Electron-transfer Reactions. I. The Application of Derivative Linear-sweep Voltammetry for the Determination of the Rate Constants for Electron Transfer between Two Different Organic Anion Radicals

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The kinetics of homogeneous electron-transfer reactions between *different* anion radicals, $A^{-\cdot}$ and $B^{-\cdot}$ [eqn. (i)] can be conveniently studied by derivative linear-sweep voltammetry under conditions where the dianions, B^{2-}, are rapidly protonated.

$$A^{-\cdot} + B^{-\cdot} \xrightarrow{\ k_i\ } A + B^{2-} \tag{i}$$

The method involves measurements of the ratio, $R'_I(A/B) = I'_A/I'_B$, where I'_A and I'_B are the maximum values of dI/dt for the reduction of A and B, at different sweep rates for solutions containing both substrates. Working curves have been calculated by digital simulation for the concentration ratios, $C^\circ_B/C^\circ_A = 1, 2, 5$ and 10. The approximate kinetic range of the method is given by expression (ii).

$$10^4 < k_1/(\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) < 10^8 \tag{ii}$$

The application of this type of measurement is illustrated by the electron transfer from the anion radicals, $A^{-\cdot}$, of several aromatic compounds to the anion radicals, $B^{-\cdot}$, of azobenzene and 4,4'-dimethylazobenzene. The fit of the experimental data to the working curves is generally excellent for substrates having similar diffusion coefficients. The measured rate constants vary from 2.5×10^6 dm^3 mol^{-1} s^{-1}, for A = phthalazine and B = azobenzene, to 2.7×10^4 dm^{-3} mol^{-1} s^{-1}, for A = anthracene and B = 4,4'-dimethylazobenzene.

One-electron transfer reactions involving organic ion radicals are widely appreciated as fundamental chemical steps, not only in electrochemical reactions,[1-5] but also in many conventional organic and photochemical reactions, some of which were earlier believed to involve non-radical intermediates.[6-12] The possible application of the Marcus theory in the analysis of organic electron-transfer reactions has further stimulated research in this area.[6,7]

The rate of electron transfer between two organic species may be investigated by conventional kinetic methods and in addition to these, ESR line-broadening experiments may give valuable kinetic information, for example for the isoenergetic electron exchange between anion radicals and the neutral parents[6,13] or anion radicals and the corresponding dianions.[14] The recent improvement of the measurement precision of many electroanalytical techniques caused by the application of digital data-acquisition instrumentation has further facilitated the recording of re-

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liable kinetic data for electron-transfer reactions. However, the reactions investigated so far have almost entirely involved electron transfer from ionic to neutral species.[6,7,9,10]

The reactions of anion radicals ($A^{-\cdot}$) with aliphatic halides (RX), resulting in cleavage of the carbon–halogen bond, eqn. (1), have received special attention[15-22] and an attempt has recently been made to expand the Marcus theory to describe dissociative electron-transfer processes.[23] Other examples of electron-transfer reactions followed by a bond-breaking or bond-forming step

$$A^{-\cdot} + RX \xrightarrow{k_1} A + R^{\cdot} + X^-\qquad(1)$$
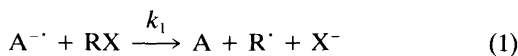
include the reactions between $A^{-\cdot}$ and aromatic halides,[24-26] aliphatic di- and trienes[27] as well as diphenyl sulfide[28] and benzyl phenyl sulfide.[29]

The kinetics of the electron transfer between two organic anion radicals have received much less interest. However, for the special case, the disproportionation reaction in which two *identical* anion radicals give the corresponding dianion and the parent compound, eqn. (2), fair estimates of k_2 can be made from measured values of $E°(A/A^{-\cdot})$ and $E°(A^{-\cdot}/A^{2-})$ provided the rate of the backward reaction is diffusion controlled. As an example of this approach, the maximum value of the disproportionation rate constant for the anthracene anion radical in N,N-dimethylformamide (DMF) has been estimated[30] to be 5×10^{-4} dm^3 mol^{-1} s^{-1}, assuming the value 5×10^9 dm^3 mol^{-1} s^{-1} for k_{-2}.

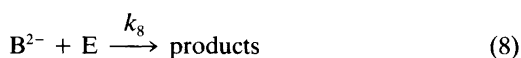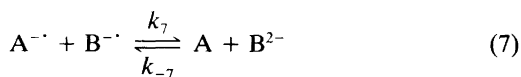$$2 A^{-\cdot} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A^{2-} + A\qquad(2)$$

Reaction (1) is a limiting case of a more general reaction scheme which involves reversible electron transfer, eqn. (3), followed by irreversible decay of the product anion radical ($B^{-\cdot}$), eqn. (4). The rate law for this mechanism, assuming the validity of the steady state approximation for $B^{-\cdot}$, is given by eqn. (5), which degenerates to the simple expression, eqn. (6), under conditions where $k_4 \gg k_{-3}[A]$. This is without doubt the case for the reduction of RX referred to above owing to the short life-time, if any,[31-34] of alkyl halide anion radicals, $RX^{-\cdot}$.

$$A^{-\cdot} + B \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A + B^{-\cdot}\qquad(3)$$

$$B^{-\cdot} \xrightarrow{k_4} products\qquad(4)$$
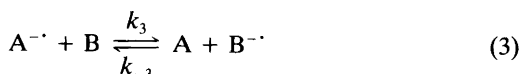
$$-\frac{d[A^{-\cdot}]}{dt} = \frac{k_3 k_4 [A^{-\cdot}][B]}{k_{-3}[A] + k_4}\qquad(5)$$

$$-\frac{d[A^{-\cdot}]}{dt} = k_3 [A^{-\cdot}][B]\qquad(6)$$

However, it is conceivable that values of the electron-transfer rate constants may also be measured in cases where the anion radicals formed by homogeneous electron transfer are not inherently unstable, but react rapidly with electrophiles (E) present in the solution. The same is true for electron transfer between two anion radicals, identical or different, eqns. (7), (8). The equivalent of rate law (6) for this mechanism is eqn. (9), provided that $k_8[E] \gg k_{-7}[A]$.

$$A^{-\cdot} + B^{-\cdot} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} A + B^{2-}\qquad(7)$$

$$B^{2-} + E \xrightarrow{k_8} products\qquad(8)$$

$$-\frac{d[A^{-\cdot}]}{dt} = k_7 [A^{-\cdot}][B^{-\cdot}]\qquad(9)$$

The aim of the present paper is to demonstrate that derivative linear-sweep voltammetry[35] (DLSV) is a convenient method for determination of the electron-transfer rate constants, k_7, in rate law (9). The examples include electron transfer *from* the anion radicals derived from a variety of aromatic substrates *to* the anion radicals of azobenzene and 4,4'-dimethylazobenzene, which result in dianions sufficiently basic[36] to be protonated rapidly by residual water (E = H_2O).

Results and discussion

The cyclic voltammogram of azobenzene (AZ) (1 mM) in DMF at two different voltage sweep rates, 50 mV s^{-1} and 50 V s^{-1}, is shown in Fig. 1. Two redox couples were observed at low sweep rates, e.g. 50 mV s^{-1}, the first of which, R^1/O^1, associated with eqn. (10), was found to be electrochemically reversible at sweep rates up to 100 V s^{-1} in agreement with previous work.[37-41] In
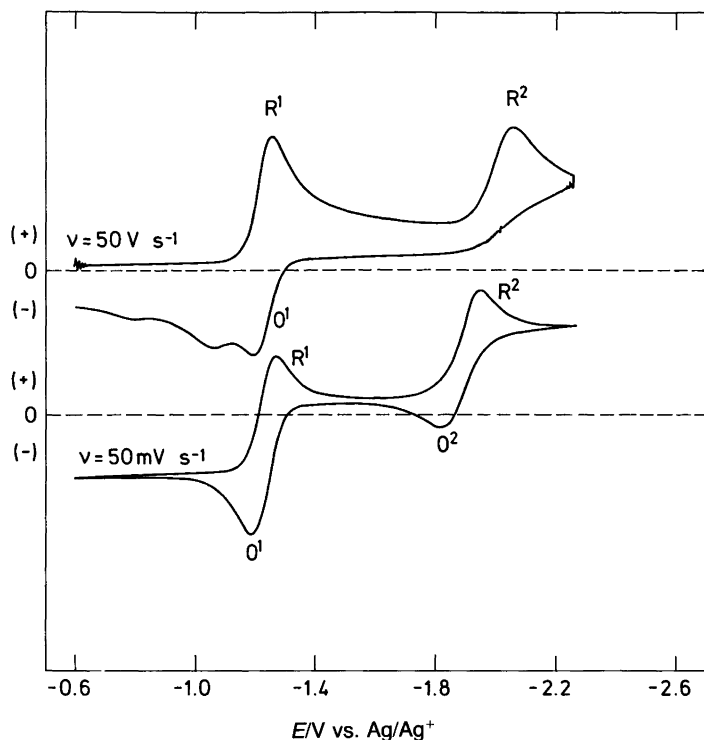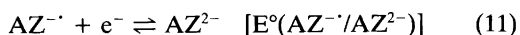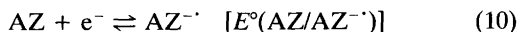
Fig. 1. Cyclic voltammetry of azobenzene (2 mmol dm^{-3}) in DMF containing Bu$_4$NPF$_6$ (0.1 mol dm^{-3}) at the sweep rates 50 V s^{-1} and 50 mV s^{-1}. $T = 21\,°C$.

contrast, the appearance of the second couple, R^2/O^2, associated with eqn. (11), was highly dependent on the sweep rate. The half-peak width, $E_{p/2} - E_p$, of the reduction peak, R^2, was found to be 75 mV at a sweep rate of 200 mV s^{-1}, confirm-

$$AZ + e^- \rightleftharpoons AZ^{-\cdot} \quad [E°(AZ/AZ^{-\cdot})] \qquad (10)$$

$$AZ^{-\cdot} + e^- \rightleftharpoons AZ^{2-} \quad [E°(AZ^{-\cdot}/AZ^{2-})] \qquad (11)$$

ing the earlier conclusion[41] that heterogeneous electron transfer to AZ$^{-\cdot}$ is quasi-reversible. The current for reoxidation of AZ^{2-} *decreased* with *increasing* sweep rate and was barely detectable at 500 mV s^{-1}. No trace of reverse current could be observed in the sweep rate range 1–2000 V s^{-1}, not even after the addition of neutral alumina to the voltammetric solution in order to diminish the water content[42,43] (cf. Fig. 1).

These observations are in agreement with earlier work[40] which demonstrated that protonation

$$AZ^{2-} + H_2O \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} AZH^- + OH^- \quad [K_{12} = k_{12}/k_{-12}] \qquad (12)$$
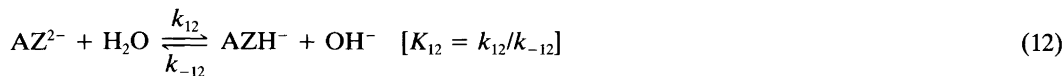
of AZ^{2-} by residual water, eqn. (12), is a reversible process. However, the backward reaction (12) is not fast enough to supply AZ^{2-} at a rate sufficient for the reoxidation of this species to take place at an appreciable rate at high sweep rates. The lack of reverse current for the oxidation of AZ^{2-} at 2000 V s^{-1} corresponds to a minimum value of 10^8 dm^3 mol^{-1} s^{-1} for k_{12}, assuming that the water concentration is less than 5 mmol dm^{-3} in the presence of neutral alumina. This illustrates the extreme basicity of AZ^{2-} [pK_a (AZH$^-$) = 38.1 in DMF[40]], which for that reason has found widespread use as an electrogenerated base.[36,39,44,45]

The voltammogram of AZ (1 mmol dm^{-3}) in DMF at 200 mV s^{-1} in the presence of anthracene (AN) (0.5 mmol dm^{-3}) is shown in Fig. 2(b). [Fig. 2(a) shows the voltammogram of AZ in the absence of AN for comparison.] The peak, R^3, due to the reduction of AN to AN$^{-\cdot}$, eqn. (13), is much higher than expected for a 0.5 mmol dm^{-3}
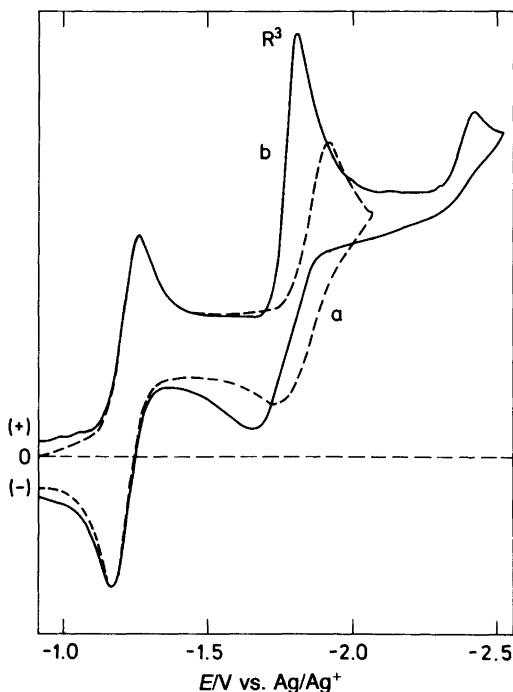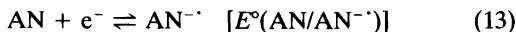
Fig. 2. Cyclic voltammetry of azobenzene (1 mmol dm^{-3}) in DMF containing Bu$_4$NPF$_6$ (0.1 mol dm^{-3}) at 200 mV s^{-1} (*a*) before and (*b*) after addition of anthracene (0.5 mmol dm^{-3}). *t* = 21 °C.

solution and the peak potential is approximately 50 mV higher than that for a solution containing only AN. This voltammetric behavior is typical

$$AN + e^- \rightleftharpoons AN^{-\cdot} \quad [E^\circ(AN/AN^{-\cdot})] \tag{13}$$

for an electrocatalytic reduction process,[46–49] in the present case the reduction of AZ$^{-\cdot}$ to AZ^{2-} by AN$^{-\cdot}$, eqn. (14), followed by reaction (12).

$$AN^{-\cdot} + AZ^{-\cdot} \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} AN + AZ^{2-} \tag{14}$$
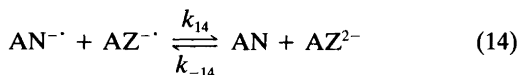
Considering that k_{12} is larger than 10^8 dm^3 mol^{-1} s^{-1}, and probably even close to the diffusion-controlled limit since reaction (12) is strongly displaced to the right ($K_{12} = 2.5 \times 10^3$)[40] and involves exchange of a proton between a nitrogen and an oxygen site,[50,51] it seems reasonable to assume that $k_{12}[\mathrm{H_2O}] \gg k_{-14}[\mathrm{AN}]$. Accordingly, the forward electron-transfer reaction

(14) is rate determining which results in rate law (15).

$$-\frac{d[\mathrm{AN}^{-\cdot}]}{dt} = k_{14}[\mathrm{AN}^{-\cdot}][\mathrm{AZ}^{-\cdot}] \tag{15}$$

Rate constants such as k_{14}, or in general k_7, can, in principle, be determined by linear-sweep voltammetry or cyclic voltammetry from the sweep-rate dependence of the magnitude and position of the catalytic peak for AN reduction by an approach similar to that described by Savéant *et al.*[46–49] However, the theoretical treatment given by these workers is not applicable to the present case owing to the interference from the AZ/AZ$^{-\cdot}$ redox couple, R^1/O^1, in front of the catalytic AN reduction peak.

Precise measurements of the height of the catalytic peak, R^3, require a well-defined baseline, which may be impossible to achieve, especially at high sweep rates. Therefore, in order to reduce the contributions from baseline imperfections, it was decided to monitor the derivative peak heights instead.[35] The derivative signals obtained during the forward going sweep for a 2:1 mixture of AZ and AN at four different sweep rates are shown in Fig. 3. The ratio, $R_1'(A/B) = I'_{AN}/I'_{AZ}$, is close to 0.5 at 100 V s^{-1} indicating that the reaction between AZ$^{-\cdot}$ and AN$^{-\cdot}$ is negligible at the time scale of this experiment. The value of $R_1'(A/B)$ was found to increase with decreasing sweep rate, being close to 2 at the lowest sweep rate, 100 mV s^{-1}.

The results shown in Fig. 3 illustrate that measurements of $R_1'(A/B)$ as a function of the sweep rate (*v*) provide a convenient method for monitoring the rate of the electron-transfer reaction between AN$^{-\cdot}$ and AZ$^{-\cdot}$. However, it should be emphasized that this approach is only experimentally feasible in cases, such as the present case, where the first electron-transfer process, eqn. (10), is reversible in the applied sweep-rate range.

Working curves, obtained by digital simulation as described in the experimental section, for $R_1'(A/B)$ at four different concentration ratios, C_B°/C_A°, are shown in Fig. 4 together with the experimental points obtained for AN (0.5 mmol dm^{-3}) and AZ at $C_{AZ}^\circ/C_{AN}^\circ = 2$ and 5, respectively. The values of k_{14}, and the equivalent rate constants, k_7, for the other substrate combinations, obtained from corresponding values of log
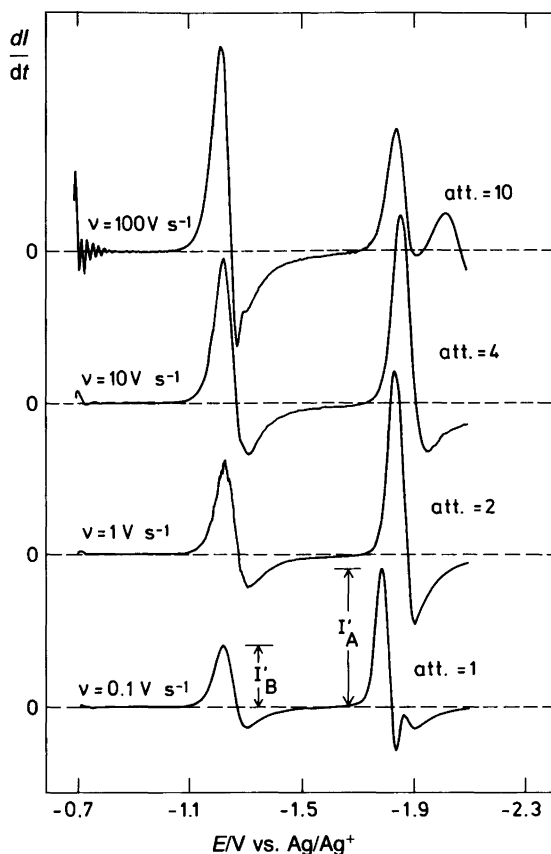
Fig. 3. Derivative peak currents for a solution of azobenzene (2 mmol dm^{-3}) and anthracene (1 mmol dm^{-3}) in DMF containing Bu$_4$NPF$_6$ (0.1 mol dm^{-3}). The sweep rates and the oscilloscope attenuation settings are shown in the figure.

(V s^{-1}/v) and log[$k_7 C_A^\circ RT/(vnF)$] (cf. Fig. 4) are summarized in Table 1.

The fit of the experimental data to the working curve was excellent in all cases except when A was 9-phenylanthracene (9-PA) for which the experimental R_i'(A/B) values were found to approach a limiting value at high sweep rates somewhat lower than that predicted by theory. The rate constants obtained at two different concentration ratios, 2 and 5, are identical for all compound combinations, within experimental error, which can be taken as evidence in favor of the proposed mechanism and the assumptions made. Comparison of the anodic shift of approximately 50 mV for R^3 reported above for and $C_B^\circ/C_A^\circ = 2$ with that predicted from the theoretical data and $k_{14} = 1.3 \times 10^6$ dm^3 mol^{-1} s^{-1}, which amounts to 48 mV, further supports the theoretical treatment.

The method allows the evaluation of k_7 values in the range given by expression (16). The lower limit corresponds to $C_B^\circ/C_A^\circ = 1$ and $C_A^\circ = 1$ mmol dm^{-3} with 100 mV s^{-1} as the lowest sweep rate and the higher limit to $C_B^\circ/C_A^\circ = 10$ and $C_A^\circ = 0.1$ mmol dm^{-3} with 100 V s^{-1} as the highest sweep

$$10^4 < k_7/(\text{dm}^{-3}\,\text{mol}^{-1}\,\text{s}^{-1}) < 10^8 \qquad (16)$$

rate. In both cases it is required that the experimental points cover approximately 50 % of the working curves given in Fig. 4.

The values of k_7 increase, as expected, with decreasing values of E°(A/A^{-}) (Table 2). For example, phthalazine is 112 mV more difficult to reduce than 1-phenylphthalazine, leading to an increase of the corresponding k_7 value by a factor of 80 from 3.2×10^4 dm^3 mol^{-1} s^{-1} to 2.5×10^6 dm^3 mol^{-1} s^{-1}. The effect of methyl substitution in AZ is more difficult to evaluate in view of the problems in assigning meaningful values to E°(B^{-}/B^{2-}) due to the acid–base equilibrium
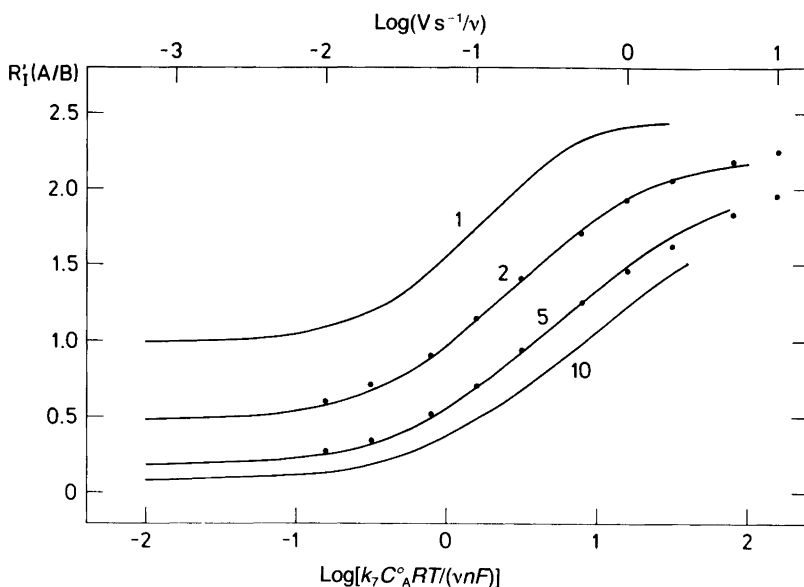
Fig. 4. Working curves for rate law (9) at $C°_B/C°_A = 1$ (*a*), 2 (*b*), 5 (*c*) and 10 (*d*) for $E°(B/B^{-·}) - E°(A/A^{-·}) = 600$ mV. [The numerical data are available on request.] The points are experimental data for the electron-transfer reaction between azobencene anion radical, AZ$^{-·}$, and anthracene anion radical, AN$^{-·}$, to yield AZ^{2-} and AN in DMF at $C°_{AZ}/C°_{AN} = 2$ and 5 and $C°_{AN} = 0.5$ mmol dm^{-3}. $T = 21$ °C.

(12). However, methyl substitution is expected to cause the $E°(B^{-·}/B^{2-})$ value to decrease, as was observed for $E°(B/B^{-·})$, and accordingly, the value of k_7 for reaction with the same anion radical, A$^{-·}$ is observed to decrease (Table 1).

Since the object of this paper is to demonstrate the convenience of DLSV for the determination of the electron-transfer rate constants, and since the amount of data obtained so far are restricted to those given in Table 1, we will desist from further discussion of the data at this place. However, we do wish to stress that the approach described provides an experimental basis for investigation of the importance of the charge–charge repulsion terms in the Marcus equations when applied to electron-transfer reactions between organic anions.

The simulations of the working curves given in

Table 1. Rate constants, k_7, for the electron-transfer process: A$^{-·}$ + B$^{-·}$ → A + B^{2-} in DMF at 21 °C.

Compound A	Compound B	k_7/(dm^3 mol^{-1} s^{-1})	$C°_B/C°_A$
Phthalazine	Azobenzene	$2.4×10^6$	2
Phthalazine	Azobenzene	$2.6×10^6$	5
2-Naphthonitrile	Azobenzene	$1.3×10^6$	2
2-Naphthonitrile	Azobenzene	$1.3×10^6$	5
Anthracene	Azobenzene	$1.3×10^6$	2
Anthracene	Azobenzene	$1.3×10^6$	5
9-Phenylanthracene	Azobenzene	$1.6×10^5$ [a]	2
9-Phenylanthracene	Azobenzene	$1.7×10^5$ [a]	5
1-Phenylphthalazine	Azobenzene	$3.1×10^4$	2
1-Phenylphthalazine	Azobenzene	$3.3×10^4$	5
Phthalazine	4,4'-Dimethylazobenzene	$6.0×10^4$	2
Phthalazine	4,4'-Dimethylazobenzene	$5.7×10^4$	5
Anthracene	4,4'-Dimethylazobenzene	$2.7×10^4$	2
Anthracene	4,4'-Dimethylazobenzene	$2.6×10^4$	5

[a]Minimum values owing to the small diffusion coefficient for 9-PA (see the text).

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Table 2. Peak potentials, half-peak potentials and relative peak currents for the reversible reduction of compounds A and B to the corresponding anion radicals.[a]

Compound	$\dfrac{-E_p\,[b]}{mV}$	$\dfrac{-E_{p/2}\,[b]}{mV}$	$\dfrac{E_{p/2}-E_p}{mV}$	$\dfrac{I_p\,[c]}{I_p(AN)}$
A				
Phthalazine	1903	1843	60	1.09
2-Naphthonitrile	1889	1830	59	0.98
Anthracene	1875	1816	59	1.00
9-Phenylanthracene	1826	1770	56	0.77
1-Phenylphthalazine	1791	1733	58	0.86
B				
4,4'-Dimethylazobenzene	1363	1306	57	0.92
Azobenzene	1263	1204	59	0.98

[a] In DMF–Bu$_4$NPF$_6$ (0.1 mol dm^{-3}) at $T = 21\,°C$. [b] Relative to Ag/Ag$^+$ in DMF–Bu$_4$NPF$_6$ (0.1 mol dm^{-3}). [c] Peak current relative to that for anthracene.

Fig. 4 were based on the assumption that the diffusion coefficients, *D,* of the two reacting anion radicals and their parents are identical. To justify this assumption, the peak currents for the reversible substrate/anion radical couples were recorded precisely under the reaction conditions for 1 mmol dm^{-3} solutions of all the compounds included in the study. The results, given relative to the peak current for AN in Table 2, show that the assumption is reasonable for all the compounds, except 9-PA for which $I_p(9\text{-PA})/I_p(AN)$ is equal to 0.77, corresponding to $D(9\text{-PA}) = 0.59D(AN)$. We believe that the deviations of the experimental data from the working curves observed for 9-PA are associated with this relatively small diffusion coefficient. A similar, but more pronounced effect, was observed for electron transfer reactions involving 9,10-diphenylanthracene anion radical and may be anticipated for other systems as well. The effects of the relative magnitudes of diffusion coefficients have been discussed previously for second-order reactions,[52–54] and will be the subject of a forthcoming paper in this series.

Experimental

Chemicals, solvent and supporting electrolyte. The compounds, A, and azobenzene were reagent grade and were used as received. 4,4'-Dimethylazobenzene was prepared by Zn–NaOH

reduction of 4-methylnitrobenzene[55] followed by recrystallization from ethanol. The identity of the product was confirmed by ^{1}H NMR spectroscopy and elemental analysis. Anal. C$_{14}$H$_{14}$N$_2$: C, H, N.

The preparation of Bu$_4$NPF$_6$ and the solvent/supporting electrolyte purification procedures have been described elsewhere.[56]

Instrumentation and measurement procedures. The electrochemical instrumentation, electrodes, cells, data handling and measurement procedures were the same as those reported earlier.[56]

Measurement precision. The values of the reversible potentials given in Table 2 are averages of 9–12 measurements. The standard deviations of the E_p and $E_{p/2}$ values were typically 0.7 and 0.4 mV, respectively. The potentials for anthracene were measured at the beginning and at the end of the series, in order to detect possible drift of the reference electrode and were found to vary less than 1 mV.

Owing to the difference in steepness of the reduction peak for A and B, the frequency (Hz) of the analog differentiator (PAR model 189) was adjusted to 20 times the sweep-rate (V s^{-1}), instead of 10 (cf. Ref. 35), in order to reduce the distortion of the resulting derivative voltammogram. Although the noise discrimination was less effective at this frequency-to-sweep-rate ratio, the overall accuracy of the measurements was found to be improved.

Theoretical data. Digital simulations were carried out by application of an explicit formulation of the diffusion problem combined with the integrated rate law for the chemical reaction.[56–57] The complete description of the homogeneous electron-transfer reactions include not only eqn. (7), but also eqns. (17) and (18). The reaction be-

$$A^{-\cdot} + B \rightarrow A + B^{-\cdot} \tag{17}$$

$$B^{2-} + B \rightarrow 2B^{-\cdot} \tag{18}$$

tween $A^{-\cdot}$ and B, eqn. (17), was assumed to be instantaneous owing to the large difference between $E^\circ(A/A^{-\cdot})$ and $E^\circ(B/B^{-\cdot})$, which in the present study were, in all cases, larger than 500 mV, and to result in complete depletion of that of the two species present in the smaller amount. Reaction (18) was neglected owing to the low concentration of B^{2-}, relative to $A^{-\cdot}$, caused by reaction (8), in other words, it was assumed that B was only consumed in solution due to reaction (17). The working curves depicted in Fig. 4 are valid for values of $E^\circ(B/B^{-\cdot}) - E^\circ(A/A^{-\cdot})$ larger than approximately 400 mV. At smaller values, working curves had to be calculated for each value of $E^\circ(B/B^{-\cdot}) - E^\circ(A/A^{-\cdot})$ owing to the varying contributions from the reduction current of B to the total current.

The simulation programs were written in VS FORTRAN and the calculations were performed on an IBM 6151 computer.

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