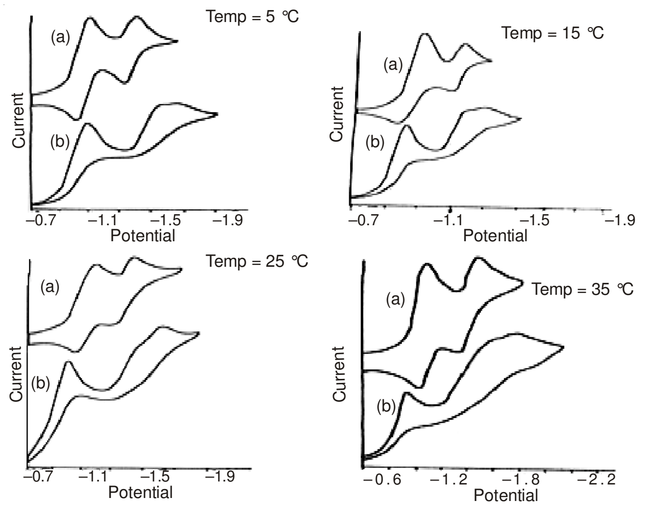


Fig. 1(ii) (a) Reversible voltammogram of 1,2-DNB in acetonitrile at HMDE (b) voltammogram after the addition of protonating agent Benzoic acid

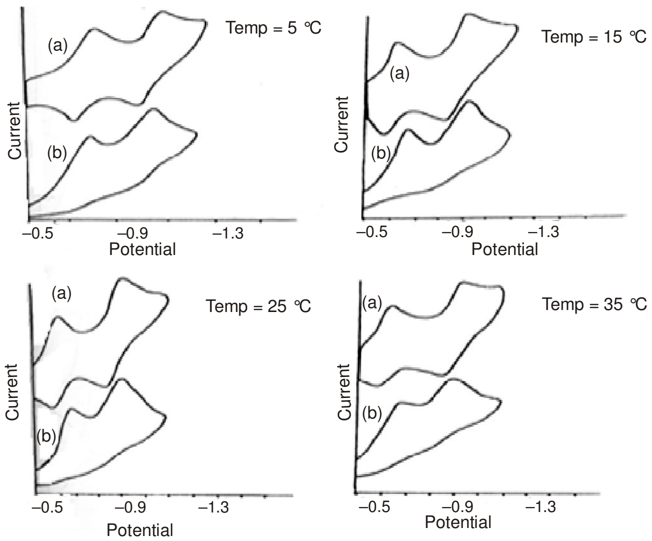


Fig. 1(iii) (a) Reversible voltammogram of 1,3-DNB in acetonitrile at GCE (b) voltammogram after the addition of protonating agent benzoic acid

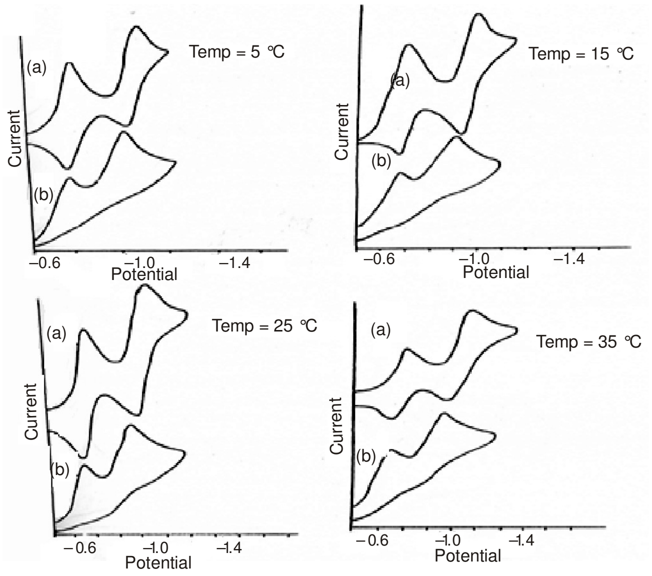


Fig. 1(iv) (a) Reversible voltammogram of 1,3-DNB in acetonitrile at HMDE (b) voltammogram after the addition of protonating agent benzoic acid

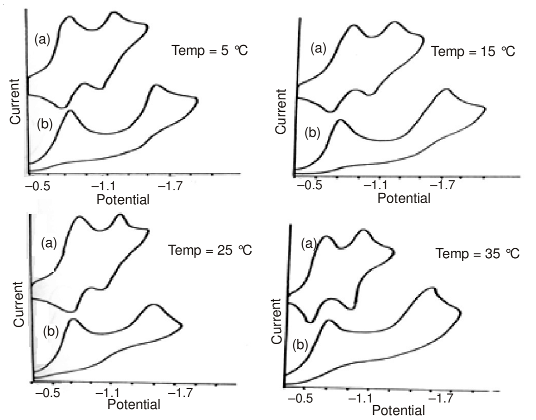


Fig. 1(v)(a) Reversible voltammogram of 1,4-DNB in acetonitrile at GCE (b) voltammogram after the addition of protonating agent benzoic acid

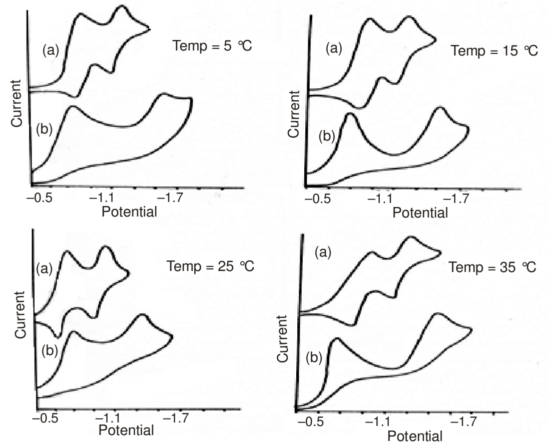


Fig. 1(vi) (a) Reversible voltammogram of 1,4-DNB in acetonitrile at HMDE (b) voltammogram after the addition of protonating agent benzoic acid

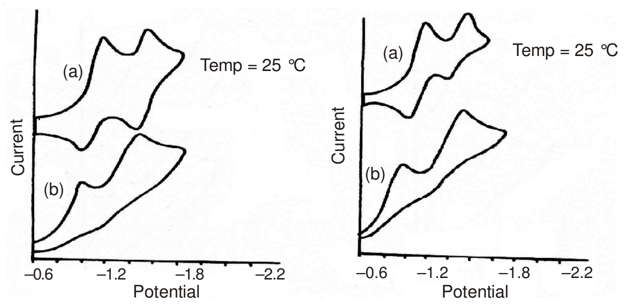


Fig. 2(i) (a) Reversiblevoltammogram of 1,2-DNB in acetonitrile at GCE (b) voltammogram after the addition of protonating agent salicylic acid (ii) (a) Reversible voltammogram of 1,2-DNB in acetonitrile at HMDE (b) voltammogram after the addition of protonating agent Salicylic acid

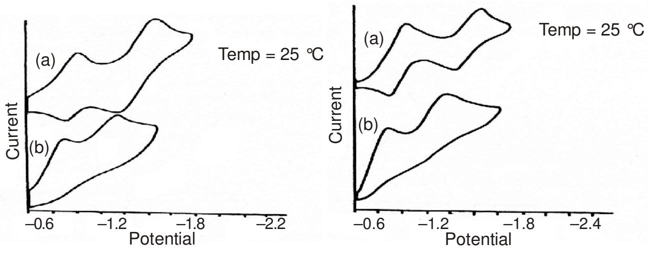


Fig. 2(iii) (a) Reversible voltammogram of 1,3-DNB in acetonitrile at GCE (b) voltammogram after the addition of protonating agent salicylic acid (iv) (a) Reversible voltammogram of 1,3-DNB in acetonitrile at HMDE (b) voltammogram after the addition of protonating agent salicylic acid

TABLE-3
HETEROGENEOUS RATE CONSTANT (k^O) FOR THE ISOMERS OF DINITROBENZENE FOR FIRST REDUCTION PROCESS IN CH_3CN CALCULATED FROM DIGITAL SIMULATION METHOD. (PROTONATING AGENT: BENZOIC ACID)

Compound	Temperature (°C)	Working electrode glassy carbon electrode				Working 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	5	-0.850	12.26	2.00	0.0211	-0.840	10.40	3.00	0.0316
	15	-0.850	91.60	-	-	-0.850	33.40	-	-
	25	-0.860	319.0	-	-	-0.870	379.0	-	-
	35	-0.880	850.0	-	-	-0.880	485.0	-	-
1,3-DNB	5	-0.815	5.09	19.00	0.2003	-0.800	7.63	20.00	0.2108
	15	-0.820	16.90	1.00	0.0105	-0.800	12.20	20.00	0.0211
	25	-0.830	22.60	1.00	0.0105	-0.800	21.90	1.00	0.0063
	35	-0.840	32.80	-	-	-0.815	34.60	-	-
1,4-DNB	5	-0.565	17.80	-	-	-0.550	91.00	-	-
	15	-0.600	91.40	-	-	-0.610	376.0	-	-
	25	-0.600	163.8	-	-	-0.610	787.0	-	-
	35	-0.615	482.0	-	-	-0.610	916.0	-	-

[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 (k^O) FOR THE ISOMERS OF DINITROBENZENE FOR FIRST REDUCTION PROCESS IN CH_3CN CALCULATED FROM DIGITAL SIMULATION METHOD. (PROTONATING AGENT: BENZOIC ACID)

Compound	Temperature (°C)	Working electrode glassy carbon electrode				Working electrode hanging mercury drop electrode			
		E_o^a (mv)	k_f (s^{-1})	RKS	HKO^d (cm s^{-1})	E^a (mv)	k_f (s^{-1})	RKS	HKO (cm s^{-1})
1,2-DNB	5	-0.825	5.80	22.00	0.2319	-0.835	6.55	18.00	0.1897
	15	-0.840	18.40	1.00	0.0105	-0.845	14.30	1.00	0.0105
	25	-0.870	471.0	-	-	-0.860	456.0	-	-
	35	-0.880	1736.0	-	-	-0.860	847.0	-	-
1,3-DNB	5	-0.800	10.20	3.00	0.0316	-0.790	4.52	32.00	0.3373
	15	-0.815	20.10	1.00	0.0105	-0.810	5.43	27.00	0.2846
	25	-0.820	47.70	-	-	-0.820	75.40	-	-
	35	-0.820	65.00	-	-	-0.820	221.0	-	-
1,4-DNB	5	-0.750	122.0	-	-	-0.780	80.20	-	-
	15	-0.775	240.0	-	-	-0.785	84.00	-	-
	25	-0.765	1111.0	-	-	-0.790	387.0	-	-
	35	-0.775	1238.0	-	-	-0.795	817.0	-	-

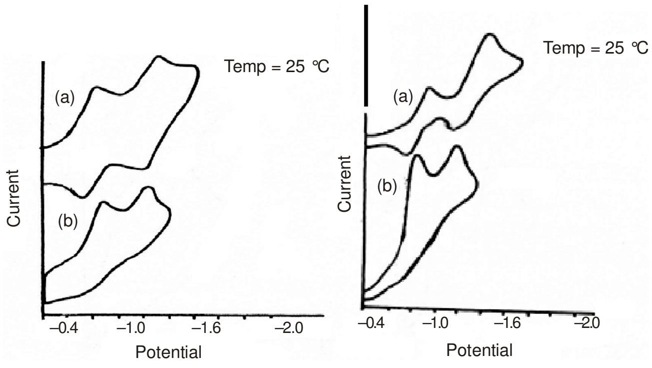


Fig. 2(v) (a) Reversible voltammogram of 1,4-DNB in acetonitrile at GCE (b) voltammogram after the addition of protonating agent salicylic acid (vi) (a) Reversible voltammogram of 1,4-DNB in acetonitrile at HMDE (b) voltammogram after the addition of protonating agent salicylic acid

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

$$\log K_D = \frac{\Delta E_{1/2}}{1.303\ RT/nF} \qquad (6)$$

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 are calculated from the following relations

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

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

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

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 and 6.

Activation energy, E_a, of protonating step is obtained by plotting $\ln k_2 \frac{1}{T}$ 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 and 8.

TABLE-5
THERMODYNAMIC PARAMETERS (ΔH°, ΔG°, ΔS°) CALCULATED FROM DISPROPORTIONATION CONSTANTS IN CH_3CN (PROTONATING AGENT = BENZOIC ACID)

Compound	Temperature (K)	Working electrode glassy carbon electrode				Working electrode hanging mercury drop electrode			
		$-\ln K_D$	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1})	$-\Delta S^\circ$ (JK^{-1} mol^{-1})	$-\ln K_D$	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1})	$-\Delta S^\circ$ (JK^{-1} mol^{-1})
1,2-DNB	278	2.91	6.74	44.19	24.10	2.92	6.74	26.69	24.17
	288	2.73	6.53		22.69	2.78	6.66		23.13
	298	3.13	7.75		26.01	2.52	6.24		20.95
	308	2.93	7.49		24.25	3.11	7.96		25.84
1,3-DNB	278	4.91	11.35	82.29	40.54	4.98	11.52	223.5	40.64
	288	5.04	12.06		41.61	1.88	11.69		39.81
	298	4.73	11.73		39.09	4.46	11.06		36.36
	308	4.74	12.14		39.18	4.40	11.27		35.86
1,4-DNB	278	3.32	7.67	226.9	26.76	2.95	6.83	207.2	23.82
	288	3.15	7.54		26.18	2.94	7.04		24.44
	298	2.89	7.16		24.04	2.52	6.24		20.95
	308	2.67	6.83		22.17	2.42	6.20		20.13

TABLE-6
THERMODYNAMIC PARAMETERS (ΔH°, ΔG°, ΔS°) CALCULATED FROM DISPROPORTIONATION CONSTANTS IN CH_3CN (PROTONATING AGENT = SALICYLIC ACID)

Compound	Temperature (K)	Working electrode glassy carbon electrode				Working electrode hanging mercury drop electrode			
		$-\ln K_D$	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1})	$-\Delta S^\circ$ (JK^{-1} mol^{-1})	$-\ln K_D$	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1})	$-\Delta S^\circ$ (JK^{-1} mol^{-1})
1,2-DNB	278	2.90	6.70	168.9	23.50	3.32	7.67	136.6	27.09
	288	2.85	6.83		23.71	2.68	6.41		22.56
	298	2.79	6.91		23.19	2.94	7.29		24.46
	308	3.48	8.92		28.97	2.79	7.16		23.26
1,3-DNB	278	5.18	11.98	11.46	43.06	4.75	10.98	193.6	38.78
	288	5.20	12.44		43.20	4.99	11.94		41.46
	298	5.17	12.82		43.02	5.56	13.78		46.25
	308	5.15	13.20		42.85	5.17	13.24		42.98
1,4-DNB	278	2.61	6.02	198.5	20.99	2.56	5.91	48.03	21.08
	288	2.57	6.16		21.38	2.45	5.86		20.36
	298	2.10	5.19		17.43	2.21	5.49		18.42
	308	2.13	5.45		17.68	2.49	6.37		20.67

TABLE-7
ACTIVATION PARAMETERS (ΔH°, ΔS°, ΔG°) OF DINITROBENZENES CALCULATED FROM HOMOGENEOUS RATE CONSTANT IN CH_3CN (PROTONATING AGENT = BENZOIC ACID)

Compound	Temperature (K)	Working electrode glassy carbon electrode				Working electrode hanging mercury drop electrode			
		E_a (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	$-\Delta S^\circ$ (JK^{-1} mol^{-1})	E_a (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	$-\Delta S^\circ$ (JK^{-1} mol^{-1})
1,2-DNB	278	99.85	51.48	97.53	165.6	99.71	51.86	97.40	163.7
	288		48.61	97.45	169.6		51.02	97.32	160.7
	298		47.29	97.37	168.1		46.86	97.24	169.0
	308		46.45	97.29	165.0		47.89	97.15	159.9
1,3-DNB	278	107.72	53.52	105.4	186.7	79.55	52.58	77.24	88.70
	288		52.45	105.3	182.9		53.44	77.16	82.35
	298		53.85	105.2	172.5		53.92	77.07	77.68
	308		54.78	105.2	163.6		54.65	76.99	72.53
1,4-DNB	278	71.37	50.62	69.06	66.31	55.15	46.85	52.84	21.54
	288		48.61	68.98	70.71		45.22	52.76	26.16
	298		50.07	68.89	63.17		45.05	52.67	25.59
	308		47.90	68.81	67.88		46.06	52.59	20.57

In aprotic solvent CH_3CN cyclic voltammograms of dinitrobenzenes show typically two reversible waves as in 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 CH_3CN at glassy carbon electrode. The $\Delta E_P = E_{Pc} - E_{Pa}$ values range between 65 mv 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 values range between 100 to 200 mV for the solvent 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 showed reversible peaks corresponding to the first and second reduction processes and

TABLE-8
ACTIVATION PARAMETERS (ΔH°, ΔS°, ΔG°) OF DINITROBENZENES CALCULATED FROM HOMOGENEOUS RATE CONSTANT IN CH_3CN (PROTONATING AGENT = SALICYLIC ACID)

Compound	Temperature (K)	Working electrode glassy carbon electrode				Working 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	278	144.6	53.21	142.3	320.6	12.84	52.93	12.61	263.3
	288		52.45	142.3	311.8		53.05	12.60	253.5
	298		46.32	142.2	321.7		46.40	12.60	267.0
	308		44.62	142.1	316.5		46.46	12.60	257.9
1,3-DNB	278	46.00	51.91	43.66	-29.66	101.3	53.79	99.02	162.7
	288		52.24	43.58	-30.05		55.37	98.94	151.3
	298		52.00	43.50	-28.51		50.86	98.85	161.0
	308		53.02	43.42	-31.17		49.89	98.77	158.7
1,4-DNB	278	60.62	46.17	58.31	43.65	60.03	47.14	57.72	38.03
	288		46.30	58.23	41.41		48.80	57.63	30.66
	298		44.19	58.14	46.80		46.81	57.55	36.05
	308		45.49	58.06	40.82		46.55	57.47	35.45

$\Delta E_P = E_{Pc} - E_{Pa}$ values for first reduction process were exactly 60 mv at hanging mercury drop electrode.

Studies on the protonation reaction of anion radicals of nitroaromatics have been carried out by many coworkers[20-23]. In the present study the anion radical is generated by reducing dinitrobenzenes (1,2-, 1,3-, 1,4-)

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

on the surface of the working electrodes *i.e.*, GCE and HMDE, 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 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).

This behaviour can be explained if we consider the resonance structures of the dinitrobenzenes as shown in Fig. 3. Looking at the resonance structures it may be seen that when

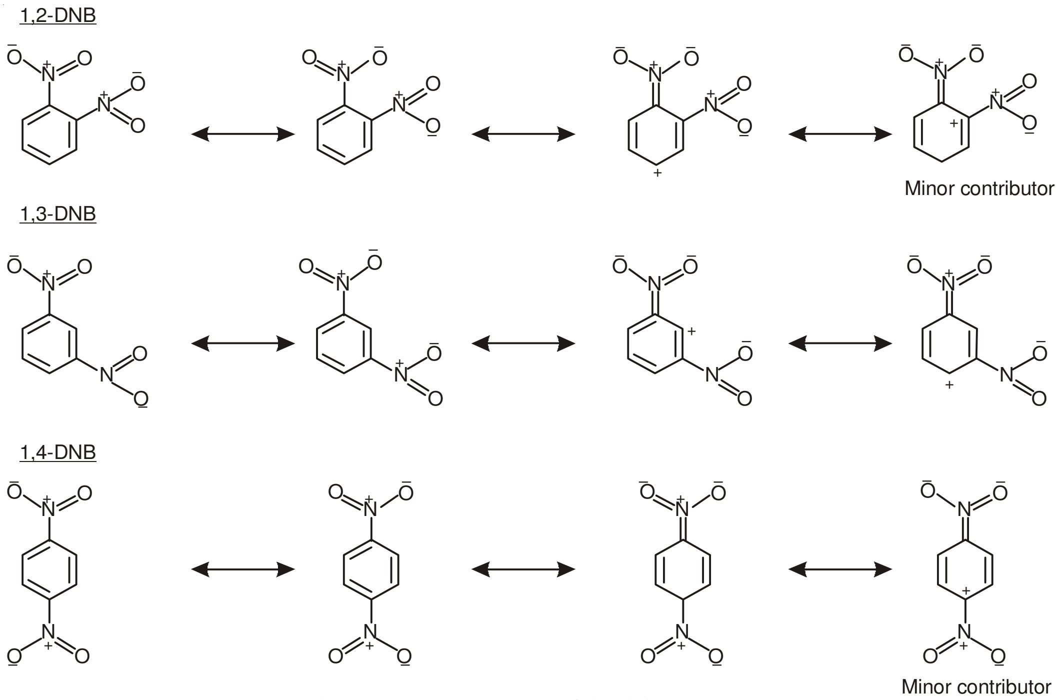


Fig. 3. Resonance structures of the dinitrobenzenes

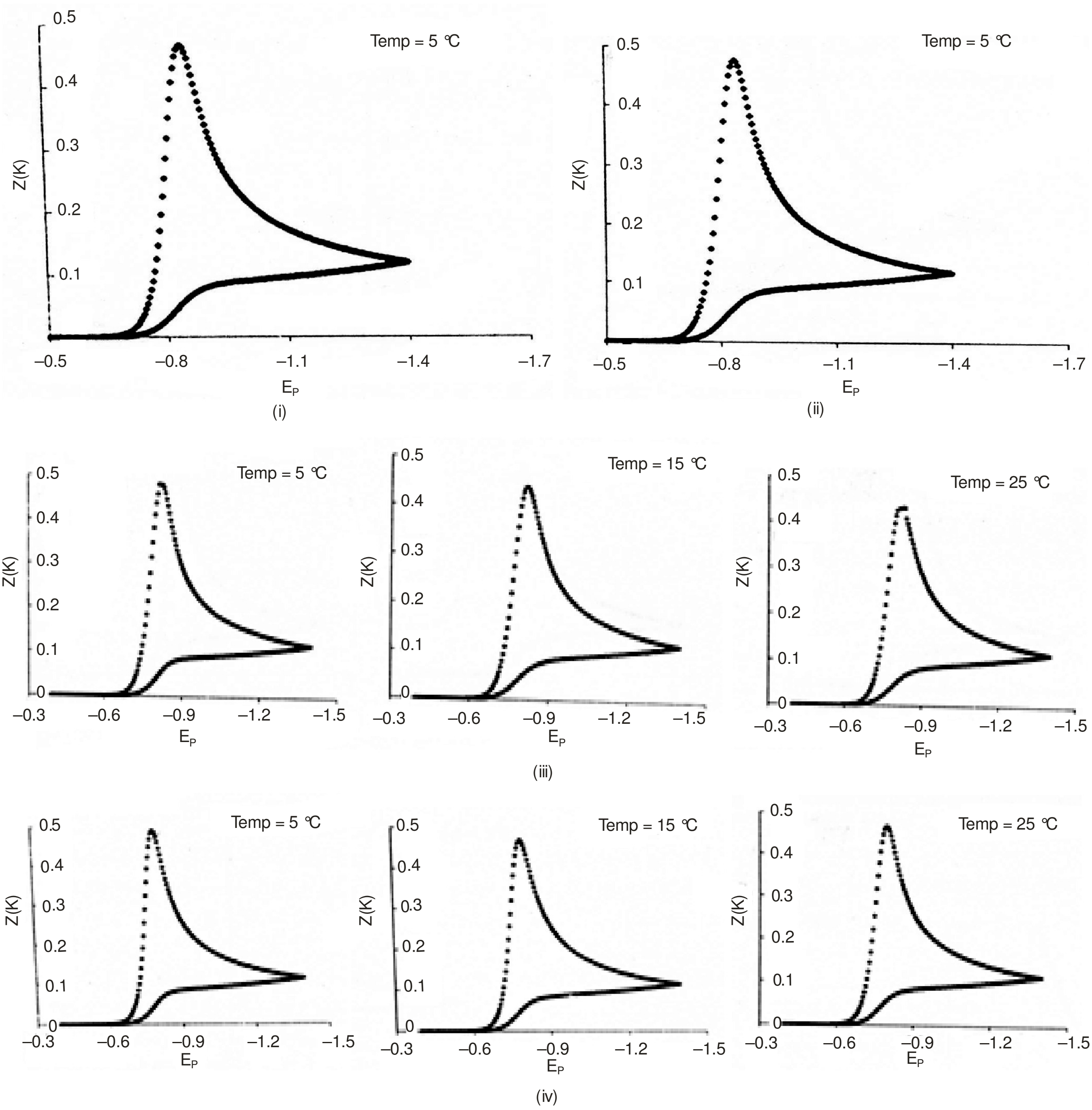


Fig. 4. (i) Simulated cyclic voltammogram of 1,2-DNB in acetonitrile at GCE (protonating agent: benzoic acid) (ii) Simulated cyclic voltammogram of 1,2-DNB in acetonitrile at HMDE (protonating agent: benzoic acid) (iii) Simulated cyclic voltammogram of 1,3-DNB in acetonitrile at GCE (protonating agent: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

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.

Digital simulation method has played an important role in the analysis of the electrochemical data[24-27]. In the present study heterogeneous electron transfer rate constant $k_{s,h}$ is calculated by simulation method as given in Tables 3 and 4. Simulated voltammograms are shown in Figs. 4 and 5.

Disproportionation for the dinitroaromatic system may be depicted as follows:

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

when benzoic acid is added as protonating agent in CH_3CN the K_D value at 5 and 15 °C of 1,2-DNB^{-} is greater than 1,4-DNB^{-} while, at 25 and 35 °C the value of disproportionation constant for 1,4-DNB^{-} becomes greater than 1,2-DNB^{-}. Same trend is observed at 25 and 35 °C with the protonating agent salicylic acid.

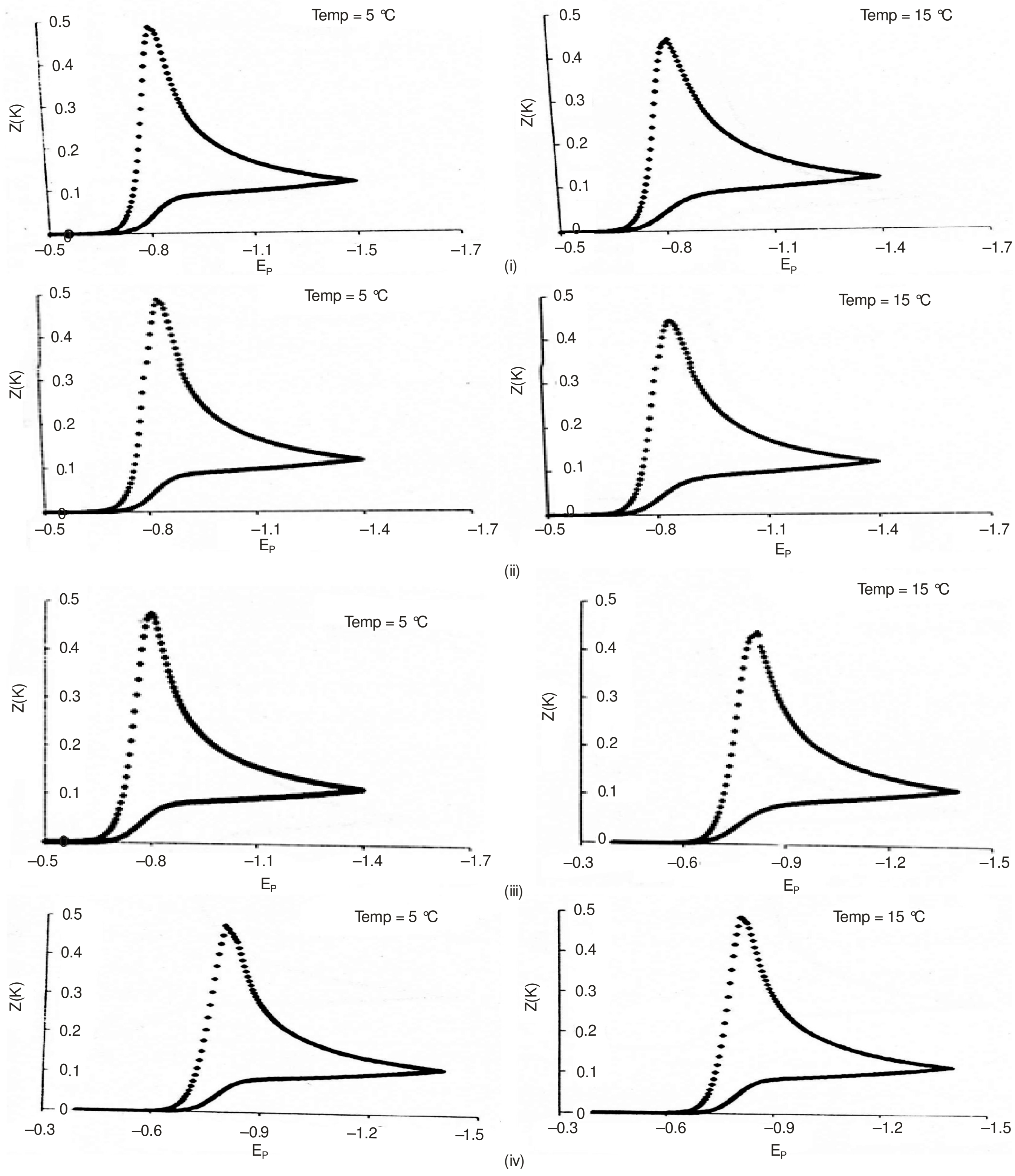


Fig. 5. (i) Simulated cyclic voltammogram of 1,2-DNB in acetonitrile at GCE (protonating agent: salicylic acid) (ii) Simulated cyclic voltammogram of 1,2-DNB in Acetonitrile at HMDE (protonating agent: salicylic acid) (iii) Simulated cyclic voltammogram of 1,3-DNB in acetonitrile at GCE (protonating agent: salicylic acid) (iv) Simulated cyclic voltammogram of 1,3-DNB in acetonitrile at HMDE (protonating agent: salicylic acid)

In order to seek information regarding the stability of the electrochemical system and its kinetic behaviour, thermodynamic and activation parameters were calculated. In addition of both protonating agents the ΔG^o values of 1,3-DNB$^-$ are higher than 1,2-DNB$^-$, 1,4-DNB$^-$ showing non spontaneous behavior, while ΔS^o are more negative indicationg decrese in disorderness. For the case of homogeneous reaction of 1,2-DNB anion radical, E_a, ΔH^* and values are found higher than for 1,3-DNB$^-$ and 1,4-DNB$^-$. In solvent acetonitrile the entropy and enthalpy of activation of 1,3-DNB$^-$ is found higher than that of 1,2-DNB$^-$. It seems that the lower value of 1,2-DNB$^-$ is due to the activated complex of 1,2-DNB$^-$ being as symmetrical and planer and more ordered. The observed decrease in ΔH^* values for the 1,4-DNB is expected as the two nitro groups are far apart.

When salicylic acid was used as protonating agent in the solvent the entropy and enthalpy of activation for the homogeneous chemical reaction of 1,2-DNB$^-$ is higher than 1,3-DNB$^-$ and 1,4-DNB$^-$. The higher values of 1,2-DNB$^-$ show that in 1,2-DNB$^-$ 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$^-$ than that of 1,3-DNB$^-$ and 1,4-DNB$^-$.

Conclusion

Nicholson and Shain polarographic method is a valid, elegant 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.

REFERENCES

1. G.H. Williams, Advances in Free Radical Chemistry, Logos Press, Academic Press, New York, vol. I (1965).
2. N.S. Kosower and E.M. Kosower, in ed.: W.A. Pryor, Free Radicals in Biology, Academic Press, New York, vol. II (1976).
3. W.J. Bowyer and D.H. Evans, *J. Org. Chem*., **53**, 5234 (1988).
4. D.H. Geske, J.L. Ragle, M.A. Bambenek and A.L. Balch, *J. Am. Chem. Soc*., **86**, 987 (1964).
5. P.H. Rieger and G.K. Fraenkel, *J. Chem. Phys*., **39**, 609 (1963).
6. J. Bard and L.R. Faulkner, Electrochemical Methods, John Wiley & Sons, New York, edn 2 (2000).
7. M. Mohammad, A.Y. Khan, M.S. Subhani, W. Begum, N. Ashraf, R. Qureshi and R. Iqbal, *Res. Chem. Intermed*., **16**, 29 (1991).
8. M.A. Syroeshkin, A.S. Mendkovich, L.V. Mikhalchenko, A.I. Rusakov and V.P. Gul'tyai, *Mendeleev Commun*., **19**, 258 (2009).
9. M.A. Syroeshkin, A.S. Mendkovich, L.V. Mikhal'chenko, A.I. Rusakov and V.P. Gul'tyai, *Russ. Chem. Bull*., **58**, 468 (2009).
10. S. Mendkovich, M.A. Syroeshkin, L.V. Mikhalchenko, M.N. Mikailov, A.I. Rusakov and V.P. Gul'tyai, *Int. J. Electrochem*., Article ID 346043 (2011).
11. M.A. Henderson, Y. Zhou, J.M. White and C.A. Mims, *J. Phys. Chem*., **93**, 3688 (1989).
12. J.T. Hupp, H.Y. Liu, J.K. Farmer, T. Gennett and M.J. Weaver, *J. Electroanal. Chem. Interfacial Electrochem*., **168**, 313 (1984).
13. K.A. Conner, T. Gennett, M.J. Weaver and R.A. Walton, *J. Electroanal. Chem*., **196**, 69 (1985).
14. M. Mohammad and M. Aslam, *J. Chem. Soc. Pak*., **33**, 12 (2011).
15. M.D. Newton and N. Sutin, *Annu. Rev. Phys. Chem*., **35**, 437 (1984).
16. D.D. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, edn 1, p. 58 (1966).
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*., **60**, 2460 (1988).
19. R.S. Nicholson and I. Shain, *Anal. Chem*., **36**, 706 (1964).
20. D.H. Evans, *Chem. Rev*., **108**, 2113 (2008).
21. Z.V. Todres, Ion-Radical Organic Chemistry: Principles and Applications, CRC Press, Taylor & Francis Group, Boca Raton, Fla, USA, edn 2 (2009).
22. A.S. Mendkovich, M.A. Syroeshkin, L.V. Mikhalchenko, A.I. Rusakov and V.P. Gultyai, *Russ. Chem. Bull*., **57**, 1492 (2008).
23. M.-J. Huang and J. Leszczynski, *J. Mol. Struct*., **592**, 105 (2002).
24. A.J. Bard and L.R. Faulkner, Electrochemical Methods, John Wiley & Sons, New York, edn 2 (2001).
25. D. Britz, Digital Simulation in Electrochemistry, Springer, Berlin (1981).
26. D.K. Gosser and P.H. Rieger, *Anal. Chem*., **60**, 1159 (1988).
27. D.K. Gosser Jr., Cyclic Voltammetry, VCH, New York and Weinheim, Germany, p. 275 (1993).