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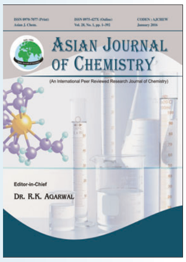

Cyclic Voltammetric Study of Protonation Reactions of Some Dinitroaromatics in Propylene Carbonate

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Cyclic voltammetric technique is used to study the protonation of anion radicals of 1,2-dinitrobenzene and 1,3-dinitrobenzene in propylene carbonate 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 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: Dinitrobenzene, Glassy carbon electrode, Hanging mercury drop electrode, Propylene carbonate.

INTRODUCTION

Cyclic voltammetry is one of the commonly employed electroanalytical techniques for the study of electro active molecules and ions, as well as their corresponding chemical reactions. This technique is also helpful in studying the kinetics and identifying the products in various electrochemical reactions [1-4]. The cyclic voltammetry is a standard technique for studying heterogeneous as well as homogenous electron transfer rates [5-8]. It provides a quantitative interpretation of the important variants of the electrochemical process in terms of their voltammetric response. Moreover, modern numerical methods facilitate calculations of voltammetric curves for complex electrochemical processes [9,10].

Nitroaromatics are considered as interesting substrates due to their applications in various pharmaceutical industries and a number of workers have carried out diverse studies on them including electron transfer kinetics [11,12]. Among the different types of electrodes, the glassy carbon electrode has been frequently applied in cyclic voltammetry for the study of reduction reactions of numerous nitro compounds in protic as well as aprotic media. The mononitro compounds undergo a chemical reaction in dipolar aprotic solvents producing an anion radical, while compounds with dinitro groups attached to an aromatic system produce an anion radical and then a dianion respectively [13].

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 dinitrobenzenes and to measure the heterogeneous electron transfer rate constants in propylene carbonate solvent at different temperatures. The substrates are the two isomers of dinitrobenzenes and the protonating agents are benzoic acid and salicylic acid.

EXPERIMENTAL

Reagent grade propylene carbonate (PC) of Fisher Scientific Company was dried over Linde 4 Å type molecular sieves, refluxed over CaO at reduced pressure (1-3 Torr) for 6 days. Then purified nitrogen was passed through it at 6 °C for one day to reduce the content of water and other low boiling components and finally distilled at 110-120 °C at reduced pressure (1-5 Torr).

All other chemicals, electrochemical cells, electrodes, instrumentation and experimental procedure are same as described earlier [14,15].

RESULTS AND DISCUSSION

Electrochemical measurements (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 as a reference electrode. All the measurements are carried out in aprotic solvent propylene carbonate at four different temperatures 5, 15, 25 and 35 °C. Tetra *n*-butyl ammonium perchlorate (TBAP) is used as a supporting electrolyte.

The reaction of the anion radical of dinitrobenzene with the protonating agent (HA) is shown in our previous work [14,15].

Cyclic voltammograms of substrates (dinitrobenzenes) are recorded in two steps: 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) was 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 Table-1.

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. 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 values are given in Table-2.

Disproportionation constant (K_D) and thermodynamic parameters are calculated by the equations as reported [14,15]. Values are given in Table-3.

Activation energy, E_a, of protonating step is obtained by plotting ln k_2 *vs.* 1/T in accordance with Arrhenius equation for the reaction rate. Other activation parameters such as free energy of activation, enthalpy of activation and entropy of activation are calculated in similar manner as in our previous research articles [14,15]. Activation parameters are given in Table-4.

Voltammograms of dinitrobenzenes in aprotic solvent propylene carbonate show typically two reversible waves. The first and the second waves correspond to the formation of radical anion and dianion respectively. The compound 1,2-dinitrobenzene shows two reductions peaks in solvent propylene carbonate but the anodic peak corresponding to the first cathodic peak was not observed in both the cases *i.e.*, at glassy carbon electrode and at hanging mercury drop electrode. The absence of the anodic peak for the first reduction process could be due to either irreversible electron transfer or coupled chemical reaction. The former possibility *i.e.*, irreversible electron transfer is ruled out as E_p-$E_{p/2}$ values observed ranged between 60 to 70 mV at the glassy carbon electrode and 40 to 43 mV at the hanging mercury drop electrode. For the second reduction process, the cathodic peak was quite dragged or drawn out, indicating an irreversible behaviour. The Ep_c-Ep_a values ranged between 200 to 230 mV while, E_p-$E_{p/2}$ values were found to be between 100 to 150 mV. In the first reduction process the absence of anodic peak shows that the first reduction product (the monoanion) is very reactive causing the second peak's appearance to be drawn out. The peak could be due to some reaction product and not due to dinitrobenzene dianion (DNB^{2-}).

The compound 1,3-dinitrobenzene also showed two reversible peaks in the propylene carbonate solvent. Both the processes (first and second reductions) showed reversible behaviour in the temperature range 5-35 °C. The E_{pc}-E_{pa} values were found between 60 to 65 mV for the 1st reduction process at both the glassy carbon electrode and the hanging mercury

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 PROPYLENE CARBONATE (SCAN RATE: 50 mV)

Compound	Concentration of protonating agent (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})
Benzoic acid						
1,2-Dinitrobenzene	1.0×10^{-2}	5	(-0.053±0.009)	(1.55±0.98)×10	(-0.024±0.008)	$(1.62\pm0.94)\times10^{2}$
		15	(0.053±0.006)	(1.82±0.36)×10	(0.023±0.007)	$(1.71\pm0.87)\times10^{2}$
		25	(0.052±0.007)	(1.87±0.93)×10	(0.018±0.007)	$(2.65\pm1.32)\times10^{2}$
		35	(0.047±0.012)	(3.70±2.70)×10	(0.014±0.008)	$(3.72\pm2.01)\times10^{2}$
1,3-Dinitrobenzene	1.0×10^{-2}	5	(-0.034±0.009)	(7.57±4.82)×10	(0.004±0.008)	$(8.07\pm3.73)\times10^{2}$
		15	(0.022±0.007)	$(1.90\pm0.97)\times10^{2}$	(0.007±0.008)	$(2.06\pm1.17)\times10^{3}$
		25	(0.034±0.007)	$(15.20\pm7.56)\times10^{3}$	(0.043±0.009)	$(3.34\pm2.20)\times10^{4}$
		35	(0.046±0.007)	$(3.31\pm1.60)\times10^{4}$	(0.059±0.007)	$(8.81\pm4.26)\times10^{4}$
Salicylic acid						
1,2-Dinitrobenzene	1.0×10^{-2}	5	(-0.030±0.005)	(8.88±3.51)×10	(-0.030±0.009)	$(1.05\pm0.67)\times10^{2}$
		15	(-0.013±0.009)	$(4.31\pm2.67)\times10^{2}$	(-0.027±0.010)	$(1.46\pm0.98)\times10^{2}$
		25	(-0.001±0.008)	$(1.03\pm0.57)\times10^{3}$	(-0.024±0.008)	$(1.72\pm0.95)\times10^{2}$
		35	(0.039±0.010)	$(2.22\pm1.41)\times10^{4}$	(0.015±0.006)	$(3.09\pm1.31)\times10^{2}$
1,3-Dinitrobenzene	1.0×10^{-2}	5	(-0.019±0.008)	$(2.52\pm1.47)\times10^{2}$	(-0.013±0.010)	$(4.05\pm2.77)\times10^{3}$
		15	(-0.007±0.012)	$(8.26\pm6.18)\times10^{2}$	(0.019±0.008)	$(5.43\pm3.08)\times10^{3}$
		25	(0.015±0.010)	$(3.96\pm2.58)\times10^{3}$	(0.020±0.012)	$(6.51\pm4.77)\times10^{3}$
		35	(0.019±0.013)	$(5.74\pm4.33)\times10^{3}$	(0.027±0.010)	$(8.97\pm5.72)\times10^{3}$

TABLE-2
HETEROGENEOUS RATE CONSTANT FOR THE ISOMERS OF DINITROBENZENE FOR FIRST REDUCTION PROCESS IN PROPYLENE CARBONATE 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 (mV)	k_f (s^{-1})	RKS	HKO (cm s^{-1})
Benzoic acid									
1,2-Dinitrobenzene	5	-0.740	0.155	20.00	0.2110	-0715	1.62	22.0	0.2319
	15	-0.730	0.182	24.00	0.2529	-0.715	1.71	30.00	0.3162
	25	-0.730	0.187	21.00	0.2214	-0.715	2.65	26.00	0.2741
	35	-0.730	0.370	24.00	0.2530	-0.715	3.72	20.00	0.2108
1,3-Dinitrobenzene	5	-0.820	0.757	25.00	0.2635	-0.820	8.07	1.00	0.0105
	15	-0.820	1.92	35.00	0.3162	-0.820	20.60	11.00	0.1159
	25	-0.840	152.0	–	–	-0.820	334.0	–	–
	35	-0.840	331.0	–	–	-0.830	881.0	–	–
Salicylic acid									
1,2-Dinitrobenzene	5	-0.830	0.888	28.00	0.2952	-0.810	1.05	30.00	0.3162
	15	-0.840	4.31	22.00	0.2319	-0.820	1.46	29.00	0.3057
	25	-0.845	10.30	10.00	0.0316	-0.825	1.72	29.00	0.3057
	35	-0.880	222.0	24.00	0.2530	-0.835	3.09	23.00	0.2424
1,3-Dinitrobenzene	5	-0.810	2.52	34.00	0.3584	-0.815	40.50	–	–
	15	-0.815	8.26	10.00	0.1054	-0.830	54.30	–	–
	25	-0.845	39.60	–	–	-0.820	65.10	–	–
	35	-0.840	57.40	–	–	-0.845	89.70	–	–

[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 FOR DINITROBENZENE IN PROPYLENE CARBONATE

Compound	Temp. (K)	Glassy carbon electrode				Hanging mercury drop electrode			
		-ln K_D	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1})	-ΔS° (J K^{-1} mol^{-1})	-ln K_D	ΔG° (kJ mol^{-1})	ΔH° (J mol^{-1})	-ΔS° (J K^{-1} mol^{-1})
Benzoic acid									
1,2-Dinitrobenzene	278	7.18	16.59	5.15.3	57.82	7.78	17.97	503.5	62.84
	288	7.12	17.05		59.20	6.70	16.04		55.71
	298	6.02	14.91		50.05	6.63	16.42		55.11
	308	5.87	15.04		48.83	6.18	15.84		51.42
1,3-Dinitrobenzene	278	4.88	11.27	173.5	39.91	4.49	10.39	156.7	36.81
	288	4.71	11.27		39.13	4.32	10.35		35.93
	298	4.50	11.14		37.40	4.21	10.43		35.01
	308	4.38	11.23		36.45	4.02	10.31		33.46
Salicylic acid									
1,2-Dinitrobenzene	278	7.39	17.09	544.5	59.53	7.78	17.97	628.7	62.39
	288	6.93	16.59		57.60	7.07	16.92		58.77
	298	6.39	15.84		53.14	6.66	16.51		55.39
	308	5.81	14.87		48.29	5.87	15.04		48.83
1,3-Dinitrobenzene	278	4.59	10.60	40.60	37.98	3.84	8.88	112.6	31.54
	288	4.58	10.98		38.11	4.29	10.26		35.64
	298	4.50	11.14		37.39	4.13	10.22		34.30
	308	4.48	11.15		37.27	4.25	10.89		35.36

drop electrode while, the E_{pc}-E_{pa} values for the second reduction process were found between 100 to 120 mV. In the later case, there may be some electrode kinetic effect as well [16].

In the present study the anion radical is generated by reducing dinitrobenzenes (1,2-DNB, 1,3-DNB):

$$\mathrm{DNB} + \bar{e} \rightleftharpoons \mathrm{DNB}^{\cdot-} \tag{1}$$

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

It is observed that cathodic peak shifted anodically and the anodic peak completely disappeared when the protonating agent is added. From the resulting voltammograms, the pseudo first order rate constant is calculated. In this case, 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 k_f/a ratio occurred when protonating agent was added. From the shift in the peak potential (E_p-$E_{1/2}$) the

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

Compound	Temp. (K)	Glassy carbon electrode				Hanging mercury drop electrode			
		E_a (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})	E_a (kJ mol^{-1})	ΔG^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
Benzoic acid									
1,2-Dinitrobenzene	278	18.51	61.59	16.20	-163.2	207.2	56.16	18.40	-135.8
	288		63.50	16.12	-164.5		58.14	18.32	-138.5
	298		65.72	16.03	-166.7		59.16	18.34	-137.3
	308		66.27	15.95	-163.4		60.34	18.16	-137.0
1,3-Dinitrobenzene	278	16.10	57.92	158.7	362.4	119.9	52.45	117.6	234.4
	288		57.89	158.6	349.6		52.18	117.5	227.0
	298		49.12	158.5	367.0		47.17	117.5	235.9
	308		48.86	158.4	355.7		46.36	117.4	230.6
Salicylic acid									
1,2-Dinitrobenzene	278	123.3	57.55	121.0	228.3	72.11	57.16	69.80	45.46
	288		55.92	120.9	225.7		58.52	69.72	38.90
	298		55.78	120.8	218.3		60.23	69.64	31.58
	308		49.89	120.8	230.1		54.94	69.55	47.46
1,3-Dinitrobenzene	278	78.25	55.14	76.00	74.81	18.25	48.72	15.94	-117.9
	288		54.37	75.85	74.61		49.86	15.85	-118.1
	298		52.46	75.77	78.24		51.22	15.77	-119.0
	308		53.35	75.69	72.53		52.21	15.69	-118.6

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).

When the protonating agent was salicylic acid, in propylene carbonate solvent the observed rate constant for 1,3-dinitrobenzene was higher than 1,2-dinitrobenzene when measured with the two electrodes (glassy carbon electrode and hanging mercury drop electrode) at 5 to 35 °C. 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 saturated calomel electrode may bring about a change in the environment near the electrode and stabilize the anion radical.

Disproportionation for the dinitroaromatic system may be depicted as follows:

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

Disproportionation constant (K_D) values for dinitroaromatics are given in Table-3. In the solvent propylene carbonate disproportionation constant for the anion radical of 1,3-dinitrobenzene is greater than 1,2-DNB$^{\cdot-}$ at all the temperatures selected for the present study. When the protonating agent is salicylic acid, the similar trend is observed.

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

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

The role of solvent is very important in determining the rate of electron transfer in solution [17]. 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 very pronounced effect on the kinetics of the electron transfer reactions [18]. On the other hand, substantial changes of electron transfer rate constants are solely observed for the dinitrobenzenes due to solvent polarity.

The dipole moment 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 the dielectric constant "ε". In order to minimize the solution resistance, solvents with substantially higher dielectric constants should be used preferably in electrochemical work. This will also minimize ohmic losses and diminish the problem of potential control error. 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. 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 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 self consistent field-Unrestricted Hartree-Fock (SCF-UHF) and Modified Neglect of Diatomic Overlap (MNDO) methods and equation is

$$\lambda_o = \frac{1}{2}\left(\frac{1}{\varepsilon_o} - \frac{1}{\varepsilon}\right)\left(\frac{q_1^2}{a_1} + \frac{q_2^2}{a_2} + \frac{2q_1q_2}{R_{12}}\right) \quad (3)$$

where, ε_o and ε are optical and effective dielectric constants respectively; q_1 and q_2 are charge 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 [19]. 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 [20].

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

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

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:

$$\Delta G^o_{th} = \frac{[\lambda + w_p]^2}{4\lambda} \quad (5)$$

The dielectric constant for an interfacial phase, however, is entirely different from the bulk phase [20] 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 for as heterogeneous rate constant is concerned the local environment of solvent molecules around the initial and transition states is most important. So instead of taking the bulk dielectric constant it is more appropriate to take an effective dielectric constant (for the evaluation of λ_o) [21]. The expression for the variation of dielectric constant as a function of distance from the centers of the charged ion is given by Booth [22] and it has been adopted for the present study. In order to study the electrode reactions, Booth's expression was used after some modifications [23]. The charge of the ion (Z) was 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). Thus, the value of ε for propylene carbonate has been considered as an effective dielectric constant in contrast to the values of 64.40 for the bulk dielectric constant. The rate constants calculations were carried out by using these values of effective dielectric constants. The theoretical heterogeneous rate constant $k^{th}_{s,h}$ is calculated from the equation

$$k^{th}_{s,h} = Z_{el} \exp\left(-\frac{\Delta G^o_{th}}{kT}\right) \quad (6)$$

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

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

Compound	$\lambda_i^{SCF-UHF}$	q_1	q_2	w	Z_{het} (cm s^{-1})	λ_o (eV)	ΔG^o_{th} (eV)	$k^{th}_{s,h}$ (cm s^{-1})
Benzoic acid								
1,2-Dinitrobenzene								
$\varepsilon = 36.12$	0.076	-0.371	-0.258	0.119	4843	0.266	0.266	0.150
$\varepsilon_o = 64.40$		-0.371	-0.258			0.270	0.270	0.125
1,3-Dinitrobenzene								
$\varepsilon = 36.12$	0.042	-0.370	-0.260	0.000	4843	0.727	0.192	2.660
$\varepsilon_o = 64.40$		-0.370	-0.260			0.756	0.197	2.210
Salicylic acid								
1,2-Dinitrobenzene								
$\varepsilon = 36.12$	0.076	-0.371	-0.258	0.119	4843	0.266	0.266	0.150
$\varepsilon_o = 64.40$		-0.371	-0.258			0.270	0.270	0.125
1,3-Dinitrobenzene								
$\varepsilon = 36.12$	0.042	-0.370	-0.260	0.000	4843	0.727	0.192	2.660
$\varepsilon_o = 64.40$		-0.370	-0.260			0.756	0.197	2.210

The analysis of electrochemical data can be performed by employing various digital simulation methods [24]. In the present study, heterogeneous electron transfer rate constant $k_{s,h}$ was calculated by simulation method. The results of these $k_{s,h}$ are presented in Table-5.

Conclusion

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.

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