J. Chem. Soc., Faraday Trans. 1, 1986, **82**, 339–347

The Solvent Effect on the Electro-oxidation of 1,4-Phenylenediamine

The Influence of the Solvent Reorientation Dynamics on the One-electron Transfer Rate

Marcin Opałło

Institute of Physical Chemistry of the Polish Academy of Sciences,
01-224 Warszawa, Kasprzaka 44/52, Poland

The one-electron electro-oxidation of 1,4-phenylenediamine to the corresponding radical cation has been studied by cyclic voltammetry at a Pt electrode in perchlorate solutions in a wide range of aprotic and hydrogen-bonded solvents. A linear relationship between the redox potential of this system and the donor number of a given solvent has been found. It has been shown that the dynamics of solvent reorientation strongly affects the heterogeneous electron transfer rate in the studied case: an almost linear relationship between the standard rate constant and the reciprocal of the longitudinal dielectric relaxation time of a given solvent has been found. It has been suggested that the solvent dynamics affects the rate of the analogous homogeneous electron-transfer reaction.

The rate constant for outer-sphere electron transfer is usually related to the overall free-energy barrier $\Delta G^\ddagger$. According to the 'encounter prequilibrium' model, the activation process follows the formation of the precursor complex with the reactants or reactant–electrode pair in homogeneous and heterogeneous reaction, respectively. Thus the rate constant k can be expressed as[1–4]

$$k = \kappa K_p \nu_n \exp(-\Delta G^\ddagger/RT) \qquad (1)$$

where κ is the electronic transmission coefficient (*i.e.* the probability of electron transfer once the transition state has been formed), K_p is the equilibrium constant of precursor complex formation and ν_n is the nuclear frequency factor (the frequency of surmounting the free energy barrier).

The important conclusion of recent theoretical works[5–9] is that the solvent reorientation dynamics strongly affects the electron transfer rate. When ν_n is controlled only by the solvent reorientation and reaction free energy is zero, it can be expressed in the following manner:

$$\nu_n = \tau_L^{-1}(\Delta G^\ddagger/4\pi RT)^{\frac{1}{2}} \qquad (2)$$

where τ_L is the longitudinal dielectric relaxation time of the solvent defined as

$$\tau_L = \tau_D\, \varepsilon_\infty/\varepsilon_s \qquad (3)$$

in which τ_D is the dielectric relaxation time and ε_s and ε_∞ are the static and high-frequency dielectric permittivity of the solvent, respectively.

It should be noted that ε_∞ is 1.5–4 times higher than the optical dielectric permittivity ε_{op}, usually approximated as equal to the square of the refractive index, n_D^2.

The equilibrium constant K_p is sensitive to the solvent only *via* electrostatic terms. Considering that $\Delta G^\ddagger$ is slightly dependent on the solvent *via* the polarity parameter[10] $(\varepsilon_{op}^{-1}-\varepsilon_s^{-1})$, the following relationship is expected:

$$k \propto \tau_L^{-1}. \qquad (4)$$

This was recently observed in the case of heterogeneous electron transfer reactions.[11–14]

These results are contrary to the collisional model, where the pre-exponential factor in eqn (1) was assumed to be equal to the gas phase collision frequency,[10] and also to the transition state formulation of 'encounter pre-equilibrium' model, where ν_n is most affected by the inner-shell bond vibration frequency.[1-4] Both these approaches predict a smaller solvent effect on the electron transfer kinetics which may be described by the relationship

$$\ln k \propto (\varepsilon_{op}^{-1} - \varepsilon_s^{-1}). \qquad (5)$$

Therefore, the studies of this effect can be seen as one of the best methods of evaluation of the theoretical predictions.

1,4-Phenylenediamine (PPD) was chosen because its radical cation is stable in aprotic solvents.[15,16] Also it is known from the literature that the PPD molecule can be oxidized at a Pt electrode in acetonitrile solution in a one-electron reversible process.[17] This electrode reaction with both reactants remaining in solution is a suitable model system. The kinetics of homogeneous electron self-exchange between a PPD molecule and its radical cation were studied in aprotic solvents,[15,16] thereby allowing a comparison between homo- and hetero-geneous electron transfer rates to be drawn.

Experimental

Materials

Acetonitrile (ACN), dimethylformamide (DMF), dimethyl sulphoxide (DMSO), propylene carbonate (PC), tetrahydrofuran (THF), hexamethylphosphotriamide (HMPT), nitrobenzene (NB) and *N*-methylformamide (NMF) were dried and purified for electrochemical use in the conventional manner.[18] Methanol (MeOH), propan-2-ol (PrOH-2), butan-1-ol (BuOH-1) and sulpholane (TMS) were spectroscopic grade and were used as received.

Analytical grade $(C_4H_9)_4NClO_4$ (TBAP) and $NaClO_4$ were dried at 60 and 120 °C, respectively, under reduced pressure. Analytical grade ferrocene (Fc) was used as received, whilst analytical grade PPD was purified by vacuum sublimation.

Apparatus

The measuring system for cyclic voltammetry was constructed from an EP-20A potentiostat and an EG-20 function generator (Elpan, Poland). Cyclic voltammetric curves were recorded on an TRP-XY recorder (Sefram, France) and on DT 516 oscilloscope (Kabid, Poland) for low (up to 0.1 V s^{-1}) and for rapid scan rates, respectively.

Measurements were performed in a conventional three-electrode cell. The Pt-disc electrode with area 0.008 cm^2 was used as the working electrode.The other electrodes were a mercury pool electrode and a saturated aqueous calomel electrode (connected to a cell by a salt bridge) as reference electrode.

All potentials were referred to an internal reference redox system, ferrocene/ferricinium (Fc),[19] in order to minimize liquid junction and diffuse potentials and their instabilities.

Procedures

All measurements were carried out at 25 ± 0.2 °C. The solutions were deoxygenated with pure argon presaturated by bubbling through solvent. The sample of PPD (0.1 – 0.5 mmol dm^{-3}) was added to the deoxygenated solution. $NaClO_4$ was used as the supporting electrolyte in concentrations given in table 2 except for NB solutions, where TBAP was used. The working electrode was polished before each use and it was cycled many times in the potential range ±0.2 V around the redox potential of studied system

Table 1. The parameters of solvents used: polarity parameter $(\varepsilon_{op}^{-1}-\varepsilon_s^{-1})$, donor number N_D, longitudinal dielectric relaxation time τ_L and solvent radius r_{solv}

solvent	$(\varepsilon_{op}^{-1}-\varepsilon_s^{-1})$	N_D	$\tau_L^a \times 10^{12}$/s	r_{solv}^b/nm	ref.[c]
ACN	0.526	14.1	0.2	0.28	44
DMF	0.462	26.6	1.3	0.31	45
DMSO	0.437	29.8	2.4	0.32	45
PC	0.481	15.1	2.6	0.32	46
THF	0.372	20.0	3.3	0.32	47
NB	0.390	4.4	3.1	0.31	48
TMS	0.432	14.8	6.5[d]	0.34	
HMPT	0.437	38.8	8.9	0.41	45
NMF	0.484	27.0	6.1	0.29	49
MeOH	0.536	19.0	3.3	0.25	50
PrOH-2	0.474	—	54.0	0.31	51
BuOH-1	0.467	—	35.8	0.33	52

[a] Calculated according to eqn (3), for alcohols the lowest value of τ_D^2 and $\varepsilon_\infty = \varepsilon_{op} = n_D^2$ was taken for the calculation of τ_L. [b] Calculated from the molecular volume assuming spherical shape of solvent molecule. [c] Sources of dielectric dispersion data. [d] Estimated using the Debye equation.[48]

Table 2. The estimated electrochemical parameters of one-electron electro-oxidation of PPD: diffusion coefficients D, redox potentials $E°$ *vs.* Fc and standard rate constants k_s[a]

solvent	electrolyte[b] concentration range/mol dm^{-3}	$D/10^{-6}$ cm^2 s^{-1}	$-E°_{PPD}$/V *vs.* Fc	k_s/cm s^{-1}
ACN	0.05–0.3	20.0	0.11_0	0.22
DMF	0.05–0.3	9.1	0.28_0	0.082
DMSO	0.05–0.3	2.8	0.31_0	0.074
PC	0.05–0.3	2.0	0.11_0	0.055
THF	0.10–0.3	12.6	0.22_0	0.074
NB	0.10	3.1	0.11_5	0.035
TMS	0.10–0.3	1.0	0.12_0	0.022
HMPT	0.10–0.3	1.5	0.51_5	0.017
NMF	0.05–0.3	3.5	0.29_5	0.10
MeOH	0.05–0.3	15.0	0.20_5	0.18
PrOH-2	0.05–0.1	3.1	0.18_0	0.017
BuOH-1	0.10	2.9	0.24_5	0.027

[a] Accuracy as follows: $D \pm 10\%$, $E° \pm 5$ mV, $k_s \pm 20\%$. [b] In all solvents $NaClO_4$ was used except with NB, where TBAP was used as the supporting electrolyte.

after immersion in the solution. Reproducible results have been obtained using this procedure, although the surface state is not well defined.

The diffusion coefficients D and the redox potentials E were estimated as previously described.[13, 14]

The standard heterogenous electron-transfer rate constants k_s were estimated from the observed differences of cathodic and anodic peak potentials, ΔE, according to the procedure of Nicholson[20] for quasi-reversible conditions. The ΔE values were measured with a precision of ± 1 mV. The $k_s/D^{\frac{1}{2}}$ values were estimated for more than five sweep rates where observed values of ΔE were > 70 mV.

In order to avoid unreliability in estimation of k_s, the positive feedback technique was used for cell resistance *IR* compensation. The *IR* drop was compensated by looking for the onset of potential oscillations on the oscilloscope screen. The reliability of the above procedure was controlled by increasing the PPD concentration and looking for a change in ΔE. Where its value remained unchanged, the uncompensated remaining *IR* drop did not influence measured ΔE values and the estimated k_s values were considered reliable. The above procedure also enabled us to avoid the effects of variations in *IR* drop in different solutions.

Results and Discussion

The cyclic voltammograms with approximately equal cathodic and anodic diffusional peak currents were obtained for all solutions (table 2). The mechanism of the studied reaction is solvent independent and it can be described as follows:

$$\mathrm{PPD} - \mathrm{e} \rightleftharpoons \mathrm{PPD}^{+}. \qquad (6)$$

Diffusion Coefficients

The approximately linear relationship between the estimated *D* values and the reciprocal of the viscosity of a given solvent as predicted by the Stokes–Einstein theory has been found. This result ascertains the mechanism of the studied process as described by eqn (6). The estimated value of the effective radius of PPD molecule ($r_{\mathrm{PPD}} = 0.34$ nm) is similar to the value obtained from crystallographic data.[15]

Redox Potentials

The E°_{PPD} *vs* Fc values has been found to vary appreciably with the solvent, but no effect of $NaClO_4$ concentration has been observed. Thus the ion-pairing phenomena can be neglected in this case.

An approximately linear relationship between E°_{PPD} and the donor number N_{D} of a given solvent as a measure of its basicity has been found (fig. 1). A strong deviation from the above dependence was observed only in the case where NB (which has a relatively low donor number) was used. Thus for other solvents, the solvent effect on E°_{PPD} can be discussed in terms of donor–acceptor interactions.[21] In the case under study the linear regression has the form

$$E^{\circ}_{\mathrm{PPD}} = -0.015\, N_{\mathrm{D}} + 0.109. \qquad (7)$$

This implies that the energies of solvation of PPD^+ are greater than those for the neutral molecule PPD. One may also observe that solvation phenomena are stronger than for the phenothiazine cation.[22] This may be understood as an effect of an excess of positive charge on nitrogen atoms of the amine groups which is expected to be larger than on the heteroatoms in the aromatic ring.

Kinetic Data

The apparent standard rate constants k_s have been found to be nearly independent of the supporting electrolyte concentration in all solvents used.

The values of E°_{PPD} in ACN and DMSO solutions are close to the estimated zero charge potentials (E_{zc}) of the Pt electrode in perchlorate solutions in these solvents.[23, 24] In most other solvents the E_{zc} value of the Pt electrode can be estimated by a comparison of the data for Pt and Hg electrodes in aqueous solutions and the data for Hg electrodes in non-aqueous solvents (using the proposals of Frumkin[25, 26]), and they are also close to the E°_{PPD} values. Therefore the measured k_s values can be further discussed as 'true' values, not influenced by the potential drop in the diffuse layer.

On the basis of the kinetic data presented in table 2, it is readily apparent that k_s varies

Table 3. Values of the ratio k_s/k_s^{th} between the experimental k_s and k_s^{th} calculated according to eqn (1), (2) and (8)–(10), assuming $r_{PPD} = 0.34$ nm, and $\kappa\delta r = 60$ pm for various distances of the reactant from the electrode surface, d

	k_s/k_s^{th}		
solvent	$d = r_{PPD}$	$d = 2r_{solv} + r_{PPD}$	$d = \infty$
ACN	0.003	0.08	0.55
DMF	0.004	0.08	0.36
DMSO	0.006	0.08	0.61
PC	0.007	0.15	0.72
THF	0.004	0.03	0.15
NB	0.003	0.02	0.10
TMS	0.005	0.05	0.29
HMPT	0.005	0.05	0.33

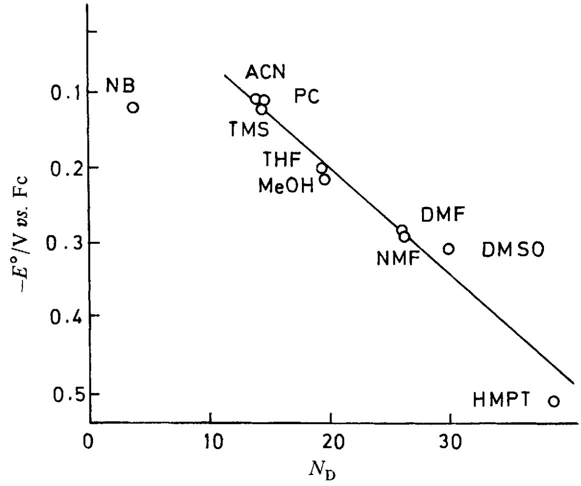

Fig. 1. Standard redox potentials, E°_{PPD}, of the couple PPD$^+$|PPD as a function of the donor number of a given solvent.

considerably with the type of solvent. This cannot be explained by the inner solvation-shell effect because no simple correlation between k_s and N_D is observed. Also the outer solvation-shell effects are not responsible for this phenomenon because no correlation between k_s and the solvent polarity parameter $(\varepsilon_{op}^{-1} - \varepsilon_s^{-1})$ is observed. On the other hand, k_s strongly depends on the τ_L value of a given solvent. Thus, the solvent reorientation dynamics play an important role in the electro-oxidation of PPD. In the case of aprotic solvents, a nearly linear correlation exists between k_s and τ_L^{-1} (fig. 2).

The interpretation of kinetic data in alcohols is more complicated because they exhibit multiplied relaxational behaviour.[27] Taking into consideration the slower τ_D it seems to be more appropriate to calculate τ_L according to eqn (3) taking $\varepsilon_\infty = \varepsilon_{op} = n_D^2$. A nearly linear correlation between k_s and τ_L^{-1} of a given hydrogen-bonded solvent is observed (fig. 2). Similar correlations were observed in the case of intramolecular electron transfer reactions.[28, 29]

The values of k_s in hydrogen-bonded solvents are higher than expected by comparison with kinetic data in aprotic solvents. This was recently observed in the case of the one-

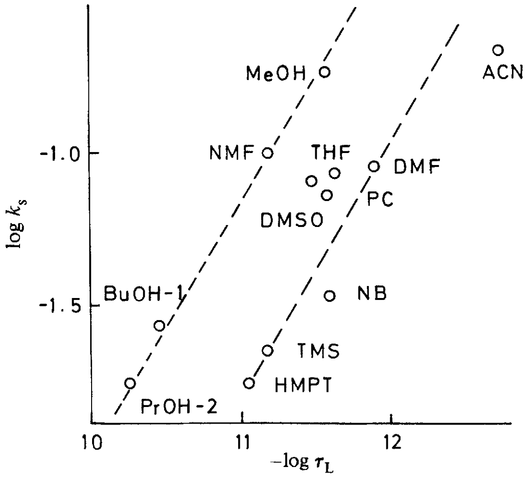

Fig. 2. Standard rate constants of the electro-oxidation of PPD k_{e1} as a function of the reciprocal of the longitudinal dielectric relaxation time of a given solvent τ_L.

electron electro-oxidation of phenothiazine.[14] Similar observations can also be made for the orientational decay of excited organic dyes where the solvent reorientation may also play an important role.[30]

The above effect may be caused by many reasons. First, the faster dielectric relaxation processes influence the electron-transfer rate which cannot be taken into account by substitution of ε_{op} for ε_∞ in eqn (3). Secondly, the polarization–diffusion mechanism of solvent relaxation can be intrinsic for solvents with relatively long τ_L.[31–33] It should also be emphasized that the existence of the discussed effect for homogeneous processes[30] indicates that this is not entirely caused by interfacial phenomena.

The Validity of the Encounter Pre-equilibrium Model involving Solvent Reorientation Dynamics

The observed relationship between k_s and τ_L^{-1} gives rise to the conclusion that the kinetic data obtained can be discussed in terms of eqn (1) and (2).

The value of the overall free-energy barrier has been assumed as being equal to the sum of the inner and outer reorganization energies:

$$\Delta G^\ddagger = \lambda_i/4 + \lambda_o/4. \tag{8}$$

The value of λ_i has been taken from ref. (16). Assuming that only one molecule is reorganized in one elementary reaction step, $\lambda_i/4 = 0.9$ kJ mol^{-1}, *i.e.* only few percent of $\Delta G^\ddagger$.

The value of λ_o can be estimated on the basis of a simple extension of Born model:[10]

$$\lambda_o = (Ne^2/8\pi\varepsilon_0) \times g(r,d) \times (\varepsilon_{op}^{-1} - \varepsilon_s^{-1}) \tag{9}$$

where N is the Avogadro number, e is the electronic charge, ε_0 is the dielectric permittivity of a vacuum and $g(r,d)$ is a distance parameter. In the spherical approximation for heterogeneous reactions, this last parameter is a function of reactant radius r and its distance from the electrode surface when electron transfer occurs, d:

$$g(r,d) = (r^{-1} - 2d^{-1}). \tag{10}$$

In this case r was taken as the effective radius of PPD, r_{PPD}, estimated as given above.

It is obvious that λ_0 calculated according eqn (9) and thus k_s is strongly dependent on the reaction site. Therefore it has been calculated using three assumptions: *viz*. the closest approach of the PPD molecule to the electrode ($d = r_{PPD}$), the separation of the PPD molecule from the electrode surface by a monolayer of solvent molecules ($d = r_{PPD} + 2r_{solv}$) and neglecting the reactant–electrode imaging interactions in the transition state ($d = \infty$).

In the heterogeneous electron transfer reaction K_p is assumed equal to the effective thickness of the 'reaction zone' δr.[3] Therefore k_s also depends on the reaction site *via* the composite term $\kappa\delta r$ which is sensitive to the dependence of κ upon the reactant–electrode separation.[3, 34, 35] The effective tunnelling probability was suggested to be unity at large distances (1–2 nm) from the electrode surface owing to the large number of electronic energy states near the Fermi level in the metal.[36, 37] However it was recently shown that in the case of electroreduction of some Cr^{III} and Co^{III} complexes bound to the electrode surface non-adiabatic tunnelling ($\kappa < 1$) is possible for smaller distances ($d \leqslant 0.6$ nm).[34, 35]

Assuming that the reaction is adiabatic only at the closest approach to the electrode surface ($\kappa \approx 1$), the value of $\kappa\delta r = 60$ pm has been taken for calculations.[34] It should be emphasized that in the above treatment the distance of closest approach is identified with the corresponding value of d, taken for calculation of λ_0.

The values of the ratios of estimated standard rate constants k_s to calculated k_s^{th} as given above, k_s/k_s^{th}, for aprotic solvents are presented in table 3. One may observe that this ratio remains independent of solvent within an order of magnitude. This indicates that the model used predicts the observed solvent effect on the rate of reaction studied. The value of k_s is closest to k_s^{th} for $d = \infty$. This may lead to the conclusion that the most probable reaction site is at the distance where reactant–electrode imaging interactions disappear. A similar conclusion can be drawn for the electro-oxidation of phenothiazine at a Pt electrode[14] and in the case of electrode reactions of some metallocene couples at an Hg electrode.[12] On the other hand, in the case of electroreduction of nitromesitilene at an Hg electrode the best agreement between the experimental value of k_s (corrected for Φ_2 potential) and the calculated value was obtained using the assumption $d = 2r_{solv} + r$.[13]

It should be emphasized that the calculations of k_s^{th} may be in serious error owing to: (*a*) the crude approximation in calculations of λ_i[15] (a different treatment gives a value of λ_i three times higher)[38] and (*b*) the neglect of non-continuum dielectric terms in $\Delta G^{\ddagger}$, which may result from specific reactant–solvent interactions.[39] In the case above, the contribution estimated from the difference between E°_{PPD} *vs*. Fc values in a given solvent and extrapolated[39] to $N_D = 0$ is in the range 1.8 (ACN) to 5.1 (HMPT) kJ mol^{-1}, whereas estimated according eqn (8)–(10) values of $\Delta G^{\ddagger}$ are in the range 10.4–14.3 kJ mol^{-1} for $d = r_{PPD}$, 15.6–22.6 kJ mol^{-1} for $d = r_{PPD} + 2r_{solv}$ and 19.9–27.7 kJ mol for $d = \infty$.

Comparison between Hetero- and Homo-geneous Electron Transfer Kinetics

The homogeneous electron self-exchange rate constant of the PPD/PPD$^+$ couple k_h was found to be proportional to the solvent polarity parameter, and it was discussed in terms of the Marcus model.[15, 16] As was emphasized in the introduction, such a correlation is expected when the frequency of surmounting the energy barrier is mostly affected by the inner-shell bond vibration frequency ν_{is}. This may indicate that mechanisms of activation in homo- and hetero-geneous processes are different.

According to the 'encounter pre-equilibrium' model, the value of k_h can be calculated assuming ν_n to be solvent independent or described by eqn (2). In calculations of the free-energy barrier for homogeneous reaction, the reorganization of two reactants has been taken into account as well as the distance parameter $g(d)$. In this case the model of two conducting ellipsoids was suggested to be more appropriate.[15] Two values of $g(d)$

Table 4. The ratio of homogeneous electron self-exchange rate constants of the PPD/PPD$^+$ couple k_h in a given solvent to those in ACN, k_h(ACN), k_h/k_h(ACN)

		k_h/k_h(ACN)			
		$g(d) = 0.74$ nm^{-1}		$g(d) = 2.74$ nm^{-1}	
solvent	expt[a]	v_{is}^{b}	v_{os}^{c}	v_{is}^{b}	v_{os}^{c}
ACN	1.0	1.0	1.0	1.0	1.0
DMF	1.4	2.0	0.3	8.8	1.3
DMSO	1.9	2.5	0.2	18.5	1.4
NM	1.1	3.5	1.5	2.0	2.3

[a] Experimental values taken from ref. (15). [b] v_n solvent independent. [c] v_n described by eqn (2).

have been used in calculations, 0.74 nm^{-1}, equivalent to the molecular distance in the radial dimers (suggested as the best approximation to empirical data),[15] and 2.34 nm^{-1}, calculated using the assumption that distance between reactants is equal to double the longest semiaxis of the ellipsoid.[15] It has also been assumed that κ and the equilibrium constant of homogeneous precursor complex formation are solvent-independent. This last assumption seems to be justified for the solvents under consideration which all have similar static dielectric permittivities: $\varepsilon_s = 37.6$, 36.7, 48.9 and 38.2 for ACN, DMF, DMSO and nitromethane, NM, respectively.

The ratios of calculated k_h in a given solvent to those in ACN, k_h(ACN), are presented in table 4. One may observe that k_h/k_h(ACN) calculated in different solvents are similar to the experimental values when v_n is solvent independent and $g(d) = 0.74$ nm^{-1}, and when v_n is solvent dependent and $g(d) = 2.34$ nm^{-1}. Thus the solvent effect on homogeneous electron self-exchange for this system can also be described by a model involving solvent reorientation dynamics, but with different assumptions about the structure of the activated complex. This is contrary to the heterogeneous case where any assumption about $g(r,d)$, taking v_n to be solvent independent, does not give the observed solvent effect on the reaction rate.

The above considerations may indicate why the different solvent dependences of the homogeneous electron-transfer rate are observed. In the case of bis(biphenyl) Cr^{I}/Cr^{0} and tris(hexafluoroacetonato) Ru^{III}/Ru^{II} couples[40, 41] and for substituted 1,4-phenylenediamines[15] the relationship (5) is observed. In the case of the ferrocene/ferricinium couple, the rate of electron self-exchange is solvent independent.[42] This is contrary to the heterogeneous case for metallocenes and bis(biphenyl) Cr^{I}/Cr^{0} couples, where the influence of solvent reorientation dynamics on the reaction rate is evident.[12] On the other hand, the rate of electron self-exchange between tetracyanoethylene and its radical anion is higher, the lower is τ_L of the solvent.[43]

One may conclude that the different structure of the activated complex may be one of the reasons that different solvent dependences of homogeneous reaction rates are observed, but it is possible that the same mechanism of activation occurs in homo- and hetero-geneous reactions influenced by solvent reorientation dynamics.

Conclusions

It has been shown that solvent reorientation dynamics has an intrinsic effect on the kinetics of one-electron electro-oxidation of PPD at a Pt electrode. On the basis of the 'encounter pre-equilibrium' model, the most expected reaction site is where the reactant–electrode imaging interactions are negligible.

On the basis of literature kinetic data of homogeneous electron-self-exchange,[15] it has been suggested that the solvent has a similar role in homo- and hetero-geneous processes.

Thanks are due to Dr Andrzej Kapturkiewicz for preliminary discussion of the above work and to Dr Zofia Borkowska for her helpful attention during the manuscript preparation. This work was carried out within Research Project 03.10.

References

1 R. A. Marcus, *Int. J. Chem. Kinet.*, 1981, **13**, 865.
2 B. L. Tembe, H. L. Friedman and M. D. Newton, *J. Chem. Phys.*, 1982, **76**, 1490.
3 J. T. Hupp and M. J. Weaver, *J. Electroanal. Chem.*, 1983, **152**, 1.
4 N. Sutin, *Progr. Inorg. Chem.*, 1983, **30**, 441.
5 L. Zusman, *Chem. Phys.*, 1980, **49**, 295.
6 I. V. Alexandrov, *Chem. Phys.*, 1980, **51**, 449.
7 D. E. Calef and P. G. Wolynes, *J. Phys. Chem.*, 1983, **87**, 3387.
8 D. F. Calef and P. G. Wolynes, *J. Chem. Phys.*, 1983, **78**, 470.
9 M. Ya. Ovchinnikova, *Russ. Theor. Exp. Chem.*, 1981, **17**, 507.
10 R. A. Marcus, *J. Chem. Phys.*, 1965, **43**, 679.
11 A. Kapturkiewicz and B. Behr, *J. Electroanal. Chem.*, 1984, **179**, 187.
12 M. J. Weaver and T. Gennett, *Chem. Phys. Lett.*, 1985, **113**, 213.
13 A. Kapturkiewicz and M. Opałło, *J. Electroanal. Chem.*, 1985, **185**, 15.
14 M. Opałło and A. Kapturkiewicz, *Electrochim. Acta*, in press.
15 G. Grampp and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.* 1984, **88**, 325.
16 G. Grampp and W. Jaenicke, *Ber. Bunsenges. Phys. Chem.* 1984, **88**, 335.
17 R. A. Adams, *Electrochemistry at Solid Electrodes* (Marcel Dekker, New York, 1969).
18 C. K. Mann in *Electroanalytical Chemistry*, ed. A. J. Bard (Marcel Dekker, New York, 1969), vol. 3.
19 G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1984, **56**, 461.
20 R. S. Nicholson, *Anal. Chem.*, 1965, **37**, 1351.
21 V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions* (Plenum Press, New York, 1969).
22 B. Paduszek and M. K. Kalinowski, *Electrochim. Acta*, 1983, **28**, 639.
23 O. A. Petri and I. G. Kchomchenko, *J. Electroanal. Chem.*, 1980, **106**, 277.
24 E. Ju. Alekseyeva, W. A. Safomov and O. A. Petri, *Electrochimiya*, 1984, **20**, 945.
25 A. N. Frumkin, *Potentialy Nulyevogo Zaryada* (Nauka, Moscow, 1979).
26 A. Kapturkiewicz and B. Behr, *J. Electroanal. Chem.*, 1984, **163**, 189.
27 C. J. F. Bottcher and P. Bordevijk, *Theory of Electric Polarization* (Elsevier, New York, 1978), vol. 2.
28 D. Hupert, H. Kanety and E. M. Kosower, *Chem. Phys. Lett.*, 1981, **84**, 48.
29 E. M. Kosower and D. Hupert, *Chem. Phys. Lett.*, 1983, **96**, 433.
30 K. G. Spears and L. E. Cramer, *Chem. Phys.* 1978, **30**, 1.
31 G. van der Zwan and J. T. Hynes, *J. Chem. Phys.*, 1982, **76**, 2993.
32 G. van der Zwan and J. T. Hynes, *J. Chem. Phys.*, 1983, **78**, 4174.
33 G. van der Zwan and J. T. Hynes, *Chem. Phys. Lett.*, 1983, **101**, 367.
34 J. T. Hupp and M. J. Weaver, *J. Phys. Chem.*, 1984, **88**, 1463.
35 T. T. T. Li and M. J. Weaver, *J. Am. Chem. Soc.*, 1984, **106**, 6107.
36 J. M. Hale, *J. Electroanal. Chem.*, 1968, **19**, 315.
37 J. M. Hale, in *Reactions of Molecules at Electrodes*, ed. N. S. Hush (Interscience, New York, 1971), chap. 4.
38 W. Jaenicke, personal communication.
39 J. T. Hupp and M. J. Weaver, *J. Phys. Chem.* 1985, **89**, 1601.
40 T. T. T. Li, M. J. Weaver and C. H. Brubaker, *J. Am. Chem. Soc.*, 1982, **104**, 2381.
41 M-S. Chan and A. C. Wahl, *J. Phys. Chem.*, 1982, **86**, 126.
42 E. S. Yang, M-S. Chan and A. C. Wahl, *J. Phys. Chem.*, 1980, **84**, 3094.
43 W. Harrer, G. Grampp and W. Jaenicke, *Chem. Phys. Lett.*, 1984, **112**, 263.
44 K. Krishaji and A. Hausingh, *J. Chem. Phys.*, 1964, **41**, 827.
45 H. Behret, F. Schmithals and J. Barthel, *Z. Phys. Chem. N.F.*, 1975, **96**, 79.
46 E. A. S. Cavel, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 78.
47 J. Crosley, S. W. Tucker and S. Weiler, *Trans. Faraday Soc.*, 1966, **62**, 576.
48 M. Davies in *Dielectric Properties and Molecular Behaviour*, ed. N. E. Hill, W. E. Vaughan, A. H. Price and M. Davies (Van Nostrand, Princeton, 1969).
49 P. Winsor IV and R. H. Cole, *J. Phys. Chem.*, 1982, **86**, 2486.
50 J. A. Saxton, R. A. Bond, G. T. Coats and R. N. Dickinson, *J. Chem. Phys.*, 1962, **37**, 2132.
51 H. A. Rizk and I. M. Elanvar, *Z. Phys. Chem. N.F.*, 1968, **62**, 225.
52 H. A. Rizk and N. Youseef, *Z. Phys. Chem. N.F.*, 1968, **58**, 100.

Paper 5/350; *Received* 1*st March*, 1985