

EPR measurements on the diffusionless homogeneous electron-self exchange kinetics of the nitrobenzene–nitrobenzene radical anion couple in nitrobenzene as solvent †



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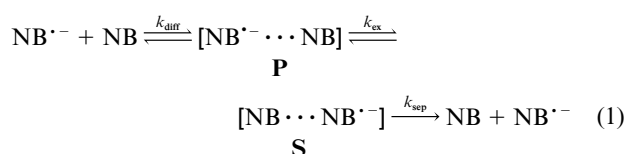
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Electron-self exchange rate constants of the nitrobenzene–nitrobenzene radical anion couple (NB/NB^{•-}) and their temperature dependence have been measured by EPR-linebroadening effects in the so-called ‘fast exchange limit’. Nitrobenzene itself serves as solvent. The first order rate constants of these diffusionless reactions vary between 2.8×10^8 and $9.7 \times 10^8 \text{ s}^{-1}$ within a temperature range of 296–353 K.

The results are compared on the basis of Marcus theory of electron transfer reactions with corresponding results of the same redox couple in solvents like DMF and CH₃CN.

Introduction

Electron self-exchange reactions as shown in reaction (1) are good examples for the application of Marcus theory, since for that type of reaction the driving force $\Delta G^\circ = 0$ and the activation energy in the sense of Marcus reduces to $\Delta G^\ddagger = \lambda/4$. λ denotes the total reorganization energy.^{1–5} Different redox couples with radical cations^{6–8} and radical anions^{9–12} are reported in the literature. The homogeneous electron-self exchange rates of all systems reported up to now were estimated in solution with organic solvents. Reaction (1) shows the



scheme that is normally used to describe an electron-self exchange reaction in solution, where P and S denote the precursor complex and the successor complex, respectively.

The first step is a diffusional one forming a precursor complex P and is normally described by an association constant K_A . In the present investigation the situation is slightly different since the diffusional step in reaction (1) is omitted. Because nitrobenzene serves as a solvent itself no diffusion is necessary. The precursor complex P is formed immediately after the nitrobenzene radical anion is generated. Also the final separation step described by k_{sep} is omitted, therefore reaction (1) is reduced to reaction (2). The electron transfer reaction takes



place with a first order rate constant k_{ex} directly from the successor complex S.

The rate for such a unimolecular reaction is given by Marcus¹ as eqn. (3), κ_{el} reflects the electronic transmission

$$k_{\text{ex}} = \kappa_{\text{el}} \nu_n \exp(-\Delta G^\ddagger/RT) \quad (3)$$

coefficient which is the deciding factor in whether the transfer is adiabatic ($\kappa_{\text{el}} \approx 1$) or diabatic ($\kappa_{\text{el}} \ll 1$). ν_n is the nuclear frequency factor. The bimolecular rate constant of a homogeneous electron-self exchange reaction in solution, according to reaction (1) is expressed by eqn. (4). The Marcus reorganiz-

$$k_{\text{et}} = K_A k_{\text{ex}} \quad (4)$$

ation energy λ is the sum of the two terms given by eqn. (5), λ_i

$$4\Delta G^\ddagger = \lambda_i + \lambda_o \quad (5)$$

describes the changes in bond lengths and angles, if any, related to the electron transfer. In a series of papers, Nelsen *et al.*¹³ pointed out that AM-1 is a useful quantum-chemical method for calculation of inner sphere reorganization energies. The outer sphere reorganization energy λ_o describes the reorientation of the solvent molecules for the charge transfer process. Within the continuum model λ_o is given by eqn. (6), where r is

$$\lambda_o = z^2 e_o^2 N_A / (4\pi\epsilon_o) (1/r + 1/d) (1/n^2 + 1/\epsilon_s) \quad (6)$$

the molecular radius, d the reaction distance and is normally taken in the closest approach approximation as $d = r_N + r_{N^{\bullet-}} = 2r$. The radius of the neutral molecule is assumed to be equal to the radius of the corresponding radical anion. r is often calculated from the molecular mass m and the density ρ of nitrobenzene as: $r = (3m/4\pi\rho N_A)^{1/3}$. n and ϵ_s are the refractive index and the static relative permittivity of the solvent, respectively, e_o is the elementary charge and N_A is Avogadro's constant.

For the association constant K_A mainly two models are discussed in the literature.

The Eigen–Fuoss model

Derived from diffusion considerations Eigen¹⁴ gave the expression eqn. (7) for K_A ; an identical expression is obtained by

$$K_A = (4/3)\pi N_A d^3 \quad (7)$$

Fuoss.¹⁵ Implicit in the Eigen–Fuoss model is the assumption of a single reaction distance.

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The reaction zone model

Sutin and Brunschwig¹⁶ proposed the reaction zone model by introducing a reaction zone thickness of roughly $\delta d = 0.8 \text{ \AA}$. Within this zone the precursor complex is formed and the reaction can occur. The association K_A then becomes eqn. (8).

$$K_A = 4\pi N_A d^2 \delta d \quad (8)$$

The aim of this paper is to report on some preliminary results of the diffusionless electron-self exchange reaction between nitrobenzene (NB) and its radical anion ($\text{NB}^{\cdot-}$) where nitrobenzene serves as the solvent itself, and to compare the results with those obtained in other organic solvents like DMF and CH_3CN . Comparison of both results should give some information about the association constant K_A .

Experimental

Nitrobenzene was a commercial sample obtained from Fluka (grade p.a.) and dried over molecular sieves (3 Å) and subsequently carefully distilled. The supporting electrolyte, tetrabutylammonium perchlorate (TBAP) (Fluka, grade p.a.) was recrystallized twice from EtOH. Nitrobenzene radical anions were generated electrochemically. An 'intra-muros' EPR-electrochemical cell was used similar to the helix-type construction published by Allendoerfer *et al.*^{17,18} A gold wire (0.5 mm) served as a working electrode and a platinum wire (0.3 mm) as a counter electrode, centered inside the gold wire helix construction. A Wenking potentiostat (type 68FR0.5) and scan generator (model VSG72) have been used to perform the electrolysis. An Ag/Ag^+ electrode serves as a reference electrode. The EPR spectra were recorded with a modified JEOL-JES 3BX spectrometer (X-band) working at 100 kHz modulation frequency and equipped with a variable temperature control unit JEOL-VT 10. The temperature has been controlled up to $\pm 0.5^\circ\text{C}$. A microwave preamplifier (type Miteq, model AFM-5S-8596-20) was installed into the microwave bridge just before the crystal detector diode to improve the S/N ratio.¹⁹

Results and discussion

If commercially available nitrobenzene is only dried over molecular sieves and then electrolysed together with 0.1 M TBAP as supporting electrolyte a stable radical anion is formed showing exactly the EPR-hyperfine pattern of the *p*-dinitrobenzene radical anion. The reported²⁰ coupling constants $a_N = 0.174$ and $a_H = 0.112$ mT fit exactly the EPR-spectrum observed. Therefore great care must be taken in drying and purifying the nitrobenzene. After a dynamic drying with molecular sieves (3 Å), an additional fractional distillation is necessary. Electrolysis of this carefully purified nitrobenzene results in an EPR-spectrum showing only one single line (see Fig. 1). The appearance of only one single EPR-line is a consequence of the high concentration (8.12 M) of neutral nitrobenzene present, which brings the EPR-spectrum into the so-called 'fast exchange limit'. The nitrobenzene radical anion concentration is in the order of 1×10^{-4} M, controlled by a coulometric procedure. Our results are in contrast to a paper of Suga and Aoyagui²¹ who find some remaining EPR-splitting even in the fast exchange-limit. We believe that some 1,4-dinitrobenzene or another impurity remained still in the sample.

Johnson and Holz²² first pointed out that eqn. (9) is applic-

$$k_{\text{ex}} = b\nabla_2/(\Delta B_{\text{pp}} - \Delta B_{\text{pp}}^\circ) \quad (9)$$

able to a homogeneous electron-self exchange reaction in the 'fast exchange limit', with $b = (2\pi)(2/\sqrt{3})g_e\beta_e/h = 28.03 \text{ MHz mT}^{-1}$. ΔB_{pp} denotes the peak-to-peak line width with electron exchange, whereas $\Delta B_{\text{pp}}^\circ$ is the true EPR-line width without any

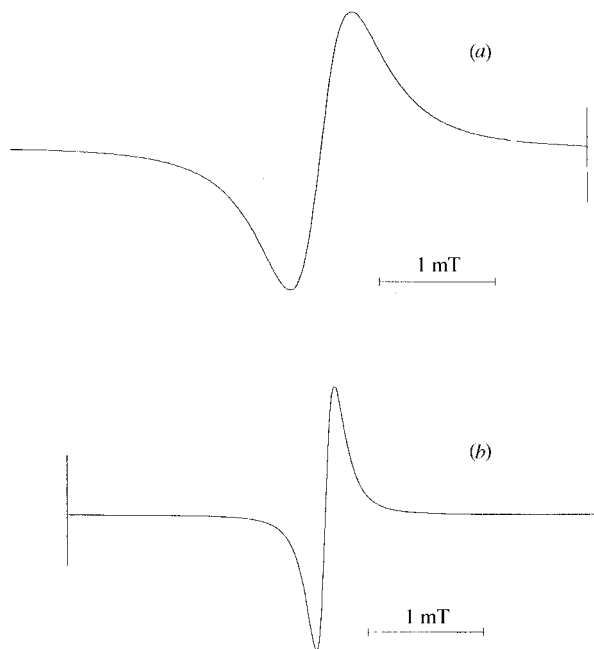


Fig. 1 EPR-spectrum in the 'fast exchange limit'. Homogeneous electron-self exchange of the $\text{NB}/\text{NB}^{\cdot-}$ couple. Solvent: nitrobenzene. (a) $T = 296 \text{ K}$, (b) $T = 353 \text{ K}$.

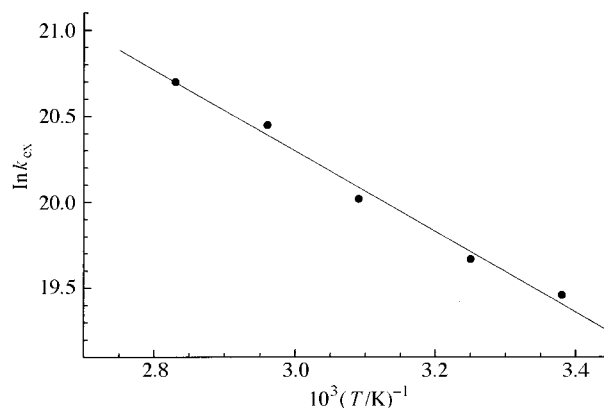


Fig. 2 Temperature dependence of the electron-self exchange rate of the $\text{NB}/\text{NB}^{\cdot-}$ couple. Solvent: nitrobenzene.

exchange reaction. From measurements of the nitrobenzene radical anion in dimethylformamide a natural linewidth of $\Delta B_{\text{pp}}^\circ = 0.020$ mT is found. ∇_2 expresses the second moment of the spectrum and can be calculated according to van Vleck's general equation, eqn. (10), where p_i is the normalized popu-

$$\nabla_n = \sum_i p_i (B_i)^n \quad (10)$$

lation factor and B_i is the resonance magnetic field of line i . With the coupling constants of nitrobenzene radical anion reported²³ as $a_N = 1.092$, $a_{\text{H}_{2,6}} = 0.339$, $a_{\text{H}_{3,5}} = 0.109$ and $a_{\text{H}_1} = 0.397$ mT one obtains values for the second and fourth moment of the nitrobenzene radical anion spectrum of 7.163 mT^2 and 960.7 mT^4 , respectively. Even the appearance of a single EPR-line is not a guarantee that we are in the fast exchange limit, only a requirement. A criterion for the applicability of eqn. (9) is given by a Z -value [eqn. (11)].²² For $Z \leq 0.2$, eqn. (9) can be

$$Z = (\sqrt{3}/2)(\Delta B_{\text{pp}} - \Delta B_{\text{pp}}^\circ) (\sqrt{\nabla_2}) \quad (11)$$

used to calculate the rate constants k_{ex} , whereas for $0.2 \leq Z \leq 0.4$ a cubic corrected equation [eqn. (12)] must be used,

$$k_{\text{ex}} = b\nabla_2/(\Delta B_{\text{pp}} - \Delta B_{\text{pp}}^\circ) [1 + (c\nabla_2 X)/k_{\text{ex}}] \quad (12)$$

Table 1 Observed EPR peak-to-peak linewidth ΔB_{pp} in the 'fast exchange limit' for the NB/NB⁻ couple in NB as a solvent, together with the exchange rates k_{ex} as a function of temperature

T/K^a	$\Delta B_{pp}/mT^b$	$k_{ex}/10^{-7} s^{-1}c$
296	0.561	28.4 ± 0.3
308	0.453	34.9 ± 0.4
323	0.319	49.5 ± 0.5
338	0.212	76.3 ± 0.8
353	0.170	97.4 ± 1.0

^a Temperature uncertainty: ± 0.5 K. ^b Uncertainty: ± 0.5 mT. ^c The uncertainties in the rate constants are mainly given by the uncertainties in ΔB_{pp} [see eqn. (9)]. Note that the errors are relatively low for this region of rate constants, since ΔB_{pp} can be measured quite accurately with a NMR-gaussmeter.

Table 2 Homogeneous electron-self exchange rate k_{ex} for the NB/NB⁻ couple in DMF and NB ($T = 296$ K)

Solvent	$k_{ex}/10^{-7} dm^3 mol^{-1} s^{-1}a$	$k_{ex}/10^{-7} s^{-1}$	Supporting electrolyte
DMF	3.1 ± 0.5^b	—	TBAP ^d
DMF	3.0 ± 0.2^c	—	TEAP ^e (0.01 mol dm ⁻³)
CH ₃ CN	0.68 ± 0.014^f	—	TBAP ^d (0.1 mol dm ⁻³)
NB	—	28.4 ± 0.3	TBAP ^d (0.1 mol dm ⁻³)

^a The reported observed bimolecular rate constants k_{obs} are close to the diffusion controlled limit and must be corrected according to: $1/k_{ex} = 1/k_{obs} - 1/k_{diff}$. A simple Smoluchowski approach is used for $k_{diff} = 8RT/3\eta$. η = solvent viscosity: η (DMF, 296 K) = 0.93 cP. ^b Ref. 25. ^c Ref. 26. ^d Tetrabutylammonium perchlorate. ^e Tetraethylammonium perchlorate. ^f Ref. 27.

with $c = (2g\beta_e/h)^2 = 3.10 \times 10^4$ MHz² mT⁻² and $X = 2 - [\nabla_4/(\nabla_2)^2]$. For the investigation described in this paper the uncorrected eqn. (9) can only be used for the spectra at $T = 353$ and 338 K. For the other spectra eqn. (12) must be used.

Table 1 gives the results of the measured ΔB_{pp} and the k_{ex} values obtained as a function of different temperatures. From an Arrhenius-like plot of $\ln k_{ex}$ vs. $1/T$ an activation energy of $\Delta G^* = 19.5$ kJ mol⁻¹ is obtained (see Fig. 2). This value can be compared with the theoretical calculated ΔG^* (theo) = 21.9 kJ mol⁻¹, calculated from both the inner and the outer sphere reorganization energies, see eqn. (5). For λ_i one obtains 15.4 kJ mol⁻¹ from an AM-1 calculation and for λ_o 72.1 kJ mol⁻¹ is obtained within the simple spherical continuum approximation from eqn. (6), assuming $r_{NB} = r_{NB^-} = 3.7$ Å. In nitrobenzene λ_o is only slightly temperature dependent, since the term $(1/n^2 - 1/\epsilon_s)$ varies only between 0.385–0.376 within the temperature range of 296–353 K. A temperature independent reaction distance is assumed. The slight difference in the observed and calculated ΔG^* values maybe due to an additional interaction not included in Marcus theory. Nitrobenzene possesses a relatively high permanent dipole moment of 4.0 Db and ion-dipole interactions are possible at these short reaction distances. The intercept of the $\ln k_{ex}$ vs. T^{-1} plot is equal to $\ln(\kappa_{el}v_n)$, see eqn. (3). Together with the average nuclear frequency factor of $v_n = 5 \times 10^{13}$ s⁻¹ one obtains a κ_{el} value of 0.015. Such a low value indicates a diabatic reaction behaviour of the electron-self exchange reaction. A detailed discussion of these effects with more sophisticated models will be given in a forthcoming paper.²⁴

Table 2 shows the results of the exchange rates for the NB/NB⁻ couple in DMF and NB as solvents. For the comparison of the association constants K_A eqns. (4) and (3) are used. Provided that the inner sphere reorganization energy and the pre-exponential factor $(\kappa_{el}v_n)$ are both solvent independent, one obtains eqn. (13) with the solvent parameters $(1/n^2 - 1/$

$$\ln K_A = \ln(k_{ex}/k_{ex}) - e_o^2 N_A / (32\pi\epsilon_o RT) [(1/n^2 - 1/\epsilon_s)_{NB} - (1/n^2 - 1/\epsilon_s)_{DMF}] \quad (13)$$

$\epsilon_s)_{NB, 296 K} = 0.386$ and $(1/n^2 - 1/\epsilon_s)_{DMF, 296 K} = 0.460$ one can calculate the association constant as $K_A = 0.43$ dm³ mol⁻¹. A similar calculation for CH₃CN, $(1/n^2 - 1/\epsilon_s)_{CH_3CN, 296 K} = 0.530$, gave $K_A = 0.37$ dm³ mol⁻¹. Theoretical calculations after the Eigen–Fuoss model, eqn. (7), and the Sutin reaction zone model, eqn. (8), gave 1.02 and 0.33 dm³ mol⁻¹, respectively. Comparison with the experimental values indicate that the Eigen–Fuoss model, derived from free volume considerations¹⁴ as well as from the forward and reverse rates of diffusion-controlled reactions,¹⁵ is less suitable for the description of the association constant in electron transfer reaction. Sutin's model, taking the association constant as an effective volume $4\pi d^2 \delta d$, where the d values over which electron transfer can still occur significantly lie between d and $d + \delta d$, is more suitable.

More detailed experiments with different liquid nitrocompounds are in progress to obtain further information about these diffusionless electron transfer reactions in solution.²⁴

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