

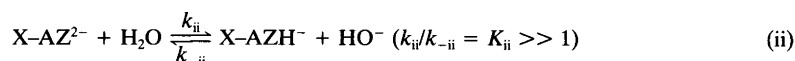
# Electron Transfer Reactions. II. The Application of the Marcus Theory in Kinetic Studies of Electron Transfer from Aromatic Hydrocarbon Anion Radicals to Halogen-Substituted Azobenzene Anion Radicals in *N,N*-Dimethylformamide

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The kinetics of electron transfer from anion radicals of aromatic hydrocarbons (A) to anion radicals of azobenzene or halogen-substituted azobenzenes (X-AZ; X = H, F, Cl, Br) [eqn. (i)] have been studied in *N,N*-dimethylformamide by derivative linear sweep voltammetry.

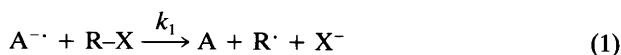


The dianions of the azobenzenes were rapidly protonated by residual water [eqn. (ii)] except for 4-bromoazobenzene and 4,4'-dibromoazobenzene where loss of bromide ion was the predominant reaction.

The measured values of the rate constant,  $k_i$ , varied from  $3.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (A = benzo[*a*]pyrene and X-AZ = azobenzene) to  $2.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (A = 9-phenylanthracene and X-AZ = 3-chloroazobenzene). The linear regression line, defined by the experimental data plotted as  $-RT \ln k_i$  against the free energy difference,  $-F[E^{\circ'}(X-AZ^{\cdot-}/X-AZ^{2-}) - E^{\circ'}(A|A^{\cdot-})] \approx \Delta G^{\circ}$ , where the formal potentials,  $E^{\circ'}$ , refer to strictly non-aqueous conditions, had a slope of 0.68. This is close to the value, 0.66, predicted by the Marcus theory considering the range and magnitudes of the free energy differences.

The rate constants,  $k_i$ , increased upon addition of water (0.1 M) to the solutions, which was accompanied by a decrease of the slope of  $-RT \ln k_i$  against  $-F[E^{\circ'}(X-AZ^{\cdot-}/X-AZ^{2-}) - E^{\circ'}(A|A^{\cdot-})]$  from 0.68 to 0.60. It is suggested that this effect is due to the participation of the hydrogen-bonded species, X-AZ<sup>·-</sup>/H<sub>2</sub>O and X-AZ<sup>2-</sup>/H<sub>2</sub>O, in reactions (i) and (ii), which results in a shift of  $\Delta G^{\circ}$  towards lower values.

The transfer of a single electron has become recognized as a fundamental step in many organic reactions and the intermediacy of ion radicals has been demonstrated for a number of reactions earlier believed to proceed by non-radical pathways.<sup>1-8</sup> The kinetics of electron transfer followed by or synchronous with bond breaking or bond forming processes have been studied intensely by electroanalytical<sup>9-12</sup> and radiolytic<sup>13,14</sup> methods. The studies have been focussed almost entirely on electron transfer from ionic to neutral species and special attention has been given to the reaction between anion radicals of aromatic compounds (A) and aliphatic halides (RX) resulting in cleavage of the R-X bond, eqn. (1).<sup>14-20</sup>



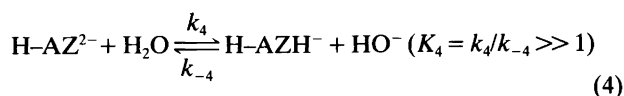
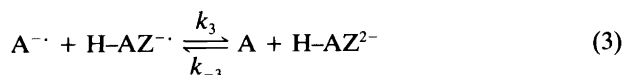
The kinetics of electron transfer between organic ions of the same polarity have not been studied except for the special case of the disproportionation of A<sup>·-</sup>, eqn. (2),<sup>21</sup> and electron transfer between the anion radical and the dianion of cyclooctatetraene.<sup>22</sup>



We have recently reported on the kinetics of electron transfer from the anion radicals of various aromatic compounds

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to the anion radical of azobenzene (H-AZ), eqn. (3), in *N,N*-dimethylformamide (DMF) and demonstrated the convenience of derivative linear sweep voltammetry (DLSV)<sup>11</sup> for obtaining the rate constants,  $k_3$ , under conditions where the azobenzene dianion is rapidly protonated by residual water, eqn. (4).<sup>23</sup>



Anion radicals derived from simple halogen-substituted aromatic compounds are known to undergo bond cleavage through loss of a halide ion,<sup>13,24-28</sup> which is a central process in the  $S_{RN}1$  reaction.<sup>29</sup> However, when the aromatic halide contains an additional electron-withdrawing group, as for example nitro or carbonyl, the anion radical generally becomes less reactive and a reversible cyclic voltammogram for the substrate-anion radical couple may be observed at low sweep rates. This provides for the further reduction to the corresponding dianion, which, in a subsequent reaction, undergoes protonation or loss of a halide ion as observed for halogen-substituted nitrobenzene<sup>30</sup> and benzo-phenone<sup>31</sup> dianions.

In this work we have extended the application of the DLSV method described earlier<sup>23</sup> to the determination of rate constants for the electron transfer from the anion radicals of aromatic compounds to the anion radicals of

halogen-substituted azobenzenes (X-AZ; X = F, Cl, Br) under conditions where the dianions,  $X-AZ^{2-}$ , react rapidly by protonation rather than by loss of a halide ion. A primary aim of this study was to examine the application of the Marcus theory for electron transfer in the description of the relationship between the rate constants and the free energy change of the reactions.

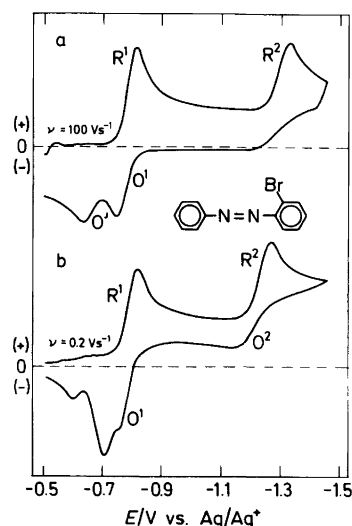


Fig. 1. Cyclic voltammograms of 2-bromoazobenzene (1 mM) in DMF containing  $Bu_4NPF_6$  (0.1 M) at (a)  $\nu = 100 \text{ V s}^{-1}$  and (b)  $\nu = 0.2 \text{ V s}^{-1}$ ;  $T = 294 \text{ K}$ . The unmarked peak at  $-0.6 \text{ V}$  observed at  $\nu = 0.2 \text{ V s}^{-1}$  is caused by adsorption.

Table 1. Peak potentials,  $E_p^{\text{red}}$ , and diffusion coefficients,  $D$ , for halogen-substituted azobenzenes and aromatic hydrocarbons in *N,N*-dimethylformamide.<sup>a</sup>

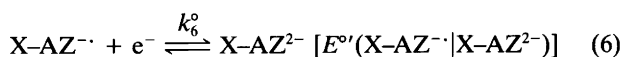
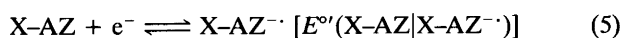
Compound	1st wave <sup>b</sup>		2nd wave <sup>c</sup>
	$E_p^{\text{red}}/\text{mV}^d$	$D/D(\text{H-AZ})^e$	$E_p^{\text{red}}/\text{mV}^d$
Azobenzene (H-AZ)	0	1.00	-764
2-Fluoroazobenzene (2-FAZ)	+111	0.96	-686
4-Fluoroazobenzene (4-FAZ)	+9	0.96	-807
4,4'-Difluoroazobenzene	+18	0.92	-853
2-Chloroazobenzene (2-ClAZ)	+155	0.76	-625
3-Chloroazobenzene (3-ClAZ)	+144	0.77	-614
4-Chloroazobenzene (4-ClAZ)	+91	0.77	-679
4,4'-Dichloroazobenzene	+180	0.83	-590
2-Bromoazobenzene (2-BrAZ)	+163	0.76	-610
3-Bromoazobenzene (3-BrAZ)	+151	0.76	-600
4-Bromoazobenzene (4-BrAZ)	+103	0.74	-
4,4'-Dibromoazobenzene (4,4'-DBrAZ)	+202	0.76	-
Anthracene (AN)	-612	1.00	-
9-Phenylanthracene (9-PA)	-567	0.64	-
Benzo[a]pyrene (BP)	-497	0.67	-

<sup>a</sup>In solvent containing  $Bu_4NPF_6$  (0.1 M) at  $T = 294 \text{ K}$ ,  $\nu = 10 \text{ V s}^{-1}$ . <sup>b</sup>The half-peak width,  $E_{p/2} - E_p$ , was between 55 and 58 mV at  $\nu = 10 \text{ V s}^{-1}$ . <sup>c</sup>The half-peak width was between 68 and 78 mV at  $\nu = 10 \text{ V s}^{-1}$ . <sup>d</sup>Potentials are given relative to  $E_p^{\text{red}}(\text{H-AZ})$ .

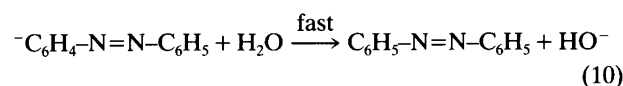
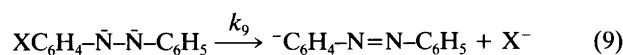
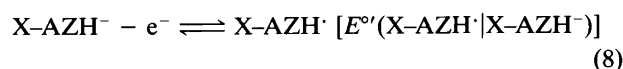
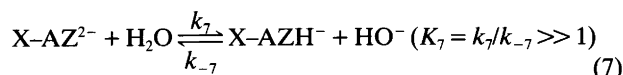
<sup>e</sup> $I_p/I_p(\text{H-AZ}) = [D/D(\text{H-AZ})]^{1/2}$ .

## Results and discussion

**Cyclic voltammetry (CV).** The peak potentials,  $E_p^{\text{red}}(\text{A})$ ,  $E_p^{\text{red}}(\text{X-AZ})$ , and  $E_p^{\text{red}}(\text{X-AZ}^{\cdot-})$  for the voltammetric reduction of the compounds A and X-AZ in DMF are given in Table 1, which also summarizes the abbreviations used for the compounds in the study. The one-electron reductions of A and X-AZ [eqn. (5) and the redox couple,  $\text{R}^1/\text{O}^1$ , in Fig. 1] were electrochemically reversible with half-peak widths,  $E_{p/2} - E_p$ , less than 60 mV at voltage sweep rates ( $\nu$ ) up to  $100 \text{ V s}^{-1}$ . Among the azobenzenes studied, cleavage of the carbon-halogen bond at the anion radical stage was only observed for 4-iodoazobenzene, which even at  $\nu = 100 \text{ V s}^{-1}$  showed no sign of reversibility,<sup>32</sup> and for that reason was excluded from the study.



In contrast with the reversible behavior observed for the substrate-anion radical redox couples, the formation of the dianions,  $\text{X-AZ}^{2-}$ , eqn. (6), was associated with relatively broad voltammetric peaks ( $\text{R}^2$  in Fig. 1), with values of  $E_{p/2} - E_p$  in the range 68–78 mV at  $\nu = 10 \text{ V s}^{-1}$ . No trace of reoxidation of the dianions could be observed at high sweep rates [e.g. Fig. 1(a)] whereas an oxidation peak [ $\text{O}^2$  in Fig. 1(b)] appeared at sweep rates below approximately  $1 \text{ V s}^{-1}$ . These observations agree with results reported earlier for azobenzene and can be attributed to quasi-reversible one-electron reduction of  $\text{X-AZ}^{\cdot-}$  followed by reversible protonation of  $\text{X-AZ}^{2-}$  by residual water, eqn. (7).<sup>23,33–35</sup> The absence of a peak corresponding to  $\text{O}^2$  at sweep rates exceeding  $1 \text{ V s}^{-1}$  indicates that backward reaction (7) is too slow to supply  $\text{X-AZ}^{2-}$  at the rate required for the observation of an oxidation peak for this species. Instead, an oxidation peak [ $\text{O}^1$  in Fig. 1(a)] was observed at a potential slightly higher than the peak potential for reoxidation of  $\text{X-AZ}^{\cdot-}$ . This peak is most likely associated with oxidation of the monoprotonated dianion,  $\text{X-AZH}^-$ , to the corresponding radical, eqn. (8),<sup>35</sup> and the voltammogram resembles, in this respect, the general voltammetric pattern observed for the reduction of many chemically related aza-aromatic compounds.<sup>36–38</sup>



Cleavage of the dianions by loss of a halide ion, eqn. (9), followed by rapid protonation of the resulting anion, eqn. (10), and reduction of the dehalogenated compound to the corresponding anion radical was observed only for 4-BrAZ and 4,4'-DBrAZ. In these two cases a third peak,  $\text{R}^3$ , corresponding to reduction of the anion radical of the dehalogenated compound to the dianion was observed in addition to  $\text{R}^1$  and  $\text{R}^2$  as illustrated by the cyclic voltammogram for 4-BrAZ [Fig. 2(a)]. The cleavage of the carbon-bromine bond could be suppressed significantly by addition of water (0.1 M) to the voltammetry solution as illustrated in Fig. 2(b). The peak,  $\text{R}^3$ , has almost vanished leaving only  $\text{R}^2$ , which indicates that protonation competes favorably with cleavage in the solution containing water.

Thus, the voltammetric results indicate that protonation of  $\text{X-AZ}^{2-}$  by residual water, eqn. (7), is faster than cleavage of the carbon-halogen bond, eqn. (9), when  $\text{X} = \text{F}$  and  $\text{Cl}$  and competes favorably also when  $\text{X} = \text{Br}$ , if the substituent is situated at the 2- or 3-position.

**Kinetic measurements.** A mechanism composed of the electron transfer reaction (11) followed by protonation (7) results in rate law (12) in the time domain in which (7) is essentially irreversible, assuming that the steady-state approximation is valid for  $\text{X-AZ}^{2-}$ .

The dianion of azobenzene is known to be an extremely strong base with a  $\text{p}K_{\text{A}}$  of the corresponding acid,  $\text{H-AZH}^-$ , equal to 38.1 in DMF<sup>35</sup> and the rate constant,  $k_4$ , for protonation by residual water has been estimated to be close to the value for a diffusion-controlled process.<sup>23</sup> The

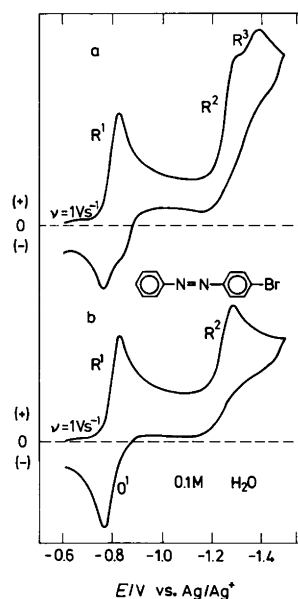
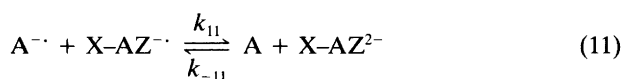


Fig. 2. Cyclic voltammograms of (a) 4-bromoazobenzene (1 mM) in DMF containing  $\text{Bu}_4\text{NPF}_6$  (0.1 M) and (b) the same solution as (a) after addition of water corresponding to 0.1 M;  $T = 294 \text{ K}$ .



$$-\frac{d[A^{\cdot-}]}{dt} = \frac{k_{11}k_7[A^{\cdot-}][X-AZ^{\cdot-}][H_2O]}{k_{-11}[A] + k_7[H_2O]} \quad (12)$$

dianions of the halogen-substituted azobenzenes are likely to be less basic than  $H-AZ^{2-}$  due to the electron-withdrawing properties of the halogen substituents, but the total absence of current for reoxidation of the dianions even at  $v = 2000 \text{ V s}^{-1}$  indicates that protonation by residual water is, in fact, also an extremely fast reaction for the halogen-substituted azobenzenes, which implies that  $k_7[H_2O] \gg k_{-11}[A]$ . Accordingly, the forward electron transfer reaction (11) is rate determining and rate law (12) degenerates to the simple eqn. (13). However, it should be emphasized that rate law (13) is only valid under conditions where the backward reaction (7) does not manifest itself kinetically. This requirement appears to be fulfilled for sweep rates larger than approximately  $1 \text{ V s}^{-1}$  for the present series of compounds as discussed in the CV section.

The electron transfer rate constants,  $k_{11}$ , were determined by the DLSV method described earlier.<sup>23</sup> In brief, the method involves recording of the ratio,  $R'_1(A/B) = I'_A/I'_{X-AZ}$ ,

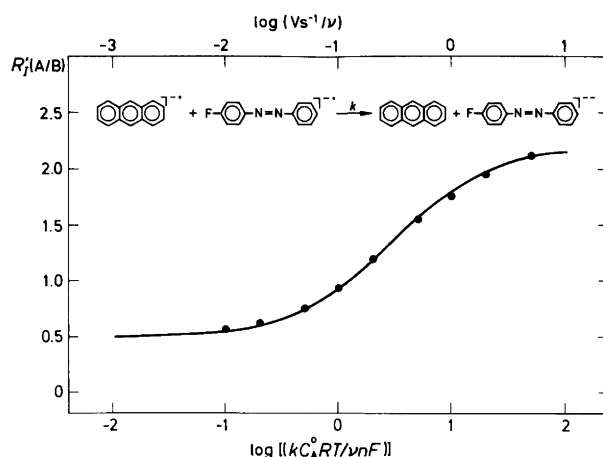


Fig. 3. Working curve for rate law (13) at  $C_{X-AZ}^0/C_A^0 = 2$  for  $E^{\circ}(X-AZ|X-AZ^{\cdot-}) - E^{\circ}(A|A^{\cdot-}) = 600 \text{ mV}$ .<sup>23</sup> The points are experimental data for the electron transfer from the anion radical of anthracene (0.5 mM) to the anion radical of 4-fluoroazobenzene (1.0 mM) in DMF containing  $Bu_4NPF_6$  (0.1 M);  $T = 294 \text{ K}$  and  $v = 0.2\text{--}100 \text{ V s}^{-1}$ .

as a function of the sweep rate, where  $I'_A$  and  $I'_{X-AZ}$  are the maximum values of the time derivatives,  $dI_A/dt$  and  $dI_{X-AZ}/dt$ , of the current,  $I$ , obtained from a solution con-

Table 2. Rate constants for electron transfer from anion radicals of aromatic hydrocarbons to anion radicals of halogen-substituted azobenzenes in *N,N*-dimethylformamide at  $T = 294 \text{ K}$ .<sup>a</sup>

Compound	$-F(\Delta E^{\circ})^b/\text{kcal mol}^{-1}$	$k_{11}/\text{M}^{-1} \text{ s}^{-1}$	
	0 mM $H_2O^c$	0 mM $H_2O^c$	100 mM $H_2O^c$
<b>Anthracene</b>			
Azobenzene	5.03	$1.5 \times 10^6$	$2.5 \times 10^6$
2-Fluoroazobenzene	3.23	$1.2 \times 10^7$	$1.5 \times 10^7$
4-Fluoroazobenzene	6.02	$7.9 \times 10^5$	$1.3 \times 10^6$
4,4'-Difluoroazobenzene	7.08	$3.3 \times 10^5$	$6.9 \times 10^5$
<b>9-Phenylanthracene</b>			
Azobenzene	6.06	$3.2 \times 10^5$	$6.7 \times 10^5$
2-Fluoroazobenzene	4.27	$3.7 \times 10^6$	$5.3 \times 10^6$
4-Fluoroazobenzene	7.06	$1.5 \times 10^5$	$3.3 \times 10^5$
4,4'-Difluoroazobenzene	8.12	$6.0 \times 10^4$	$1.6 \times 10^5$
2-Chloroazobenzene	2.86	$1.9 \times 10^7$	$2.3 \times 10^7$
3-Chloroazobenzene	2.61	$2.9 \times 10^7$	$3.6 \times 10^7$
4-Chloroazobenzene	4.10	$5.5 \times 10^6$	$7.9 \times 10^6$
<b>Benzo[a]pyrene</b>			
Azobenzene	7.68	$3.8 \times 10^4$	$1.3 \times 10^5$
2-Fluoroazobenzene	5.88	$5.0 \times 10^5$	$1.1 \times 10^6$
2-Chloroazobenzene	4.47	$4.1 \times 10^6$	$6.0 \times 10^6$
3-Chloroazobenzene	4.22	$7.0 \times 10^6$	$1.0 \times 10^7$
4-Chloroazobenzene	5.72	$9.4 \times 10^5$	$1.7 \times 10^6$
4,4'-Dichloroazobenzene	3.67	$1.0 \times 10^7$	$1.8 \times 10^7$
2-Bromoazobenzene	4.13	$4.8 \times 10^6$	$7.0 \times 10^6$
3-Bromoazobenzene	3.90	$7.5 \times 10^6$	$1.2 \times 10^7$
4-Bromoazobenzene	— <sup>d</sup>	— <sup>d</sup>	$2.8 \times 10^6$

<sup>a</sup> $C_A^0 = 0.5 \text{ mM}$  and  $C_{X-AZ}^0 = 1.0 \text{ mM}$ . <sup>b</sup>Equal to  $-F[E^{\circ}(X-AZ^{\cdot-}|X-AZ^{2-}) - E^{\circ}(A|A^{\cdot-})]$ . <sup>c</sup>Concentration of added water. <sup>d</sup>Not measurable because of dehalogenation of  $X-AZ^{2-}$  (see the text).

taining both A and X-AZ. The rate constants result from the fit of the experimental  $R_i(A/B)$ -sweep rate data to the working curve calculated for rate law (13) by digital simulation.

$$-\frac{d[A^{\cdot-}]}{dt} = k_{11}[A^{\cdot-}][X-AZ^{\cdot-}] \quad (13)$$

As a first approximation the simulations were based on the assumption that the diffusion coefficients,  $D$ , were identical for all species in solution, and for several combinations of A and X-AZ the fit of the experimental data to the resulting working curve was excellent as illustrated in Fig. 3 for A = anthracene (AN) and X-AZ = 4-fluoroazobenzene (4-FAZ) for which the ratio,  $D(4-FAZ)/D(AN)$ , equals 0.96 (Table 1). However, it was observed that the fit to the working curve was generally poor when the  $D$ -ratio deviated significantly from unity. This problem, being particularly pronounced for the large compounds, A = 9-phenylanthracene (9-PA) and benzo[*a*]pyrene (BP), was solved by calculation of a series of working curves taking into account the proper  $D$ -ratios (Table 1) and then use of these working curves for the evaluation of  $k_{11}$ . Comparison of the working curves for different  $D$ -ratios demonstrated that attempts to evaluate  $k_{11}$  without the proper incorporation of  $D$  in the simulation may result in rate constants that are 50–100% too low. The details of the simulations, which are not trivial, will be discussed elsewhere.<sup>39</sup>

The rate constants,  $k_{11}$ , determined as described above, are given in Table 2. The values vary from  $3.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  (BP and H-AZ) to  $2.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (9-PA and 3-ClAZ), but before going into the discussion of these data we wish to make two more points concerning the quality of the measurements.

The accuracy of rate constants obtained by the DLSV method is dependent mainly on the assumptions made for the relative rates of the chemical steps and the goodness of the fit of the experimental data to the working curve as already indicated. The rate constants for the slow reactions, corresponding to  $k_{11} < 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , were necessarily based on  $R_i(A/B)$  ratios obtained at fairly low sweep rates, typically in the range,  $\nu = 0.5\text{--}5.0 \text{ V s}^{-1}$ , where the CV experiments have shown that interference from the reversibility of the protonation of X-AZ<sup>2-</sup>, eqn. (7), may occur. This interference will be increasingly severe with decreasing sweep rate. As a consequence, the measured values of  $R_i(A/B)$  will be too small and the fit to a working curve, which does not take backward reaction (7) into account, will result in values of the rate constants that are too small as well. The maximum error introduced in this way is estimated to be 20–30% for  $k_{11} < 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . No attempts were made to correct for this since there was no way in which the error could be evaluated quantitatively. For the fast reactions, corresponding to  $k_{11} > 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , the measurements require, in principle, sweep rates well above  $100 \text{ V s}^{-1}$  in order that data points can be accumulated over a range sufficiently large to allow evaluation of the good-

ness of the fit to the working curve. However, due to the restrictions imposed on the measurement procedure by the rates of the heterogeneous charge transfer processes for A and X-AZ, which in the simulations have to be assumed to be Nernstian, the applied sweep rate range seldom included  $\nu$ -values higher than  $100\text{--}150 \text{ V s}^{-1}$ . Consequently, the evaluation of the rate constants had to be based on only few data points and may for that reason be less precise than the rate constants in the  $10^5\text{--}10^7 \text{ M}^{-1} \text{ s}^{-1}$  region, where the measurements could be made over a large sweep rate range (cf. Fig. 3).

*The relationship between  $k_{11}$  and  $E^\circ(X-AZ^{\cdot-}|X-AZ^{2-}) - E^\circ(A|A^{\cdot-})$ .* Discussions of the magnitudes of electron transfer rate constants,  $k$ , are usually based upon the relationship between  $-RT \ln k$  and the free energy difference,  $\Delta G^\circ$ .<sup>40–44</sup> The latter is often approximated by  $-F(\Delta E^\circ)$ , in the present case corresponding to  $-F[E^\circ(X-AZ^{\cdot-}|X-AZ^{2-}) - E^\circ(A|A^{\cdot-})]$ .

$$E_p^{\text{red}}(A) - E^\circ(A|A^{\cdot-}) = -0.0285 \text{ V} \quad (14)$$

The values of  $E^\circ(A|A^{\cdot-})$  for the reversible A|A<sup>·-</sup> couples in DMF are easily calculated from the corresponding peak potentials,  $E_p^{\text{red}}(A)$ , via eqn. (14).<sup>45,46</sup> However, the determination of  $E^\circ(X-AZ^{\cdot-}|X-AZ^{2-})$  for the quasi-reversible electron transfer reactions, eqn. (6), requires much more consideration since the potential difference,  $E_p^{\text{red}}(X-AZ^{\cdot-}) - E^\circ(X-AZ^{\cdot-}|X-AZ^{2-})$ , is a complicated function,  $f(k_6^\circ, k_7, \nu, \alpha)$ , of the rate constants for the heterogeneous electron transfer process, eqn. (6), and the chemical follow-up reaction, eqn. (7), the sweep rate,  $\nu$ , and the charge transfer coefficient,  $\alpha$ , eqn. (15).<sup>47</sup> For the present series of compounds, the value of  $f(k_6^\circ, k_7, \nu, \alpha)$  at  $\nu = 10 \text{ V s}^{-1}$  could be demonstrated to be close to 0.04 V (see the Appendix), which allows for the evaluation of  $E^\circ(X-AZ^{\cdot-}|X-AZ^{2-})$  for the azobenzenes from the voltammetric data given in Table 1 and thus, the free energy differences.

According to the Marcus theory<sup>40–42,44,48</sup> the relationship between the free energy of activation,  $\Delta G^\ddagger$ , and the free energy difference,  $\Delta G^\circ$ , is given by expression (16), where  $w_r$  and  $w_p$  are the free energies required to form the encounter complex between the reactants and the products, respectively, and  $\Delta G_0^\ddagger$  is the so-called intrinsic barrier, corresponding to the free energy of activation within the encounter complex at  $\Delta G^\circ - w_r + w_p = 0$ . Accordingly, the slope of a plot of  $-RT \ln k$  against  $\Delta G^\circ$  is given by eqn. (17). It is seen from eqn. (17) that the slope at  $\Delta G^\circ - w_r + w_p = 0$  is equal to 0.5 and is predicted to be larger than 0.5 for  $\Delta G^\circ - w_r + w_p > 0$ .

A plot of  $-RT \ln k_{11}$  against  $-F[E^\circ(X-AZ^{\cdot-}|X-AZ^{2-}) - E^\circ(A|A^{\cdot-})] \approx \Delta G^\circ$  is shown in Fig. 4 and since the range of the  $k_{11}$  values only covers approximately three orders of magnitude it is not surprising that an almost linear relationship between the parameters is observed. The slope of the linear regression line was calculated to be 0.68 and the

$$E_p^{\text{red}}(\text{X-AZ}^{\cdot-}) - E^{\circ'}(\text{X-AZ}^{\cdot-}|\text{X-AZ}^{2-}) = f(k_6^{\circ}, k_7, \nu, \alpha) \quad (15)$$

$$\Delta G^{\ddagger} = w_r + \Delta G_0^{\ddagger} \left[ 1 + \frac{\Delta G^{\circ} - w_r + w_p}{4\Delta G_0^{\ddagger}} \right]^2 \quad (16)$$

$$\begin{aligned} -RT \left[ \frac{\partial \ln k}{\partial \Delta G^{\circ}} \right]_{\Delta G_0^{\ddagger}, w_r, w_p} &= \left[ \frac{\partial \Delta G^{\ddagger}}{\partial \Delta G^{\circ}} \right]_{\Delta G_0^{\ddagger}, w_r, w_p} \\ &= \frac{1}{2} \left[ 1 + \frac{\Delta G^{\circ} - w_r + w_p}{4\Delta G_0^{\ddagger}} \right] \end{aligned} \quad (17)$$

question is now, how does this slope compare with that predicted by eqn. (16)?

The values of the work terms,  $w_r$  and  $w_p$ , are dominated by electrostatic contributions<sup>42,49</sup> and since one of the products, A, in reaction (11) is uncharged the value of  $w_p$  may be set to zero. The value of  $w_r$  (in kcal mol<sup>-1</sup>) may be estimated from the simplified Debye-Hückel expression (18)<sup>42,49,50</sup> valid for  $r_1 \approx r_2$ , where  $r_1$  and  $r_2$  are the radii of

$$w_r = \frac{2.39 \times 10^{-11} z_1 z_2 N e^2}{\epsilon_s r_{12} \left[ 1 + r_{12} \left( \frac{8\pi N e^2 \mu}{1000 \epsilon_s k_B T} \right)^{1/2} \right]} \quad (18)$$

the reacting species. [In eqn. (18),  $z_1$  and  $z_2$  are the charge numbers of the reactants,  $N$  is the Avogadro constant,  $e$  is the charge of the electron,  $\epsilon_s$  is the bulk dielectric constant of the solvent,  $r_{12}$  is the distance between the reactive centers in the encounter complex, which may be approximated by  $r_1 + r_2$ ,  $\mu$  is the ionic strength,  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature; cgs units are assumed]. Values of  $r_1$  and  $r_2$  were evaluated by eqn. (19) from the molecular weight ( $M_w$ ) and the density of the substrate,  $\rho$ , in the cases where  $\rho$  was available. The radii were generally close to  $4 \times 10^{-8}$  cm and were found to vary only little with structure. Therefore,  $r_{12} = r_1 + r_2 = 8 \times 10^{-8}$  cm was used in eqn. (18), which together with  $\epsilon_s = 36.7$  and  $\mu = 0.1$  M resulted in the average value  $0.51$  kcal mol<sup>-1</sup> for  $w_r$ .

$$r = \left( \frac{3M_w}{4\pi N \rho} \right)^{1/3} \quad (19)$$

From eqn. (16) it is seen that  $\Delta G_0^{\ddagger}$  may be determined as the intercept at  $\Delta G^{\circ} - w_r + w_p = 0$  of a plot of  $-RT \ln k$  against  $\Delta G^{\circ} - w_r + w_p$ . In our case ( $k = k_{11}$ ) parabolic extrapolation resulted in a value of  $3.8$  kcal mol<sup>-1</sup> assuming the bimolecular collision frequency in solution is  $10^{11}$  M<sup>-1</sup> s<sup>-1</sup>.<sup>51</sup>

The range of  $-F[E^{\circ'}(\text{X-AZ}^{\cdot-}|\text{X-AZ}^{2-}) - E^{\circ'}(\text{A}|\text{A}^{\cdot-})]$  for the present series of compounds corresponds to  $5.5$  kcal mol<sup>-1</sup> with the minimum value being  $2.6$  kcal mol<sup>-1</sup>. In-

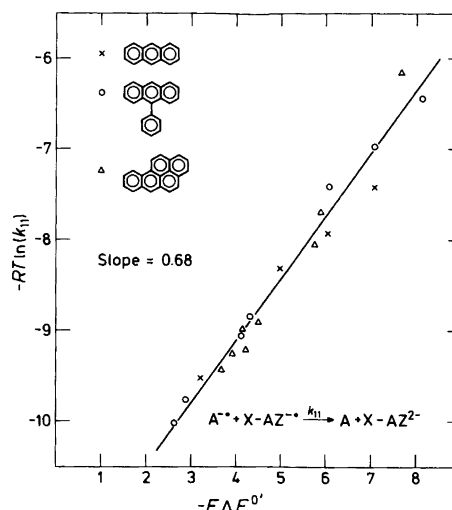


Fig. 4. The relationship between  $-RT \ln k_{11}$  and  $-F[E^{\circ'}(\text{X-AZ}^{\cdot-}|\text{X-AZ}^{2-}) - E^{\circ'}(\text{A}|\text{A}^{\cdot-})]$  for rate constants obtained in the *N,N*-dimethylformamide containing  $\text{Bu}_4\text{NPF}_6$  (0.1 M) and residual water only. The values on both scales are given in kcal mol<sup>-1</sup>.

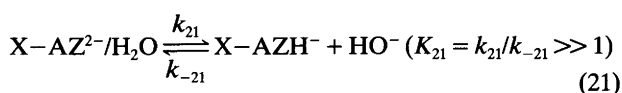
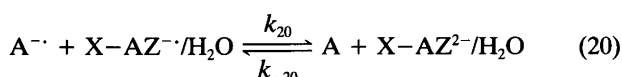
production of these values together with  $\Delta G_0^{\ddagger} = 3.8$  kcal mol<sup>-1</sup> and  $w_r = 0.51$  kcal mol<sup>-1</sup> in eqn. (16) results in a predicted slope of 0.66 for the plot in Fig. 4, which is very close to the experimentally observed value, 0.68.

Thus, we conclude that the mechanism consisting of eqns. (11) and (7) offers a satisfactory description of the electron transfer from  $\text{A}^{\cdot-}$  to  $\text{X-AZ}^{\cdot-}$  in DMF containing  $\text{Bu}_4\text{NPF}_6$  (0.1 M) and that the observed relation between the electron transfer rate constants and the free energy differences can be accounted for by the Marcus theory.

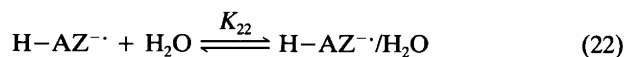
*The influence of water on the magnitudes of  $k_{11}$  and  $E^{\circ'}(\text{X-AZ}^{\cdot-}|\text{X-AZ}^{2-}) - E^{\circ'}(\text{A}|\text{A}^{\cdot-})$ .* The solvent used in the measurements described above was distilled prior to use, but apart from passing the solvent-electrolyte mixtures through a column filled with activated neutral alumina immediately before adding the substrates, no special precautions were taken to control the water content, which under these conditions has been determined to be typically 5–20 mM.<sup>52</sup> However, it was repeatedly observed that the values of  $k_{11}$  depended appreciably on the actual water content of the voltammetry solutions and that extreme care should be taken in the manipulation of the voltammetry solutions to avoid unnecessary scatter of the rate constants. In order to gain some more insight into the influence of water on the electron transfer rates a series of measurements were carried out in DMF to which water was added to increase the concentration by 0.1 M (Table 2). The general effect of addition of water is enhancement of the electron transfer rates relative to those obtained in the presence of residual water only. Inspection of Table 2 shows that the effect increases with decreasing values of the rate constants and as a result of this the slope of  $-RT \ln k_{11}$  against  $-F[E^{\circ'}(\text{X-AZ}^{\cdot-}|\text{X-AZ}^{2-}) - E^{\circ'}(\text{A}|\text{A}^{\cdot-})]$  is lowered from 0.68 to 0.60 (Fig. 5). We postulate that the

reason for this observation is that the mechanism consisting of eqns. (11) and (7) alone is not a satisfactory description of the electron transfer reaction in the presence of large concentrations of water.

Anion radicals of aromatic compounds that contain oxygen or nitrogen atoms formally carrying a lone pair are known to form hydrogen-bond complexes in DMF containing water or alcohols,<sup>53-57</sup> a property even more pronounced for dianions.<sup>58</sup> Therefore, reactions (20)–(21), in which the slash represents a hydrogen bond, may be expected to contribute to determining the kinetics in DMF containing 0.1 M water.



The equilibrium constant,  $K_{22}$ , for the formation of  $H-AZ^{\cdot-}/H_2O$ , eqn. (22), was determined to be equal to  $0.66 M^{-1}$  from the shift of the reversible peak potential,  $\Delta E_p^{\text{red}}(H-AZ) = E_p^{\text{red,water}}(H-AZ) - E_p^{\text{red}}(H-AZ)$ , upon addition of water, eqn. (23).<sup>59</sup> This value is in the range,  $0.3\text{--}1.5 M^{-1}$ , typically found for anion radicals of aromatic compounds containing more than one electron-withdraw-



$$K_{22} = \frac{\exp\{\Delta E_p^{\text{red}}(H-AZ)/[RT/F]\} - 1}{[H_2O]} \quad (23)$$

ing heteroatom.<sup>55,57</sup> As a consequence of the moderate value of  $k_{22}$ , the concentration of  $H-AZ^{\cdot-}/H_2O$  in the voltammetric solutions containing only residual water will amount to less than 1% of the total concentration of  $H-AZ^{\cdot-}$ . On the other hand, in a solution with  $C_{\text{water}}^0 = 0.1 M$  the concentration of  $H-AZ^{\cdot-}/H_2O$  close to the electrode surface will be approximately 6% of the total concentration. Obviously, the kinetic contributions from reactions (20)–(21) are expected to become increasingly important with increasing concentration of water.

Since the dianions,  $X-AZ^{2-}$ , are expected to be more strongly coordinated to water than the anion radicals<sup>58</sup> the overall effect of hydrogen bonding will be that  $-F[E^{\circ'}(X-AZ^{\cdot-}|X-AZ^{2-}) - E^{\circ'}(A|A^{\cdot-})]$  in the presence of water is smaller than the value referring to essentially non-aqueous conditions. This causes the values of  $\Delta G^{\circ}$  based on the estimates of  $E^{\circ'}(X-AZ^{\cdot-}|X-AZ^{2-})$  under water-free conditions to be too large. Values of  $E^{\circ'}(X-AZ^{\cdot-}|X-AZ^{2-})$  in the presence of 0.1 M water are unfortunately not available and therefore it is tempting to use eqn. (16) to make an estimate of the  $\Delta G^{\circ}$  shift necessary to change the slope from 0.68 to 0.60. A series of iterative calculations demon-

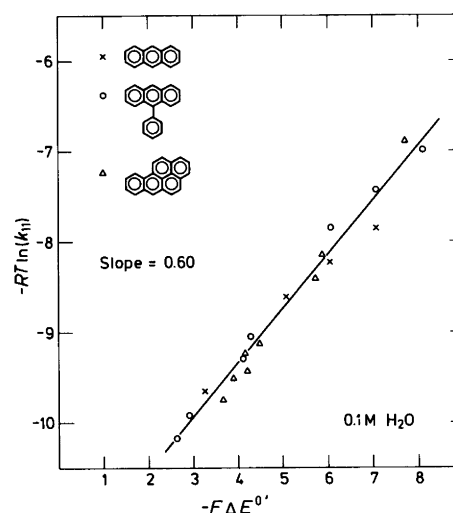


Fig. 5. The relationship between  $-RT \ln k_{11}$  and  $-F[E^{\circ'}(X-AZ^{\cdot-}|X-AZ^{2-}) - E^{\circ'}(A|A^{\cdot-})]$  for rate constants obtained in the *N,N*-dimethylformamide containing  $Bu_4NPF_6$  (0.1 M) and deliberately added water (0.1 M). The values on both scales are given in  $\text{kcal mol}^{-1}$ .

strates that the shift amounts to  $2.4 \text{ kcal mol}^{-1}$  corresponding to 0.1 V. With a value of  $K_{22}$  equal to  $0.66 M^{-1}$  the effect on  $E^{\circ'}(H-AZ|H-AZ^{\cdot-})$  of increasing the water concentration by 0.1 M is only 2 mV. This means that the shift of 0.1 V is almost entirely due to the effect of water on  $E^{\circ'}(H-AZ^{\cdot-}|H-AZ^{2-})$  and therefore that the value of the potential difference,  $E^{\circ'}(H-AZ|H-AZ^{\cdot-}) - E^{\circ'}(H-AZ^{\cdot-}|H-AZ^{2-})$ , that is consistent with our data obtained in the presence of 0.1 M water is 0.73 V.

Further work that focuses on the effects of hydrogen-bonding on electron transfer rates, and the effects of ion-pairing, is now in progress.<sup>60</sup>

## Appendix

The problem of evaluating  $E^{\circ'}(X-AZ^{\cdot-}|X-AZ^{2-})$  would be simplified considerably if the voltammetric measurements could be carried out in the strict absence of water where the kinetic complications introduced through reaction (7) vanish. Under such conditions it would be possible to observe reverse current for the reoxidation of  $X-AZ^{2-}$  and a good estimate of  $E^{\circ'}(X-AZ^{\cdot-}|X-AZ^{2-})$  might be obtained as the midpoint potential,  $[E_p^{\text{ox}}(X-AZ^{2-}) + E_p^{\text{red}}(X-AZ^{\cdot-})]/2$ . This approach, which unfortunately requires a rather elaborate experimental set-up, has been used for unsubstituted azobenzene in DMF in the presence of either  $Me_4NPF_6$ <sup>35</sup> or  $Bu_4NBF_4$ <sup>61</sup> as the supporting electrolyte. Inspection of the published voltammograms reveals that both the rate constant for the heterogeneous charge transfer process,  $k_0^{\text{e}}$ , as judged from the peak potential difference,  $E_p^{\text{ox}}(H-AZ^{2-}) - E_p^{\text{red}}(H-AZ^{\cdot-})$ , and the standard potential difference,  $E^{\circ'}(H-AZ|H-AZ^{\cdot-}) - E^{\circ'}(H-AZ^{\cdot-}|H-AZ^{2-})$ , are notably dependent on the nature of the supporting electrolyte. The values we have measured from these voltammograms are the following:

$$\left. \begin{aligned} E_p^{\text{ox}}(\text{H-AZ}^{2-}) - E_p^{\text{red}}(\text{H-AZ}^{\cdot-}) &\approx 0.063 \text{ V} \\ E^{\circ'}(\text{H-AZ}|\text{H-AZ}^{\cdot-}) - E^{\circ'}(\text{H-AZ}^{\cdot-}|\text{H-AZ}^{2-}) &= 0.75 \text{ V} \end{aligned} \right\} \text{Me}_4\text{NPF}_6 (0.1 \text{ M})$$

$$\left. \begin{aligned} E_p^{\text{ox}}(\text{H-AZ}^{2-}) - E_p^{\text{red}}(\text{H-AZ}^{\cdot-}) &\approx 0.100 \text{ V} \\ E^{\circ'}(\text{H-AZ}|\text{H-AZ}^{\cdot-}) - E^{\circ'}(\text{H-AZ}^{\cdot-}|\text{H-AZ}^{2-}) &= 0.83 \text{ V} \end{aligned} \right\} \text{Bu}_4\text{NBF}_4 (0.1 \text{ M})$$

The results indicate that the heterogeneous charge-transfer process is faster and that the resulting dianion, H-AZ<sup>2-</sup>, is thermodynamically more stable relative to H-AZ<sup>·-</sup> in the presence of Me<sub>4</sub>NPF<sub>6</sub>. The most likely explanation of these differences is that the results obtained in the presence of the smaller Me<sub>4</sub>N<sup>+</sup> ion may be affected by the formation of ion pairs, e.g. Me<sub>4</sub>N<sup>+</sup>, H-AZ<sup>2-</sup>.<sup>\*</sup> Consequently, we will use the value, 0.83 V, obtained in the presence of Bu<sub>4</sub>N<sup>+</sup>, which is also the counter ion in the present study, as our standard for  $E^{\circ'}(\text{H-AZ}|\text{H-AZ}^{\cdot-}) - E^{\circ'}(\text{H-AZ}^{\cdot-}|\text{H-AZ}^{2-})$  in the discussion to follow. We are not aware of similar studies for the substituted azobenzenes, but we will show below that, with this value at hand, fair estimates of  $E^{\circ'}(\text{X-AZ}^{\cdot-}|\text{X-AZ}^{2-})$  for the full series of compounds may be calculated from the corresponding  $E_p^{\text{red}}(\text{X-AZ}^{\cdot-})$  values.

Since the protonation equilibrium, eqn. (7), is strongly displaced to the right and can be assumed to be fast, the overall process may be treated as a quasi-reversible electron transfer reaction followed by a fast, irreversible chemical step, and E<sub>q</sub>C<sub>1</sub>-type process. Moreover, the azobenzenes used in this study are structurally very similar and since the rate of the protonation step, eqn. (7), approaches the limit for a diffusion-controlled process, the dependence of  $k_7$  on the structure of X-AZ is bound to be very small. We will, in the following, assume a high, nearly constant value of  $k_7$  for the entire series of compounds. This means that the voltammetric response of the X-AZ<sup>·-</sup>|X-AZ<sup>2-</sup> systems conforms to a kinetic region where the shape of the voltammetric peak is determined almost exclusively by the rate of the heterogeneous charge-transfer process, i.e., by the magnitudes of  $k_6^0$  and  $\alpha$ . If, in addition, we assume that these two parameters are constant or nearly constant for all the azobenzenes, again considering the close structural relationship between the compounds, the shape of the voltammetric peaks will be almost identical. The validity of these assumptions is supported by the observations that  $E_{p2} - E_p$  for the X-AZ<sup>·-</sup>|X-AZ<sup>2-</sup> couples only vary between 68–78 mV at  $\nu = 10 \text{ V s}^{-1}$  and that plots of  $E_p^{\text{red}}(\text{X-AZ}^{\cdot-})$  against  $\log \nu$  were observed to be linear with slopes in a rather narrow range, 48–53 mV/decade. An important

\* This conclusion implies that the value, 38.1, reported<sup>35</sup> for the pK<sub>A</sub> of H-AZH<sup>-</sup> may be a slight underestimate. The value was based on an observed difference of 0.2 V between  $E^{\circ'}(\text{X-AZ}^{\cdot-}|\text{X-AZ}^{2-})$  measured in scrupulously dried DMF and DMF containing equimolar amounts of H-AZ and H<sub>2</sub>O. Since the effect of ion-pairing is expected to be more pronounced in the dry solvent, the  $E^{\circ'}$  difference may well be more than 0.2 V in the absence of ion-pairing and accordingly, the resulting pK<sub>A</sub> will be higher than 38.1. This, however, has no consequences for our experimental approach or the arguments put forward in the present paper.

consequence of this analysis is that  $f(k_6^0, k_7, \nu, \alpha)$  is not likely to vary more than 5–10 mV at a given sweep rate for the entire series of compounds corresponding to 0.1–0.2 kcal mol<sup>-1</sup>. The nearly constant value of  $f(k_6^0, k_7, \nu, \alpha)$  was estimated to be approximately 0.04 V from the  $E^{\circ'}$  difference of 0.83 V for azobenzene and the peak potentials,  $E_p^{\text{red}}(\text{H-AZ})$  and  $E_p^{\text{red}}(\text{H-AZ}^{\cdot-})$ .

## Experimental

**Reagents, solvent and electrolyte.** The halogen-substituted azobenzenes were prepared by reduction of the appropriate nitrobenzenes with zinc or by coupling of suitably substituted anilines and nitrosobenzenes in acetic acid.<sup>62,63</sup> The nitrosobenzenes were prepared by reduction of the corresponding nitrobenzenes with zinc to the hydroxylamine stage followed by reoxidation with dichromate or iron (III).<sup>63,64</sup> The identity and purity of the halogen-substituted azobenzenes was ascertained by elemental analysis, <sup>1</sup>H NMR spectroscopy, cyclic voltammetry and determination of melting points.

The solvent, DMF, was distilled at reduced pressure prior to use and passed through a column filled with neutral alumina (Woelm W 200, activity grade I) before and after addition of the supporting electrolyte, Bu<sub>4</sub>NPF<sub>6</sub>, which was prepared analogously to the procedure described for Bu<sub>4</sub>NBF<sub>4</sub>.<sup>65</sup>

**Instrumentation.** The potentiostat was a PAR 173/176 driven by a PAR 175 signal generator. Differentiation was achieved by a PAR 189 selective amplifier with the frequency-to-sweep rate ratio set to 20 as reported earlier.<sup>23</sup> The resulting data were recorded on a Nicolet 310 digital oscilloscope interfaced to a Hewlett Packard Vectra ES computer equipped with a Basic language processor. The cells and electrodes were as reported earlier.<sup>65</sup>

**Measurements.** The peak potentials were recorded by linear sweep voltammetry as outlined in Ref. 65. The values given are averages of 6 to 12 measurements and the standard deviations were between 0.5 and 1.0 mV. The rate constants for the electron transfer reactions between the aromatic hydrocarbon anion radicals and the anion radicals of the azobenzenes were reproducible to within 30 % over an extended period of time and for different samples of the supporting electrolyte and solvent.

**Digital simulation.** The working curve calculated under the assumption of identical diffusion coefficients for all species in solution was the same as presented previously.<sup>23</sup> The



simulations that incorporated different diffusion coefficients for the A and the X-AZ systems required, in general, more time steps to attain the required accuracy than those for which it could be assumed that  $D(A) = D(X-AZ)$ .<sup>39</sup>

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