

Electron self-exchange kinetics between 2,3-dicyano-5,6-dichloro-*p*-benzoquinone (DDQ) and its radical anion.

Part 1. Solvent dynamical effects †



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Rate constants of the electron self-exchange between 2,3-dicyano-5,6-dichloro-*p*-benzoquinone (DDQ) and its radical anion (DDQ^{•-}) are measured by means of EPR-line-broadening effects in different solvents at $T = 293$ K. Solvents of different polarity like CHCl₃, CH₂Cl₂, CH₃CN, benzonitrile and acetone were used. No correlation is found in the sense of the classical Marcus theory, where $\ln k_{\text{et}}$ should depend linearly on the solvent parameter $\gamma = 1/n^2 - 1/\epsilon_s$ (n = refractive index, ϵ_s = static relative permittivity of the solvent). The investigated γ -range was $0.270 \leq \gamma \leq 0.530$. The diffusion corrected rate constants k_{et} cover a range of 8.9 to $36.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and clearly show a solvent-dynamical effect, expressed by the longitudinal relaxation time τ_1 dependence of the solvents used. The observed dynamical friction solvent effects clearly indicate an adiabatic reaction behaviour of this electron self-exchange reaction.

Introduction

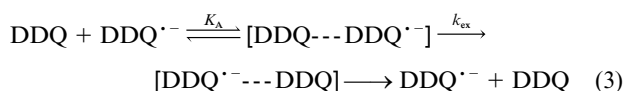
Electron self-exchange reactions are simple examples for testing the Marcus theory of electron transfer in solution.¹⁻¹² No bonds are broken or new ones formed during this type of reaction and the driving force $\Delta G^\circ = 0$. Only an electron is transferred (eqn. (1)). If the resonance splitting energy V between the



precursor and successor potential energy surfaces is small enough, the activation energy ΔG^* is approximately given by $\Delta G^* = 1/4 \lambda$. λ denotes the total Marcus reorganization energy and is expressed by: $\lambda = \lambda_i + \lambda_o$. λ_i describes the inner sphere reorganization caused by the changes of mainly bond lengths and bond angles. The solvent dependence of an electron transfer reaction is described by a Born based continuum equation¹³⁻¹⁵ expressing the outer sphere reorganization, eqn. (2). The Marcus solvent parameter γ is given by:

$$\lambda_o = \frac{e_0^2 N_L}{4\pi\epsilon_0} \left(\frac{1}{r} - \frac{1}{d} \right) \gamma \quad (2)$$

$\gamma = (1/n^2 - 1/\epsilon_s)$. Herein, the solvent is characterized by its refractive index n and its static relative permittivity ϵ_s . r denotes the radius of the reacting species. r (DDQ) and r (DDQ^{•-}) are assumed to be equal. d is the reaction distance in the transition state and is normally approximated by $d = 2r$. Following the well-established reaction scheme¹⁶ of eqn. (3), one gets



expression (4) for the overall transfer rate constant, where k_{ex} is

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

given by eqn. (5). ν_n denotes the nuclear barrier frequency. K_A is

$$k_{\text{ex}} = \nu_n \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (5)$$

the association constant forming the precursor complex. Assuming both a similar transition state independent of the solvent used and a solvent independent inner sphere reorganization one gets relation (6) for the solvent dependence, at

$$\ln k_{\text{et}} = a - b\gamma \quad (6)$$

constant temperature. A linear dependence between $\ln k_{\text{et}}$ and $\gamma = (1/n^2 - 1/\epsilon_s)$ is predicted. For highly non-polar solvents, n^2 equals ϵ_s (Maxwell relation) and γ tends to 0. For solvents with high relative permittivity ϵ_s , only the term $1/n^2$ dominates γ . The theoretical range of γ is therefore $0 \leq \gamma \leq 0.55$.

There exist only a few papers on the solvent dependence of electron self-exchange reactions.¹⁻⁶ The published results are controversial. Good correlations, according to eqn. (6), are found for various *p*-phenylenediamines and their corresponding radical cations (Wurster's cations).^{1,2} But even for the TMPPD/TMPPD^{•+} couple (TMPPD is *N,N,N',N'*-tetramethyl-*p*-phenylenediamine) for example, the observed rate constants increase by a factor of 6 only on changing the solvent from CHCl₃ ($\gamma_{293\text{K}} = 0.270$) to CH₃CN ($\gamma_{293\text{K}} = 0.530$), whereas eqn. (2) predicts an 80-fold increase.¹⁷ The difference is explained by additional ion-dipole and induced dipole-ion interactions.³ A similar behaviour is observed for the [Cr(bipy)₂]^{0/+} redox couple.^{5,6} The increase is only by a factor of 2.5, changing $\gamma_{298\text{K}}$ from 0.3 to 0.51 by using solvent mixtures in part, whereas a 5.2-fold increase is predicted by eqn. (6).¹⁷ The last two examples gave at least linear plots of $\ln k_{\text{et}}$ vs. γ , whereas other systems completely fail. The self-exchange rates of sesquibicyclic hydrazines for example have been measured in many different solvents. The experimental rates do not correlate with the Marcus solvent parameter γ .¹⁸

From recent experimental and theoretical considerations it

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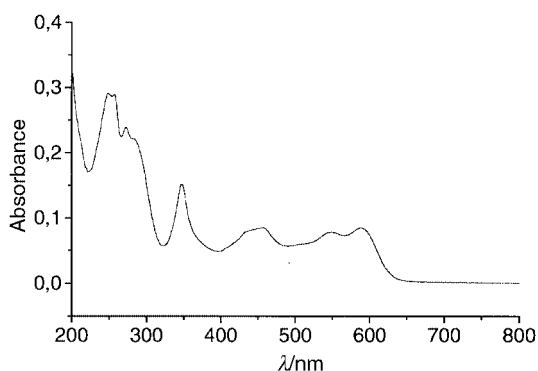


Fig. 1 UV-VIS spectrum of the DDQ^{•-} radical anion in CH₃CN.

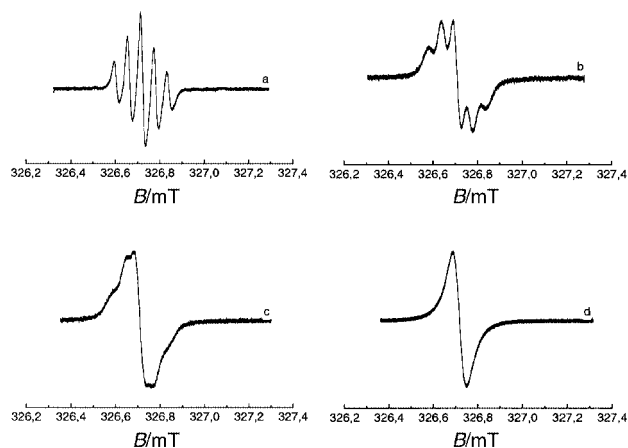
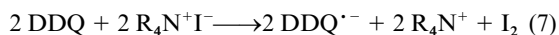


Fig. 2 EPR-spectra of DDQ^{•-} as a function of different neutral concentrations [DDQ], in acetonitrile at 293 K. The radical concentration is always 0.5 mM. (a) [DDQ] = 0 mM, (b) [DDQ] = 1.5 mM, (c) [DDQ] = 2.5 mM, (d) [DDQ] = 9.5 mM.

was found that, in contrast to former assumptions, the internal inner reorganisation energy can also be a major contributor to the activation barrier of many electron transfer reactions.^{17–21} It seems that in particular electron self-exchange reactions are not always marginally influenced by solvent environmental factors.²² In continuing our research on electron self-exchange reactions, we would like to report on the solvent dependence of the DDQ/DDQ^{•-} redox couple.

Experimental

EPR-spectra were recorded with a JEOL-X-band-EPR-spectrometer, type PE-3X connected to a 10-inch AEG-magnet at 100 kHz field modulation. Field measurements were achieved by an NMR-Gaussmeter, Drusch MNR-2. A microwave pre-amplifier, MITEQ type AMF 5S was installed before the crystal diode detector to improve the signal-to-noise ratio.²³ All solvents were of analytical grade (p.a.) and dynamically dried over molecular sieves (3 Å) and distilled afterwards. 2,3-Dicyano-5,6-dichloro-*p*-benzoquinone (Fluka, 98%) was used as received. Radical generation followed eqn. (7).



To avoid ion-pairing effects, the large R = tetrabutylammonium ion was used as the counterion. A detailed description of various ion-pairing effects on DDQ^{•-} has recently been given by Compton *et al.*²⁴ The resulting stable DDQ^{•-} radical anion is deep red in colour and its UV-VIS absorption spectrum is shown in Fig. 1. A temperature-controlled self-made flow-through capillary system is used to maintain the same experimental conditions inside the EPR-cavity. This is necessary to avoid changes in signal intensity *etc.* caused by different filling

factors, different sample tubes and positions, *etc.* Microwave power is controlled by a power meter type hp 432A. Normally three field scans under equal conditions were made to determine the linewidth. The EPR-hyperfine coupling constant measured as $a^N = 0.058$ mT, is in good agreement with the values reported in the literature.^{25,26} A computer simulation and fitting program similar to the one published by Kirste²⁷ is used to estimate coupling constants and linewidths. To simulate and fit the line broadening effects resulting from the electron self-exchange reactions, an additional computer program based on the density matrix formalism of Kaplan and Alexander is used.²⁸ The program covers all appearing cases from the “slow” exchange to the “fast” exchange limit. Radical concentration was always 5×10^{-4} M and various concentrations of the neutral compound up to 1×10^{-2} M were used. A detailed description of the experimental conditions to be followed was recently given elsewhere.²⁹

Results and discussion

Fig. 2a–c shows the line broadening effect on the EPR-spectra of DDQ^{•-} with increasing concentration of the neutral compound. With increasing DDQ concentration the whole hyperfine splitted EPR-spectrum collapses to one single line (see: Fig. 2c). But, this does not mean that the “fast” exchange limit is reached, because the criterion (8) must be fulfilled.²⁹ ΔB_{pp} is the

$$Z = \frac{\sqrt{3}}{2} \times \frac{(\Delta B_{pp} - \Delta B_{pp}^0)}{\sqrt{\nabla^{(2)}}} \leq 0.2 \quad (8)$$

observed broadened peak-to-peak linewidth of the collapsed line, ΔB_{pp}^0 the natural linewidth without exchange. $\nabla^{(2)} = \sum p_i \Delta B_i^2$ is the second moment of the spectra. p_i denotes the normalized population factor of line i at B_i the magnetic field strength at that position. $\nabla^{(2)} = 3.74 \times 10^{-3}$ mT² for the DDQ^{•-} radical anion.

The electron self-exchange rate constants found for the different solvents are listed in Table 1. Since the experimentally observed rate constants k_{obs} are close to the diffusion-controlled limit, they must be corrected, according to eqn. (9).

$$\frac{1}{k_{\text{et}}} = \frac{1}{k_{\text{obs}}} - \frac{1}{k_{\text{diff}}} \quad (9)$$

The diffusion controlled rate constant k_{diff} can be simply expressed by the Smoluchowski equation (10), since the radii of

$$k_{\text{diff}} = \frac{8RT}{3\eta} \quad (10)$$

both neutral compound and radical anion are nearly identical, where η describes the solvent dynamic viscosity.

Table 1 lists the corrected rate constants k_{et} for acetonitrile, chloroform, methylene chloride, acetone and benzonitrile. The γ -values vary between $0.270 \leq \gamma \leq 0.530$. Fig. 3 shows this independence of $\ln k_{\text{et}}$ vs. γ , contradicting Marcus theory. A completely different type of solvent dependence from that in eqn. (6) is reported in the case of an adiabatic solvent dynamical behaviour of the electron transfer reaction. The longitudinal relaxation time of the solvent τ_L then appears in the preexponential factor of the rate equation (11).^{4,10,11,30–33} Eqn. (11) can be linearized to eqn. (12). In the case of a solvent

$$k_{\text{et}} = K_A \times \frac{1}{\tau_L} \left(\frac{\lambda_0}{16\pi RT} \right)^{1/2} \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (11)$$

$$\ln(k_{\text{et}}\tau_L\gamma^{-1/2}) = a' + b'\gamma \quad (12)$$

dynamical effect on the rate constant, a plot of the left side term versus γ should result in a straight line. Such a behaviour is

Table 1 Observed rate constants k_{obs} and diffusion corrected rates k_{et} for the DDQ/DDQ⁻ couple in different solvents at $T = 293$ K. η denotes the solvent viscosity and τ_L the longitudinal solvent relaxation time. $\gamma = (1/n^2 - 1/\epsilon_s)$ is the solvent parameter according to the Marcus theory (Pekar factor)

Solvent	$k_{\text{et}}/10^8 \text{ M}^{-1} \text{ s}^{-1}$	$k_{\text{obs}}/10^8 \text{ M}^{-1} \text{ s}^{-1}$	$k_{\text{diff}}/10^8 \text{ M}^{-1} \text{ s}^{-1a}$	η/cP (293 K) ^b	τ_L/ps^b	γ (293 K) ^b
CH ₃ CN	29.2 ± 0.3	25.3 ± 0.3	190	0.341	0.20	0.530
Acetone	15.5 ± 0.6	14.4 ± 0.6	206	0.316	0.3	0.494
Benzonitrile	1.1 ± 0.05	8.9 ± 0.05	52.4	1.24	6.9	0.388
CH ₂ Cl ₂	48.5 ± 0.2	36.7 ± 0.2	151	0.43	0.33	0.380
CHCl ₃	33.7 ± 1.5	26.0 ± 1.5	114	0.57	2.9	0.270

^a From eqn. (10). ^b For detailed references on solvents, see ref. (4).

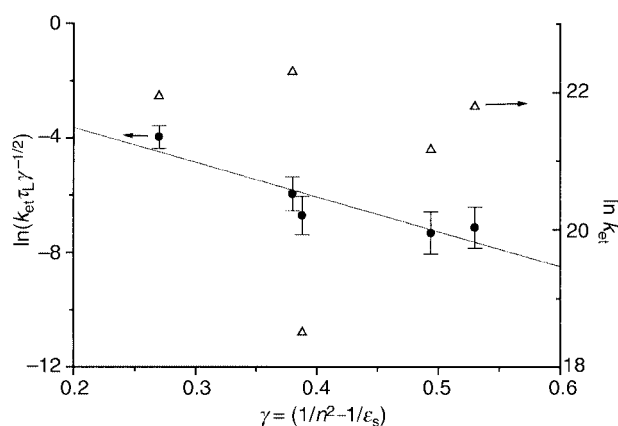


Fig. 3 Solvent dependence of $\ln k_{\text{et}}$ (right side) and $\ln(k_{\text{et}}\tau_L\gamma^{-1/2})$ (left side) versus the solvent parameter $\gamma = (1/n^2 - 1/\epsilon_s)$.

found for the homogeneous electron self-exchange reactions of the TCNE/TCNE⁻, TCNQ/TCNQ⁻ and TTF/TTF⁺ couples (TCNE = tetracyanoethylene, TCNQ = tetracyanoquinodimethane, TTF = tetrathiafulvalene).^{4,34-36} Also several heterogeneous electrochemical electron transfer reactions are reported showing a solvent dynamical effect.³⁷⁻⁴¹

Fig. 3 also shows the results for $\ln k_{\text{et}}$ and $\ln(k_{\text{et}}\tau_L\gamma^{-1/2})$ versus γ . A straight line confirms the influence of τ_L on the solvent dynamical effect. A rough calculation of the outer sphere reorganization energies using the continuum sphere model approximation of eqn. (2), gave $\lambda_o = 81.9 \text{ kJ mol}^{-1}$ for acetonitrile and 41.7 kJ mol^{-1} for chloroform, respectively. Theoretical calculations of λ_i result in 42.1 kJ mol^{-1} using the PM3 procedure and 45.3 kJ mol^{-1} from the AM1-method.⁴²

Temperature dependent measurements are in progress to get more detailed information about the activation parameters of the reaction.

Conclusions

The DDQ/DDQ⁻ electron self-exchange couple clearly shows a solvent dynamical effect in its solvent behaviour. This indicates an adiabatic reaction behaviour.

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