PCCP

Solvent effects on intramolecular electron exchange in the 1,4-dinitrobenzene radical anion

J. P. Telo,[*a] **G. Grampp**[b] **and M. C. B. L. Shohoji**[a]

[a] *Instituto Superior Técnico, Química Orgânica, Av. Rovisco Pais, P-1096 Lisboa Codex, Portugal*
[b] *Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, Technikerstrasse 4/I, A-8010 Graz, Austria*

Accepted and transferred from Berichte Bunsen-Gesellschaft 25th August 1998

The rate constants of the intramolecular electron exchange reaction in the 1,4-dinitrobenzene radical anion in linear alcohols were determined from alternating line-broadening effects in EPR spectra. Rate constants at 293 K range from 2.9×10^9 s^{-1} in methanol to 2.7×10^8 s^{-1} in octan-1-ol. The rate constant was found to depend on the reverse of the longitudinal correlation time of the solvent, τ_L, as expected for a solvent-controlled adiabatic reaction. Applying Marcus theory and the ellipsoidal cavity model for evaluating λ_0, the amount of transferred charge between nitro groups, z, and the outer-sphere reorganisation energy were determined. z changes from 0.56 at 273 K to 0.52 at 313 K. λ_0 at 293 K changes from 61 kJ mol^{-1} in octan-1-ol to 80 kJ mol^{-1} in methanol. The activation energies were obtained from the temperature dependence of the rate constants, changing from 26 kJ mol^{-1} in methanol to 36 kJ mol^{-1} in octan-1-ol. The variation of this energy clearly reflects the increase in the exponential term of τ_L for the more viscous alcohols. The results for the 1,4-dinitrobenzene radical anion were compared with those previously reported for the radical anion of 1,3-dinitrobenzene. Rate constants are smaller in the former, by three orders of magnitude, due to conjugation of the nitro groups.

1 Introduction

There is current interest in the kinetics of both intra- and intermolecular electron transfer reactions, since these are the fundamental chemical steps in numerous biological processes. A great investment has been made in the design of organic molecules for testing electron transfer theories. In particular, the understanding of intramolecular electron transfer has evolved to a high degree.[1] The verification of the Marcus inverted region was first established for intramolecular electron transfer reactions.

Most of the studies of intramolecular electron transfer focus on photoinduced charge separation, involving different donor and acceptor moieties to achieve a suitable driving force $\Delta G°$.[3] Studies on intramolecular degenerated symmetrical electron exchange reactions with $\Delta G° = 0$ are rare. Nelsen *et al.*[4] studied the self-exchange within various hydrazine derivatives by optical and EPR methods. Combination of both methods made possible the estimation of the coupling matrix element H_{12}.[5]

The kinetics of intramolecular electron exchange (IEE) in the radical anion of 1,3-dinitrobenzene (1,3-DNB) have been studied previously by EPR spectroscopy. Rate constants, k, are *ca.* 10^6 s^{-1} in alcohols and 10^9 s^{-1} in aprotic solvents. The reaction was found to be adiabatic and uniform in the sense of classic transition state theory.[6,7]

It is generally accepted that the absence of direct resonance between the donor and the acceptor is necessary for the occurrence of alternating line-broadening effects caused by IEE in the EPR spectra of free radicals. The examples found in the literature, where the two groups are either in non-conjugated *meta* positions, as in the radical anions of 1,3-DNB and 2,7-dinitronaphthalene (2,7-DNN),[8] or sterically forced out of planarity, as in the radical anion of dinitrodurene[9,10] seemed to confirm this idea. However, line-broadening effects due to IEE were recently found in the EPR spectra of the 2,6-dinitrophenolate radical dianion, where resonance structures can be drawn delocalising the electron through the two nitro groups.[11]

In this work, the solvent-induced IEE within the conjugated 1,4-dinitrobenzene (1,4-DNB) radical anion is studied in linear alkanols. The effect of the solvent on the kinetics of the reaction is discussed.

2 Theory

According to Marcus theory,[12–14] the rate constant of an adiabatic electron transfer reaction is expressed by

$$k = \nu \exp(-\Delta G^*/RT) \qquad (1)$$

where ν is the effective nuclear frequency of the reactants. For a degenerated intramolecular electron transfer reaction $\Delta G° = 0$ and the activation energy is simply given by

$$\Delta G^* = \frac{\lambda_i + \lambda_0}{4} - H_{12} \qquad (2)$$

In intramolecular reactions with aromatic spacers, the overlap between the orbitals of the donor and acceptor is extensive and the resonance energy splitting H_{12} may be considerably larger than RT. Since the activation energies are normally not very large for adiabatic electron transfer reactions, it is necessary to include H_{12} in eqn. (2).

The inner-sphere reorganisation energy λ_i depends on the changes in the bond lengths between the reactants and the products. According to Marcus, λ_i can be calculated by eqn. (3), from the changes in bond orders Δq_j between the reactants and products and from the corresponding force constants

$f_j^{\mathrm{R,P}}$. In the limiting case of totally excited vibrational states we have

$$\lambda_i^{\infty} = \sum_j \frac{f_j^{\mathrm{R}} f_j^{\mathrm{P}}}{f_j^{\mathrm{R}} + f_j^{\mathrm{P}}} (\Delta q_j)^2 \qquad (3)$$

However, the relevant vibrational frequencies are only partially excited at room temperature. A simple correction for the temperature dependence of λ_i was proposed by Holstein[15]

$$\lambda_i(T) = \sum_j (\lambda_i^{\infty})_j \left[\frac{4kT}{\hbar\omega_j} \tanh \frac{\hbar\omega_j}{4kT}\right] \qquad (4)$$

The sum can be substituted by one term with a mean frequency $\omega/2\pi \approx 5 \times 10^{13}\ \mathrm{s^{-1}}$. In the range of temperature under consideration, eqn. (4) can be approximated by a straight line

$$\lambda_i(T) = \lambda_i^{\infty}(m + nT) \qquad (5)$$

with $m = 0.092$ and $n = 0.001\,36\ \mathrm{K^{-1}}$.[16,17]

The outer-sphere reorganisation energy λ_0 is associated with the reorientation of the solvent molecules along the reaction coordinate. We have shown previously that the ellipsoidal cavity model is a satisfactory approximation to calculate λ_0 for IEE reactions in aromatic organic molecules.[6–8] In this model, the molecule is located in an ellipsoidal cavity surrounded by the solvent, considered as a dielectric continuum.[18,19] The ellipsoid has semi-axes a and b. If the charge ze_0 is transferred over a distance d, λ_0 is given by

$$\lambda_0 = \frac{(e_0 z)^2 N_{\mathrm{L}}}{4\pi\varepsilon_0 R_{\mathrm{f}}} \left[\left(\frac{1}{\varepsilon_{\mathrm{in}}} - \frac{1}{\varepsilon}\right) \sum_{n=1}^{\infty} \frac{X_n}{I_n(\varepsilon_{\mathrm{in}}, \varepsilon)} - \left(\frac{1}{\varepsilon_{\mathrm{in}}} - \frac{1}{\varepsilon_{\mathrm{op}}}\right) \sum_{n=1}^{\infty} \frac{X_n}{I_n(\varepsilon_{\mathrm{in}}, \varepsilon_{\mathrm{op}})}\right] \qquad (6)$$

where

$$X_n = 2(2n + 1)[1 - (-1)^n] P_n^2(\xi) Q_n(\chi)/P_n(\chi) \qquad (7)$$

and

$$I_n(\varepsilon_i, \varepsilon_j) = 1 - \frac{\varepsilon_i}{\varepsilon_j} \left[\frac{\chi - P_{n+1}(\chi)/P_n(\chi)}{\chi - Q_{n+1}(\chi)/Q_n(\chi)}\right] \qquad (8)$$

where ε_0 is the permittivity of the vacuum and ε and $\varepsilon_{\mathrm{op}}$ are the static and optical relative permittivities of the solvent. Usually $\varepsilon_{\mathrm{op}}$ is taken as the square of the refractive index, $\varepsilon_{\mathrm{op}} \approx n_{\mathrm{D}}^2$. Inside the ellipsoidal cavity the relative permittivity in $\varepsilon_{\mathrm{in}}$. The commonly used value for this parameter is $\varepsilon_{\mathrm{in}} \approx 2$, a value of ε usual for hydrocarbons. The shape of the ellipsoidal cavity is described by $\chi = \sqrt{a^2/(a^2 - b^2)}$ and $\xi = d/R_{\mathrm{f}}$ where $R_{\mathrm{f}} = 2\sqrt{a^2 - b^2}$ is the interfocal distance. $P_n(\chi)$ and $Q_n(\chi)$ are the Legendre polynomials of the first and second kind. A computer program was developed for calculating λ_0 from eqn. (6)–(8).

It can be recognised from eqn. (6)–(8) that, in this model, λ_0 is not an explicit function of the solvent polarity parameter γ, given by eqn. (9)

$$\gamma = \frac{1}{\varepsilon_{\mathrm{op}}} - \frac{1}{\varepsilon} \approx \frac{1}{n_{\mathrm{D}}^2} - \frac{1}{\varepsilon} \qquad (9)$$

However, by calculating λ_0 for a given ellipsoid and for the set of solvents used, a simple linear relation between λ_0 and γ was previously found,[6,7]

$$\lambda_0 = z^2 p \gamma \qquad (10)$$

where z is the fraction of transferred charge and p is a parameter depending only on the shape of the ellipsoid.

Rips and Jortner pointed out that, for a uniform adiabatic reaction, the moment of inertia of the solvent molecule, I, should be included in the pre-exponential factor ν, given by[20]

$$\nu = \frac{1}{2\pi} \left[\frac{2\varepsilon + \varepsilon_{\mathrm{op}}}{6\varepsilon} (k_{\mathrm{B}} T/I)\right]^{1/2} \qquad (11)$$

In the uniform adiabatic regime, the reagents and transition state are in equilibrium and the system obeys the conditions of transition state theory. This happens because the solvent acts as a reversible energy source or sink, providing or absorbing energy instantaneously to or from the system. If, on the contrary, relaxation of the solvent occurs on a timescale larger than that of electron transfer, irreversible reactant–solvent energy dissipation is expected to occur and the rate constant of the reaction is controlled by the solvent dynamics. In this solvent diffusion regime, the pre-exponential factor is given by[21,22]

$$\nu = 1/\tau_{\mathrm{L}}(\lambda_0/16RT)^{1/2} \qquad (12)$$

where τ_{L} is the longitudinal relaxation time of the solvent. Eqn. (1) and (12) set an upper limit of *ca.* $1/\tau_{\mathrm{L}}$ for the rate of the reaction.

3 Experimental

1,4-DNB (Fluka) was purified by elution with toluene from a short column packed with basic alumina. The solid was further sublimed and recrystallised from ethanol. The alcohols (Merck, p.a. or extra pure) were dried with molecular sieves (Union Carbide 3 Å, dried at 400 °C under vacuum). Triethylamine (Merck) was dried over potassium hydroxide, distilled and stored over molecular sieves.

Solutions contained, typically, 1–3 mM of the parent compound and 7–10 mM of triethylamine. The solutions were deaerated with argon, thermostatted at constant temperature between 250 and 320 K by passing through a glass heat exchanger, and allowed to flow through a quartz flat cell placed in the EPR cavity. The temperature inside the cell was measured with a Pyrex-coated platinum thermocouple placed in the upward solution stream immediately above the flat part of the cell. The standard flow rate was *ca.* 0.2 ml $\mathrm{s^{-1}}$. Radicals were generated by *in situ* photolysis using an optically focused high pressure Hg–Xe 1000 W lamp. Spectra were recorded with a Bruker 200D X-band EPR spectrometer.

Under the experimental conditions used, a photoinduced electron transfer occurs yielding the radical anion of the nitro compound and the radical cation of triethylamine. The unstable radical cation of the triethylamine decays fast on the EPR timescale and is not observed.

$$\mathrm{R{-}NO_2 + NEt_3} \xrightarrow{h\nu} \mathrm{RNO_2^{\bullet -}} + \underset{\downarrow\ \text{dec.}}{\mathrm{NEt_3^{\bullet +}}} \qquad (13)$$

Values of the solvent longitudinal relaxation time were obtained from Barthel *et al.*[23] (methanol, ethanol and propan-1-ol, 298 K) and from Garg and Smith[24] (butan-1-ol to octan-1-ol, 273 and 293 K). The values of τ_{L} at 273, 293 and 313 K not available in the literature, were extrapolated using eqn. (21) (see below) and values for H_{L} from Fawcett[25] (methanol, ethanol and propan-1-ol) and Garg and Smith[24] (butan-1-ol to octan-1-ol). The values of the solvent polarity parameter γ were calculated at the same temperatures from the corresponding values of the relative permittivity and refractive index.[24,26,27]

4 Results and discussion

4.1 EPR spectra

EPR spectra of the radical anion of 1,4-DNB were recorded in linear alcohols, from methanol to octan-1-ol, at temperatures between 250 and 320 K. For the higher alcohols, the minimum temperature achieved was *ca.* 275 K, due to viscosity limitations. All spectra showed temperature-dependent line-broadening effects. The spectra are in the fast region of exchange, since only one averaged coupling constant is measured for the two nitrogen atoms. The mean nitrogen coupling constant at 293 K changes from 3.83 G in methanol to 3.14 G in octan-1-ol. The continuous decrease of this constant rules out the possibility of ion pair formation in the less polar alcohols. At low temperatures, broadening occurs, not only of the lines of the nitrogen quintet but also of the lines corresponding to the hydrogens [Fig. 1(c)]. In analogy to the *meta* isomer,[6,7] this effect was interpreted as resulting from the modulation of the hyperfine coupling constants by IEE between the two nitro groups induced by asymmetric solvation, as shown in Scheme 1. Additionally, the spectra show asymmetric line-broadening effects caused by the slow tumbling of the radical due to the viscosity of the medium.

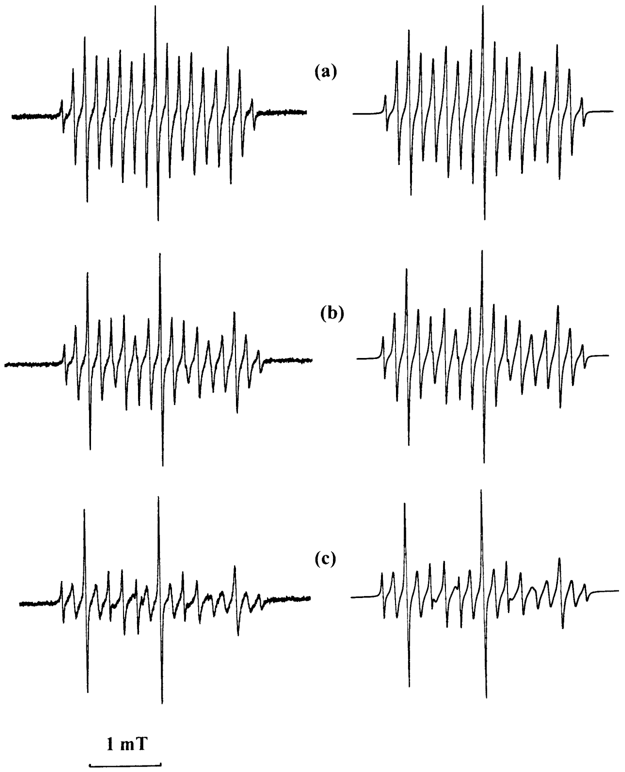
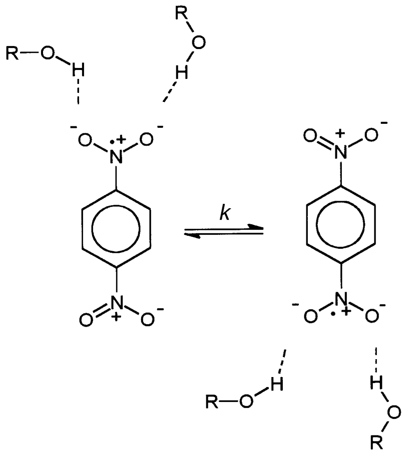


Fig. 1 EPR spectra (left-hand side) and computer simulations (right-hand side) of the 1,4-DNB radical anion in ethanol at different temperatures: (a) spectrum at 293 K and simulation with $k = 1.1 \times 10^9$ s^{-1}, $a_{N1} = 0.759$ mT, $a_{N4} = -0.078$ mT, $a_{H2,6} = -0.272$ mT, $a_{H3,5} = 0.053$ mT, $A = 11$ μT, $B = -0.36$ μT and $C = 0.53$ μT; (b) spectrum at 271 K and simulation with $k = 5.1 \times 10^8$ s^{-1}, $a_{N1} = 0.776$ mT, $a_{N4} = -0.079$ mT, $a_{H2,6} = -0.276$ mT, $a_{H3,5} = 0.056$ mT, $A = 11$ μT, $B = -1.0$ μT and $C = 0.76$ μT; (c) spectrum at 246 K and simulation with $k = 1.9 \times 10^8$ s^{-1}, $a_{N1} = 0.792$ mT, $a_{N4} = -0.081$ mT, $a_{H2,6} = -0.281$ mT, $a_{H3,5} = 0.059$ mT, $A = 11$ μT, $B = -1.8$ μT and $C = 1.07$ μT.



Scheme 1

The spectra were simulated by solving the appropriate Bloch equations for a two-jump model. In the fast region of exchange, the interchangeable coupling constants values are not accessible experimentally, since only mean constants are measured. In these cases the coupling constants must be obtained from spectra in the slow region of exchange (from ion pairs, for example) or estimated from HMO calculations. For this purpose, HMO-McLachlan calculations of the spin densities in the radical anion of 1,4-DNB were performed. The parameters used were $\gamma_{CN} = 1.06$, $\gamma_{NO} = 1.67$, $\gamma_{CO} = 1.0$ and $\delta_N = 2.2$.[28] The effect of asymmetric solvation was included by using different oxygen Coulomb integral parameters for the two nitro groups. For the less solvated nitro group a value of $\delta_O = 1.4$ was used, whereas for the more solvated nitro group δ_O was varied between 1.6 and 1.8. The formulae relating spin densities and coupling constants were obtained from the literature.[28]

The calculations show that the two interchangeable nitrogen coupling constants, a_{N1} and a_{N2}, have different signs. The same happens with the interchangeable hydrogen coupling constants and both these results are independent of the choice of parameters used in the calculations. The fluctuation $\Delta a_N = a_{N1} - a_{N4}$ of the calculated nitrogen coupling constants is a linear function of the averaged constant $\langle a \rangle_N^{calc} = (a_1 + a_4)/2$ [eqn. (14)], as found before for the radical anions of 1,3-DNB and 2,7-DNN.

$$\Delta a_N^{calc} = 2.40\langle a \rangle_N^{calc} + 0.18 \tag{14}$$

This equation was used to estimate a_{N1} and a_{N4} from the experimental values of $\langle a \rangle_N$. The few values of nitrogen coupling constants reported in the literature for spectra of 1,4-DNB radical anion in the slow region of exchange (in ion pairs[29,30]) fit eqn. (14) quite well, confirming the validity of the method used to estimate a_{N1} and a_{N4}. The same method was also used to estimate the interchangeable hydrogen hyperfine coupling constants.

The asymmetric line-broadening effects were simulated by making the intrinsic linewidth Γ of each line dependent on its nitrogen nuclear quantum number M, according to the equation

$$\Gamma(M) = A + BM + CM^2 \tag{15}$$

The values of the intrinsic line-width parameters A, B and C and the rate constant of the IEE reaction, k, were adjusted by fitting each experimental spectrum with a computer simulation. Three EPR spectra of the 1,4-DNB radical anion in ethanol at different temperatures are shown in Fig. 1, together with their simulations.

4.2 Solvent dependence of the rate constants

The rate constants for the IEE reaction within the 1,4-DNB radical anion are shown in Table 1, together with values of the solvent parameter γ and longitudinal relaxation time of the corresponding solvent, τ_L. For comparison, rate constants for the same reaction in 1,3-DNB radical anion, obtained from the literature,[6,7] are also shown.

The main difficulty in evaluating experimentally the solvent dependence of the rate constant is to separate the effects of the solvent on the pre-exponential factor and on the activation energy. The rate constant can be expressed as

$$\ln k = \ln \nu - (z^2 p/4RT)\gamma - (\lambda_i/4 - H_{12})/RT \tag{16}$$

The last term on the right-hand side of eqn. (16) is independent of the solvent,[31] but the same does not apply for the first two terms. In the uniform adiabatic regime, the solvent dependence of ν [eqn. (11)] is small compared with the solvent dependence of λ_0. In this case, eqn. (16) predicts that $\ln k$ should decrease with increasing γ. Such behaviour is indeed found for the kinetics of the electron exchange in the 1,3-DNB

Table 1 Solvent parameters, rate constants and outer-sphere reorganization energies, at 293 K, and activation parameters for the IEE reaction in the 1,3-DNB[6,7] and 1,4-DNB radical anions (energies in kJ mol^{-1})

				$1,3\text{-DNB}^{\bullet -}$				$1,4\text{-DNB}^{\bullet -}$			
Solvent	γ_{293}	$\tau_{L293}/10^{-12}$ s	H_L	k_{293}/s^{-1}	$\lambda_{0\ 293}$	ΔG^*	ln A	k_{293}/s^{-1}	$\lambda_{0\ 293}$	ΔG^*	ln A
Methanol	0.537	4.85	11.8	2.7×10^6	107	43	29.7	2.9×10^9	80	26 ± 2	36.2
Ethanol	0.500	20.2	14.1	2.9×10^6	100	42	29.4	1.1×10^9	74	22 ± 1	33.8
Propan-1-ol	0.476	44.6	15.9	—	—	—	—	8.7×10^8	71	26 ± 2	35.2
Propan-2-ol	0.474	44.8	—	5.0×10^6	96	43	30.1	—	—	—	—
Butan-1-ol	0.455	80	19.9	—	—	—	—	5.1×10^8	68	29 ± 2	35.8
Pentan-1-ol	0.444	130	21.6	—	—	—	—	3.8×10^8	66	30 ± 3	36.0
Hexan-1-ol	0.423	182	23.7	—	—	—	—	3.7×10^8	63	35 ± 2	38.2
Octan-1-ol	0.393	356	26.5	—	—	—	—	2.7×10^8	61	36 ± 3	38.0

radical anion (Table 1), which was previously shown to follow this regime. However, the rate constants for 1,4-DNB radical anion show an opposite trend. From Table 1, one can notice an increase in the rate constant with increasing γ. As noted elsewhere,[1] such behaviour suggests that the reaction follows the diffusive adiabatic regime.

In the diffusive adiabatic regime, both the pre-exponential factor [eqn. (12)] and λ_0 depend on the solvent. However, the solvent dependence of the pre-exponential factor dominates, in most cases, the equation of the rate constant. The positive correlation between the rate constants of IEE in 1,4-DNB and γ, found in Table 1, occurs because τ_L decreases with γ. In fact, for the present set of solvents, a good empirical linear correlation between ln τ_L and γ ($r = 0.992$ at 293 K), with a negative slope, is obtained

$$\ln \tau_L = a\gamma + b \qquad (17)$$

$$a = -29.7 \pm 1.6; \quad b = -9.8 \pm 0.7 \ (293\ \mathrm{K})$$

This correlation between τ_L and γ was found before for alcohols[1] and is responsible, in the present case, for the correlation between k and γ with a positive slope. Rate diminution caused by the increase in the activation energy with γ is more than offset by the increase of the term $\ln(1/\tau_L)$, and the overall effect is an increase in the rate constant of the reaction. This observed behaviour is direct evidence for the role of solvent relaxation of the reactions dynamics and indicates the presence of a diffusive regime.

4.3 The amount of transferred charge *z* and the outer-sphere reorganisation energy λ_0

One approach commonly used for separating the solvent effects on v and on λ_0 is to correct the rate constant for the anticipated solvent dependence of the pre-exponential factor. Following this idea, the rate constant can be rewritten as

$$\ln(k\tau_L/\gamma^{1/2}) = 1/2\ \ln(z^2p/16RT) - (z^2p/4RT\gamma - (\lambda_i/4 - H_{12})/RT \qquad (18)$$

A plot of $\ln(k\tau_L/\gamma^{1/2})$ *versus* γ should be linear with slope equal to $-z^2p/4RT$. However, this is only true if the parameters τ_L and γ do not correlate with each other, otherwise the plot will also reflect the dependence of τ_L on γ. Since, for the present set of solvents, τ_L and γ do correlate with each other, eqn. (18) cannot be used.

In the present case, one has to combine eqn. (12), (16) and (17) to obtain

$$\ln(k/\gamma^{1/2}) = [-a - z^2p/4RT]\gamma + 1/2\ \ln(z^2p/16RT) - (\lambda_i/4 - H_{12})/RT - b \qquad (19)$$

Fig. 2 shows a plot of $\ln(k/\gamma^{1/2})$ *versus* γ for the IEE reaction in 1,4-DNB radical anion at 293 K. As predicted by eqn. (19), a linear correlation is obtained experimentally:

$$\ln(k/\gamma^{1/2}) = (15.4 \pm 1.8)\gamma + (13.6 \pm 0.8); \quad r = 0.967 \qquad (20)$$

In order to estimate the shape of the ellipsoidal cavity a molecular model of the 1,4-DNB molecule based on bond distances and on van der Waals radii was constructed. The best fit was obtained for an ellipsoidal cavity with semi-axes of $a = 4.6$ Å and $b = 2.7$ Å. The distance between redox centres is $d = 5.75$ Å. With these parameters a value of $p = 428$ kJ mol^{-1} is calculated from eqn. (6)–(8) for the set of solvents used.

Knowing the value of p, one can calculate the fraction of the transferred charge z from the slope of eqn. (19). The value obtained at 293 K, $z_{\mathrm{exp}} = 0.54 \pm 0.07$, is shown in Table 2, together with the values obtained previously for the radical anions of 1,3-DNB and 2,7-DNN. In qualitative terms, z_{exp} shows the expected effect of the structure of the two radicals. The transferred charge is lower for 1,4-DNB because, in this radical, the two nitro groups are in a conjugated *para* position and the charge, at any instant, is more equally distributed between the two nitro groups. In the non-conjugated 1,3-DNB and 2,7-DNN radical anions, the instantaneous difference in charge between the two groups is much higher because the unpaired electron is almost completely localised in one of the nitro groups. The same qualitative agreement can be foreseen in the values of the transferred charge calculated from the difference in the spin densities on the two nitro groups obtained from the HMO-McLachlan calculations (Table 2). The theoretical calculations do not reproduce well the experimental values of z in protic solvents, as found before for 1,3-DNB and 2,7-DNN radical anions.[6,7,14] Although the calculated values

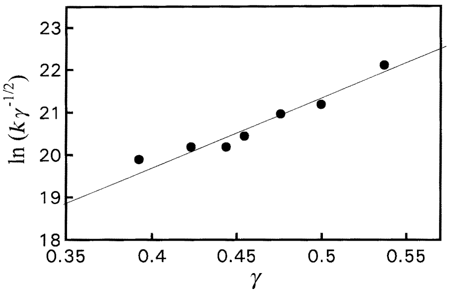


Fig. 2 Dependence of the IEE rate constants on the solvent parameter γ at 293 K, according to eqn. (16).

Table 2 Fraction of transferred charge between the two nitro groups in radical anions of dinitro compounds at 293 K

Radical anion	z_{exp}	z_{calc}[a]
2,7-DNN[b]	0.99	0.70
1,3-DNB[c]	0.94	0.73
1,4-DNB	0.54[d]	0.31

[a] From HMO calculations. [b] Ref. 14. [c] Ref. 6, 7. [d] From the slope of eqn. (19).

are systematically lower than the experimental ones, z_{calc} follows the same trend as z_{exp}, being lower for 1,4-DNB radical anion than for the other two radicals.

The outer-sphere reorganisation energies, calculated from z_{exp} and eqn. (10), are shown in Table 1 for each solvent at 293 K. For a given solvent, the value of this energy depends, under the ellipsoidal cavity model, on the amount of transferred charge z and on the shape of the molecule through the parameter p. This parameter is higher for 1,4-DNB than for 1,3-DNB ($p = 224$ kJ mol^{-1}) owing to the more elongated shape of the former molecule and to the longer distance between redox centres.[32] The experimental values of λ_0 for 1,4-DNB are, however, lower than those for 1,3-DNB, reflecting instead the higher differences in $(z_{exp})^2$.

4.4 Inner-sphere reorganisation energy λ_i and the resonance energy splitting H_{12}

From the intercept of eqn. (19) the experimental value of $(\lambda_i/4 - H_{12})$ can be extracted. At 293 K the calculations yield $(\lambda_i/4 - H_{12}) = -7.6$ kJ mol^{-1}. Calculation of λ_i^{∞} from eqn. (3) yields $\lambda_i^{\infty} = 6.8$ kJ mol^{-1}. If we correct this value according to eqn. (5) we get $\lambda_i^{293} = 3.3$ kJ mol^{-1}. Both these values are much smaller than λ_0. A value of $H_{12} = 8.4$ kJ mol^{-1} is obtained from λ_i^{293} ($H_{12} = 9.3$ kJ mol^{-1} if we use λ_i^{∞}). This relatively high value for the resonance energy splitting is usual for these type of intramolecular reactions where $H_{12} \gg RT$.[4,33]

4.5 Temperature dependence of the rate constants and activation parameters

The rate constants of the IEE reaction in 1,4-DNB radical anion at several temperatures were used to calculate the activation energy of the reaction. One difficulty was to define the temperature dependence of the pre-exponential factor, eqn. (12). One should note that the longitudinal relaxation time is approximately proportional to the viscosity and depends strongly on the temperature through an exponential term [eqn. (21)]

$$\tau_L = h/kT \exp(-S_L/R)\exp(H_L/RT) = c/T \exp(H_L/RT) \quad (21)$$

Including the dependence of τ_L on temperature in the expression for the rate constant we have

$$k = AT^{1/2} \exp(-\Delta G^*/RT) \quad (22)$$

with

$$\Delta G^* = \frac{\lambda_i + \lambda_0}{4} - H_{12} + H_L \quad (23)$$

and

$$A = 1/c(\lambda_0/16R)^{1/2} \quad (24)$$

Although $\lambda_0 = z^2 p\gamma$ depends on the temperature by z and γ, the temperature dependence of λ_0 in eqn. (24) was neglected, since γ and z (see below) vary only slightly within the range of temperatures used and in opposing directions (in methanol $\gamma = 0.534$ at 273 K and $\gamma = 0.539$ at 313 K).

The activation parameters of IEE extracted from the slope of the plots of $\ln(kT^{-1/2})$ *versus* $1/T$ for the various alcohols are presented in Table 1. The increase in ΔG^* from methanol to octanol clearly reflects the increase in H_L for the more viscous solvents, since λ_i and H_{12} do not depend on the solvent and λ_0 decreases with decreasing γ. Adding the value of $(\lambda_i/4 - H_{12}) = -7.6$ kJ mol^{-1} found before, to $\lambda_0/4$ and H_L for each solvent, according to eqn. (23), the experimental values of the activation energies ΔG^* are almost perfectly reproduced. The differences between the two values are within 10%.

4.6 Temperature dependence of z

A calculation of the fraction of the transferred charge at 273 and 313 K was performed, using rate constants for the IEE reaction at these temperatures. The slope of the plots of $\ln(k/\gamma^{1/2})$ *vs.* γ [eqn. (16)] vary from 20.1 at 273 K to 11.3 at 313 K. Surprisingly, the calculated z_{exp} values vary only slightly, from $z_{exp} = 0.56$ at 293 K to $z_{exp} = 0.52$ at 313 K. This happens because the change in the slope of the $\ln \tau_L$ *vs.* γ relation [parameter "a" in eqn. (16)] varies in the same magnitude, from -36.5 at 273 K to -23.8 at 313 K, that is, the change in the rate constant with temperature is due mainly to the change in τ_L with T and not to the activation term. This is another proof of the diffusive character of the reaction mechanism.

Since the specific solvation is lower at higher temperatures, z decreases with increasing temperature. This decrease is less significant if the interaction between the solvent and the radical anion is stronger, as found before for 1,3-DNB and 2,7-DNN radical anions in alcohols as compared with aprotic solvents.[6–8]

5 Conclusions

The present data clearly demonstrate the role of solvent dynamics on the kinetics of IEE in the 1,4-DNB radical anion. This reaction obeys a diffusive adiabatic regime, while the same reaction in the isomeric 1,3-DNB radical anion in alcohols follows a uniform adiabatic reaction behaviour. The difference reflects the faster reaction in the 1,4-DNB radical, where the electron transfer occurs on a timescale where solvent-relaxation processes controls the reaction rate. For the 1,3-DNB radical, solvent relaxation, being much faster than the electron transfer step, does not affect the reaction dynamics.

The EPR spectra of 1,4-DNB radical anion reported in the literature in aprotic solvents[34] do not show evidence of alternating line-broadening effects. In such solvents, the fraction of transferred charge z (and hence λ_0) is substantially lower than in alcohols, due to a lower specific solvation. Since, in most aprotic solvents, the values of $1/\tau_L$ are higher than in alcohols, the reaction is, under these conditions, too fast to exert discernible alternating line-broadening effects on the EPR spectra.

The 1,4-DNB radical anion is the first example where alternating line-broadening effects caused by a solvent-induced IEE reaction are found in the EPR spectra of a free ion conjugated aromatic system. Previous examples occurred in spectra of radicals substituted in non-conjugated *meta* positions, in radicals where the two groups are sterically forced out of planarity or in ion-pairs, in which the counter-ion jumps simultaneously with the electron.

The classical resonance theory postulates that all the resonance structures have equal energy and that no activation barrier exists between them. The results presented here show that, in the case of the 1,4-DNB radical anion, these conditions are not valid if solvation stabilises, by hydrogen bonding, the structures where the charge is localised in one of the nitro groups, as compared to those where the charge is in the aromatic ring.

Acknowledgements

The financial support of FCT (Fundação para a Ciência e Tecnologia) through its Centro de Processos Químicos da Universidade Técnica de Lisboa is gratefully acknowledged. G.G. thanks the EC-Socrates program, the Austrian Academic

Exchange Service (ÖAD) and the VW-Foundation for financial support.

References

1 M. J. Weaver, *Chem. Rev.*, 1992, **92**, 463.
2 G. L. Closs and J. R. Miller, *Science*, 1988, **240**, 440.
3 P. F. Barbara, F. J. Meyer and M. A. Ratner, *J. Phys. Chem.*, 1996, **100**, 13148.
4 S. F. Nelsen, R. F. Ismagilov and D. R. Powell, *J. Am. Chem. Soc.*, 1997, **119**, 10213.
5 S. F. Nelsen, R. F. Ismagilov and D. A. Trieber II, *Science*, 1997, **278**, 846.
6 G. Grampp, M. C. B. L. Shohoji and B. Herold, *Ber. Bunsen-Ges. Phys. Chem.*, 1989, **93**, 8.
7 G. Grampp, M. C. B. L. Shohoji, B. Herold and S. Steenken, *Ber. Bunsen-Ges. Phys. Chem.*, 1990, **94**, 1507.
8 J. P. Telo, M. C. B. L. Shohoji, B. J. Herold and G. Grampp, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 47.
9 J. H. Freed and G. K. Fraenkel, *J. Phys. Chem.*, 1962, **37**, 1156.
10 S. Mahmood, B. J. Tabner and V. A. Tabner, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3253.
11 J. P. Telo and M. C. B. L. Shohoji, *J. Chem. Soc., Perkin Trans.* 2, 1998, 711.
12 R. A. Marcus, *Annu. Rev. Phys. Chem.*, 1964, **15**, 155.
13 R. A. Marcus, *J. Phys. Chem.*, 1964, **43**, 679.
14 R. A. Marcus and N. Sutin, *Biochem. Biophys. Acta*, 1985, **818**, 265.
15 T. Holstein, *Philos. Mag. B*, 1978, **37**, 499.
16 G. Grampp and W. Jaenicke, *Ber. Bunsen-Ges. Phys. Chem.*, 1984, **88**, 325.
17 G. Grampp and W. Jaenicke, *J. Chem. Soc., Faraday Trans.* 2, 1985, **81**, 1035.
18 B. S. Brunschwig, S. Ehrenson and N. Sutin, *J. Phys. Chem.*, 1986, **90**, 3657.
19 B. S. Brunschwig, S. Ehrenson and N. Sutin, *J. Phys. Chem.*, 1987, **91**, 4714.
20 I. Rips and J. Jortner, *J. Phys. Chem.*, 1987, **87**, 2090.
21 H. A. Kramers, *Physica* (*Amsterdam*), 1940, **7**, 284.
22 L. D. Zusman, *Chem. Phys.*, 1980, **49**, 295.
23 J. Barthel, K. Bachhuber, R. Buchner and H. Hetzenauer, *Chem. Phys. Lett.*, 1990, **167**, 62.
24 S. K. Garg and C. P. Smith, *J. Phys. Chem.*, 1965, **69**, 1295.
25 W. R. Fawcett, *Chem. Phys. Lett.*, 1992, **199**, 153.
26 J. A. Dean, *Handbook of Organic Chemistry*, McGraw-Hill, New York, 1987.
27 *CRS-Handbook of Chemistry and Physics*, CRC Press, Boca Raton, 57th edn., 1977.
28 F. Gerson, *High Resolution ESR Spectroscopy*, Wiley, Verlag Chemie, Weinheim, 1970.
29 M. Branca, A. Gamba and C. Oliva, *J. Magn. Reson.*, 1983, **54**, 216.
30 G. Bartoli, R. Dalpozzo and L. Grossi, *J. Chem. Soc., Perkin Trans. 2*, 1989, 573.
31 G. Grampp and G. Rauhut, *J. Phys. Chem.*, 1995, **99**, 1815.
32 N. Sutin, B. S. Brunschwig, C. Creutz and J. R. Winkel, *Pure Appl. Chem.*, 1977, **8**, 391.
33 S. F. Nelsen, H. Q. Tran and M. A. Nagy, *J. Am. Chem. Soc.*, 1998, **20**, 298.
34 Landolt-Börnstein New Series, *Magnetic Properties of Free Radicals*, Springer, Berlin, 1980, group II, vol. 9d1, pp. 634–639.

Paper 8/06679E