

HETEROGENEOUS ELECTRON TRANSFER RATE CONSTANTS FOR THE SECOND REDUCTION PROCESS OF SOME DINITROAROMATICS

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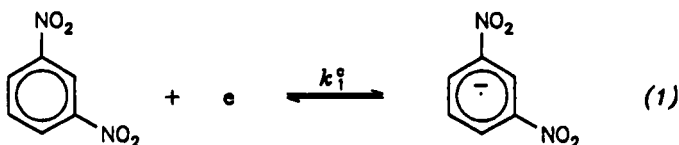
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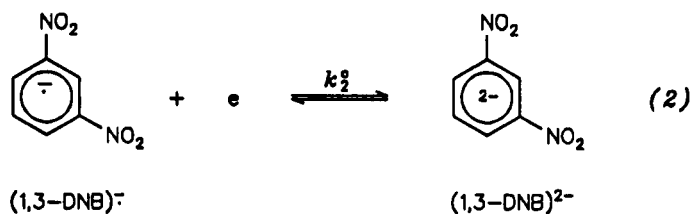
Standard heterogeneous electron transfer rate constants k^0 for the second reduction process of 1,2-, 1,3-, and 1,4-dinitrobenzenes were evaluated by the Gilcadi method. The temperature dependences of k^0 were investigated using Marcus' and other expression for ΔG^* . However, it was found that to explain the values of k^0 and its variation with temperature, it might be prudent to take into consideration the dielectric constant near the site of the reactant (the anion radical) and the product (the dianion).

The heterogeneous electron transfer rate constant is of theoretical as well as technological interest. Because of the development of the theory for the heterogeneous electron transfer process and its technological application, interest has grown in the recent past in the determination of the heterogeneous electron transfer rate constant¹⁻⁵.

Interestingly, studies in the determination of the heterogeneous rate constant k^0 have been mostly confined to the first reduction process¹⁻⁴. Very rarely attempt has been made to determine k^0 for the second reduction process⁵⁻⁷. The obvious reasons are that the reduced moieties produced are very reactive and the second reduction processes are generally coupled with chemical reactions. Nevertheless, there are compounds, for example dinitroaromatics⁶⁻⁷, which follow well defined reversible electrode processes. Equations (1) and (2) show the electrochemical processes which e.g. 1,3-dinitrobenzene (1,3-DNB) undergoes



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where $(1,3\text{-DNB})^{\bullet-}$ is the radical anion and $(1,3\text{-DNB})^{2-}$ the dianion. Thus dinitroaromatics are most suitable compounds for the determination of the heterogeneous electron transfer rate constant, k_2^0 , for the second reduction process (Eq. (2)).

In view of the importance of the heterogeneous electron transfer rate constants, several experimental (electrochemical) techniques have been developed e.g. cyclic voltammetry, AC impedance and polarography, digital simulations etc.⁸⁻⁹. A review of these techniques is available¹⁰. Of the various techniques used for determining k_2^0 , cyclic voltammetry is well established and had the advantage of being rapid and reliable. In the present report we present the results of our studies on the determination of heterogeneous electron transfer rate constants of the second reduction process of 1,2-, 1,3-, and 1,4-dinitrobenzenes utilizing cyclic voltammetry. Rate constants (k_2^0) were determined at various temperatures and an attempt is made to interpret results in the light of Marcus and related theories¹⁻⁵.

EXPERIMENTAL

Chemicals. Spectrograde dimethylformamide used as a solvent was dried over preheated molecular sieve^{6,11-12}. Tetrabutylammonium perchlorate (TBAP) (Fisher) was used without further purification. Dinitrobenzenes (DNB) were purified by standard methods¹¹. 1,2-Dinitrobenzene (m.p. 117 °C, ref.¹¹ 118.5 °C), 1,3-dinitrobenzene (m.p. 89.5 °C, ref.¹¹ 90.0 °C), 1,4-dinitrobenzene (m.p. 173 °C, ref.¹¹ 174 °C).

Nitrogen gas was purified by passing through traps of vanadous sulfate over zinc amalgam, water, paraquat + zinc in dimethylformamide, molecular sieve and dimethylformamide. Generally 1 mM solutions of DNB with 0.1 M TBAP were used for recording cyclic voltammogram.

In all the cases reversible waves for first as well as second reduction processes (Eqs (1) and (2)) were obtained (Fig. 1) confirming the absence of protonation of the radical anion and dianion.

Instrumentation. Cyclic voltammograms were recorded using Princeton Applied Research Polarographic analyzer 174A in conjunction with an X-Y recorder for slow scan rates (20, 50, 100, 200, 500 mV/s). For faster scan rate (0.5, 1.0, 2, 10, 20 V/s) PAR Universal Programmer 175, potentiostat 173 and Tektronix model 564 storage oscilloscope with differential amplifiers 5A20, 5B10N were used.

Hanging mercury drop electrode fabricated as described earlier¹³ was used as working electrode. Counter electrode was a thick platinum wire while calomel electrode was used as a reference electrode. A thermostat (LAUDA K-4R) was used for controlling temperature.

The three voltammetric methods generally used in determining the standard heterogeneous rate constant k^0 are a) Nicholson¹⁴ method of potential separation ΔE_p as modified by Schmitz¹⁵, b) $E_p^a - E_p^c$ method of Kochi¹⁶ and c) Gileadi¹⁷ method of relationship between k^0 and critical scan rate. All the three methods were employed but the Gileadi methods was preferred.

Gileadi method¹⁷ is simple for the evaluation of k^0 . In this method transition to an irreversible process is observed. If the peak potential is drawn against the logarithm of the scan rate (Fig. 2), the curve is horizontal for low scan rates. For sufficiently high scan rates an ascending linear branch is obtained. The toe of this second branch, formed by the linear extrapolation, is the critical scan rate V_c which is a measure of k^0 according to Eq. (3):

$$\log k^0 = -0.48 \alpha + 0.52 + 1/2 \log [(nFD\alpha V_c) / (2.303 RT)] , \quad (3)$$

where D is the diffusion coefficient and α is the transfer coefficient.

RESULTS AND DISCUSSION

In Table I, $E_{1/2}$ values of the three isomeric dinitrobenzenes are collected. In Table II, $(E_p)_c$, ΔE_p and k^0 , as calculated by Nicholson method for the second step reduction process (anion radical reduced to dianion, Eq. (2)) of 1,2-DNB at 25 °C are collected as an illustrative example. From ΔE_p and other similar data for the three isomeric dinitrobenzene anion radical at 278, 288, 298 and 308 K, k^0 were calculated and are included in Table III.

In Table IV, the experimental free energies of activation (ΔG^*) obtained from Eq. (4) are collected together with thermal velocities (Z) of reacting particles (Eq. (5)):

$$k^0 = Ze^{-\Delta G^*/kT} \quad (4)$$

$$Z = [(kT)/(2\pi m)]^{1/2} , \quad (5)$$

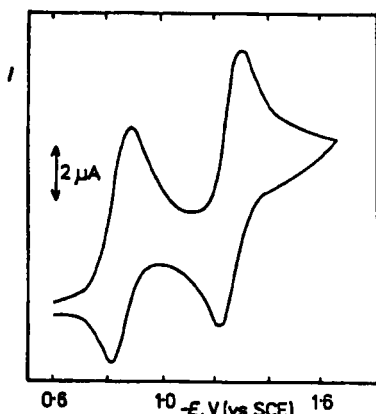


FIG. 1
Cyclic voltammogram of 1,3-DNB in DMF. Scan rate 50 mV/s, temperature 298 K

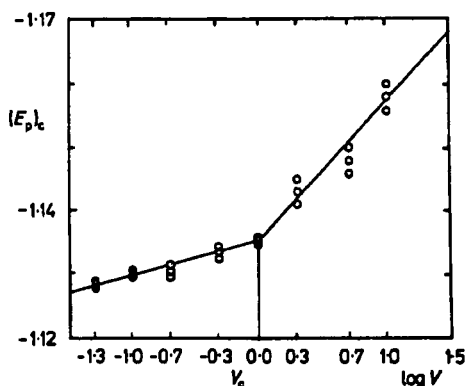


FIG. 2
Gileadi plot: $(E_p)_c$ vs $\log V$ for 1,2-DNB. V scan rate (V/s), V_c critical scan rate at 308 K

where m is the mass of the reacting particle.

According to the Marcus theory, ΔG^* is given¹ by

$$\Delta G^* = \lambda/4 = (\lambda_i + \lambda_o)/4, \quad (6)$$

where λ_i and λ_o are the inner and outer reorganization energies.

TABLE I
Electrochemical data for the three isomeric dinitrobenzenes $E_{1/2}$ (in V) vs SCE; D_0 in m^2/s

Compound	Temperature, K	$E_{1/2}$	$(E_{1/2})_2$	$(E_{p_2})_c$
1,2-DNB	288		-1.052	-1.078
	298	-0.755	-1.075	-1.100
	308		-1.132	-1.148
	288		-1.251	-1.281
1,3-DNB	298	-0.850	-1.263	-1.284
	308		-1.277	-1.320
	288		-0.878	-0.906
1,4-DNB	298	-0.617	-0.896	-0.920
	308		-0.920	-0.940

TABLE II
Heterogeneous electron transfer rate constant k^0 (in 10^{-2} cm/s) for 1,2-DNB at 298 K, Nicholson method. Scan rate in V/s; $(E_p)_c$ (in V) vs SCE

Scan rate	$-(E_p)_c$	E_p	k^0 ^a
0.05	1.100	0.070	1.38
0.1	1.105	0.078	1.15
0.2	1.110	0.085	1.09
0.5	1.122	0.090	1.40
1.0	1.125	0.093	1.80
2.0	1.129	0.101	1.93
5.0	1.132	0.129	1.65
10.0	1.140	0.149	1.76

^a Avc 1.52 ± 0.30 .

TABLE III
Temperature dependance of heterogeneous electron transfer rate constant k^0 (in 10^{-2} cm/s). Scan rates given in the text, scan rates above 20 000 mV/s gave results, thus excluded

Compound	Method	Temperature, K			
		278	288	298	308
1,3-DNB	Gileadi ^a	–	0.56	0.68	0.81
	Nicholson– Schmitz ^b	–	0.65 (±0.20)	0.79 (±0.20)	1.05 (±0.55)
1,2-DNB	Gileadi	2.2	1.77	1.37	1.22
	Nicholson– Schmitz	2.45 (±0.76)	1.91 (±0.48)	1.52 (±0.30)	1.35 (±0.30)
	Gileadi	1.27	1.25	1.23	1.08
1,4-DNB	Nicholson– Schmitz	1.40 (±0.60)	1.31 (±0.25)	1.28 (±0.32)	1.14 (±0.25)

^a Maximum error 10%; ^b for comparison, note the error in k^0 .

TABLE IV
Experimental values of chosen thermodynamic characteristics of the systems under study ($k^0 = Z \exp(-\Delta G^*/kT)$, $Z = (kT/2\pi m)^{1/2}$ (1 eV = $1.66 \cdot 10^{-19}$ J))

Compound	Temperature, K	k^0 10^{-2} cm/s	Z_{bet} cm/s	ΔG^* eV	$k^0 T^{1/2}$
1,2-DNB	308	1.22	4 923	0.343	0.214
	298	1.37	4 842	0.328	0.236
	288	1.77	4 760	0.310	0.300
	278	2.21	4 677	0.294	0.368
1,3-DNB	308	0.81	4 923	0.354	0.142
	298	0.68	4 842	0.346	0.117
	288	0.66	4 760	0.339	0.095
1,4-DNB	308	1.08	4 923	0.346	0.189
	298	1.23	4 842	0.331	0.212
	288	1.25	4 767	0.319	0.212
	278	1.27	4 677	6.307	0.212

Since $\lambda_i < 0.1 \lambda_0$ it may be assumed that

$$\Delta G^* \approx \lambda_0/4 \quad (7)$$

$$\lambda_0 = (e_0^2 / 8\pi\epsilon_0 a) [(1/n^2) - (1/\epsilon)] , \quad (8)$$

where e_0 is the charge of an electron, ϵ_0 is the permittivity of the vacuum, n is the refractive index, ϵ is the static dielectric constant and a is the radius of the electroactive species ΔG_T^* (i.e. ΔG^* at various temperatures) can be computed if n and ϵ are known at various temperatures.

One can calculate entropy of activation from the relationship

$$\partial\Delta G^*/\partial T = -\Delta S^* . \quad (9)$$

Since λ_i is independent of temperature, ΔS^* may be obtained according to Eq. (9) from Eq. (6) or Eqs (7) and (8). Hence

$$\Delta S^* = (-e_0^2 / 32\pi\epsilon_0 a) (\partial/\partial T) [(1/n^2) - (1/\epsilon)] \quad (10)$$

$$= (-e_0^2 / 32\pi\epsilon_0 a) B . \quad (11)$$

In order to calculate ΔS^* from Eq. (11) the coefficient B for DMF is required which according to Russel and Jaenicke¹⁸ is $1.2 \cdot 10^{-4} \text{ K}^{-1}$. Thus calculated ΔS^* from the experimental ΔG^* values of Table IV are collected in Table V.

It is clear from Table V that ΔS^* (experimental) and ΔS^* (theoretical) values do not agree at all. The result is in total contrast to the results obtained for pyrazine derivatives by Russel and Jaenicke¹⁸. The reasons for this disparity in the case of the second reduction process of dinitrobenzene may be qualitatively investigated.

Obviously either the simple expression for ΔG^* (Eqs (6) and (7)) does not apply to the present case or else the use of the bulk dielectric constant and its variation with

TABLE V

Radius of the neutral molecule and experimental (Eq. (9)) and theoretical (Eq. (11)) entropy of activation ΔS^* (in the units of k Boltzman constant, value of B for DMF is $1.62 \cdot 10^{-4} \text{ K}^{-1}$)

Compound	a , pm	$-\Delta S_{\text{exp}}^*$	$-\Delta S_{\text{theor}}^*$
1,3-DNB	348	8.7 ± 3.0	1.09
1,2-DNB	330	18.6 ± 2.0	0.99
1,4-DNB	345	15.1 ± 2.2	1.0

temperature is inapplicable, or both. Furthermore, the temperature dependence of pre-exponential factor could be other than that given in Eq. (5) (ref.¹⁹).

According to Marcus theory ΔG^* is given by¹⁻⁵

$$\Delta G^* = w_0 + (w_R - w_0 + \lambda)^2/4\lambda, \quad (12)$$

where w_0 is the work required to transport the reactant [O] from the bulk of the electrolyte to the plane at which electron transfer occurs. Similarly w_R is defined for the product [R]. Obviously Eqs (6) and (7) are the simplified versions of Eq. (12) i.e., w_0 and w_R are assumed very small as compared to λ . Generally w_0 and w_R are quite small. For example, $w_0 = 0$ and $w_R > 0$, but small for R/R⁻ system studied by Russel and Jaenicke¹⁸.

Parameter w is given²⁰ by $Ze\Phi_2$, where Φ_2 is the potential at the outer Helmholtz plane at which the electron transfer is assumed to occur. The Gouy–Chapman–Stern diffuse layer model enables in obtaining Φ_2 . It varies with temperature since the debye length (X) is temperature dependent. In the present case neither w_0 nor w_R is zero and their temperature coefficient may not be zero as well.

The second factor influencing k^0 and its temperature dependence is contained in Eq. (8). According to Marcus theory ϵ is the bulk dielectric constant. The dielectric constant for an interfacial phase, however, is entirely different from the bulk phase²¹⁻²⁴ and it is the interfacial dielectric constant which may be relevant here. Furthermore it has been shown by detailed calculations on some redox systems¹⁰ that ϵ in Eq. (8) does not represent the bulk dielectric constant but it is a Langevin function of distance. It was found that at OHP (the reaction site) the dielectric constant for DMF is 6 in contrast to the value of 36 for the bulk dielectric constant¹⁰. Temperature coefficient of the dielectric constant at the reaction site is not known but it may be substantial. It seems that in the case of substituted pyrazines¹⁸ there is some cancellations of these contributions and hence the agreement in ΔS_{exp}^* and $\Delta S_{\text{theor}}^*$ is obtained. In the present case the reduction of dinitrobenzene anion radicals to dianions does not lead to cancellation of the various contributions. Also the dianions having $Z = 2$ will polarize

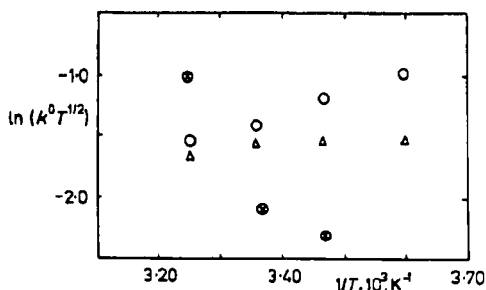


FIG. 3

The dependence of $\ln(k^0 T^{1/2})$ vs $1/T$ for 1,2-DNB (O), 1,3-DNB (●) and 1,4-DNB (Δ)

the surrounding medium more strongly than the monoanion radicals. Hence the dielectric constant of the surrounding may be entirely different from the bulk dielectric constant. Furthermore, if the reaction site varies with temperature, getting closer to the electrode at lower temperature, then the dielectric constant will be also lower. As a result λ_0 (i.e. $\Delta S_{\text{theor}}^{\ddagger}$) decreases and hence the rate constant is increased at lower temperature as observed in the cases of 1,2-DNB and 1,4-DNB.

As mentioned above Jaenicke¹⁸⁻¹⁹ investigated the temperature dependence of k^0 in the light of Marcus theory with pre-exponential factor as given in Eqs (4) and (5) (ref.¹⁸) and Eq. (13) (ref.¹⁹).

$$k^0 = K_{el} \delta r \tau_L^{-1} (\lambda_0 / 16 \pi k T)^{1/2} \exp [-(\lambda_0 + \lambda_i) 4kT], \quad (13)$$

where K_{el} is the (electronic) transmission coefficient, and δr is the small range of distance in which the electron transfer occurs, τ_L is the longitudinal relaxation time of the given solvent. In this expression the pre-exponential and exponential terms both are temperature dependent. Also τ_L depends upon temperature¹⁹.

$$\tau_L^{-1} = A_L \exp [-H_L / kT] \quad (14)$$

Thus a simple expression for the temperature dependence of k^0 can not be obtained. However, as pointed out by Kapturkiewicz and Jaenicke¹⁹ if the temperature dependence of λ_0 is ignored (being small), a plot between $\ln(k^0 T^{1/2})$ and $1/T$ would be linear with the slope equal to $1/k [\lambda_i/4 + \lambda_0/4 + H_L]$ and intercept equal to $A_L K_{el} \delta r (\lambda_0 / 16 \pi k)^{1/2}$. While Kapturkiewicz and Jaenicke did obtain the expected linear plots for their system¹⁹, unfortunately the same was not true in the present case (see Fig. 3, wrong slope). Thus it seems the expression given in Eq. (13) does not explain the behaviour of temperature dependence of k^0 for the second reduction process of dinitroaromatics. Or else the mechanism of the electron transfer for the three isomers is not the same.

It is hence concluded that in order to explain the standard heterogeneous electron transfer rate constant k_2^0 for the second reduction process (Eq. (8)) by Marcus theory it may be prudent to consider the dielectric constant near the reaction site and the work terms of the reactant and the product.

REFERENCES

1. Hale J. M. in: *Reaction of Molecules at Electrodes* (N. S. Hush, Ed.), p. 229. Wiley, New York 1971.
2. Mohammad M., Khan A. Y., Qureshi R., Iqbal R.: *Bull. Electrochem. J.* 429 (1985).
3. Kojima H., Bard A. J.: *J. Electroanal. Chem.* 63, 117 (1975).
4. Yoshimori A., Kakitani T., Mataga N.: *J. Phys. Chem.* 93, 3694 (1989).
5. Russel C., Jaenicke W.: *Z. Phys. Chem. (Neue Folge)* 139, 97 (1984); *J. Electroanal. Chem.* 199, 139 (1986).
6. Mohammad M., Dost N. P., Jalil M., Qureshi R., Saleem M., Khan A. Y.: *Bull. Electrochem.* 4, 287 (1988).

7. Geski D. H., Maki A. H.: *J. Am. Chem. Soc.* **82**, 2671 (1960).
8. Bard A. J., Faulkner L.: *Electrochemical Methods*. Wiley, New York 1980.
9. Mohammad M., Ashraf N., Begum W., Qureshi R., Khan A. Y.: *Bull. Electrochem.* **4**, 75 (1988).
10. Qureshi R.: *Thesis*. Quaid-i-Azam University, Islamabad, Pakistan 1990.
11. Perrin D. D., Armargo W. L. F., Perrin P. R.: *Purification of Laboratory Chemicals*. Pergamon, New York 1968.
12. Mohammad M., Iqbal R., Khan A. Y., Zahir K., Jahan R.: *J. Electroanal. Chem.* **124**, 139 (1981).
13. Mohammad M., Iqbal R., Khan A. Y., Bhatti M. D., Zahir K., Jahan R.: *J. Phys. Chem.* **85**, 2816 (1981).
14. Nicholson R. S.: *Anal. Chem.* **37**, 1351 (1965).
15. Schmitz J. E.: *Anal. Chem.* **54**, 1879 (1982).
16. King R. J., Kochi J. K.: *J. Phys. Chem.* **85**, 1731 (1981).
17. Gileadi E., Eisiner U.: *J. Electroanal. Chem.* **28**, 82 (1970).
18. Russel C., Jaenicke W.: *Electrochim. Acta* **27**, 1745 (1982).
19. Kapturkiewicz A., Jaenicke W.: *J. Chem. Soc., Faraday Trans. 1* **83**, 2727 (1987).
20. Kojima H., Bard A. J.: *J. Am. Chem. Soc.* **97**, 6317 (1975).
21. Moelwyn-Hughes E. A.: *Physical Chemistry*, p. 948. Pergamon, London 1961.
22. Booth F.: *J. Chem. Phys.* **19**, 391 (1951).
23. Grahame D. C.: *J. Chem. Phys.* **87**, 903 (1950).
24. Fawcett W. R., Jawarski J. S.: *J. Phys. Chem.* **87**, 2973 (1983).