

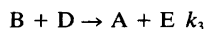
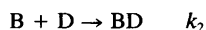
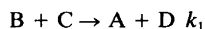
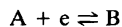
Simulated Data for Simple Electrochemical Determination of Rate Constants for Homogeneous Electron Transfer (SET) Reactions and Competition Parameter for Second-Order Follow-up Reactions. II. Coupling and Second SET Reaction between Mediator and Reduced Form of the Substrate

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The kinetic equations for catalytic solution electron transfer (SET) followed by two competing second-order reactions, a coupling reaction and a second SET reaction:



where the follow-up reactions are assumed to be much faster than the first SET reaction, are solved by digital simulation for linear sweep voltammetry (LSV), cyclic voltammetry and finally for double potential step chronoamperometry. Simulated data for simple and fast measurements of the homogeneous electron transfer rate constant by four standard methods are presented. The methods allow measurement of k_1 for a broad range of fast and slow systems. The best method for measurement of the competition parameter $q = k_2/(k_2+k_3)$ is found to be LSV.

The methods have been shown to be applicable experimentally to the systems anthracene/*sec*-butyl bromide methylbenzoate/*n*-butyl bromide and perylene/benzyl chloride in DMF.

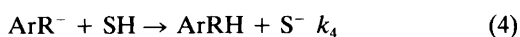
The indirect reduction of aromatic and aliphatic halides employing aromatic or heteroaromatic catalysts has been intensively studied (Refs. 1-6, and references therein). The key step in indirect electrolysis is the single electron transfer reaction in solution (SET) between an electrogenerated mediator and the substrate.

A number of reaction mechanisms in which the SET reaction is followed by different kinds of chemical reactions have been studied (Ref. 1 and references therein). In Ref. 1 we reported a study of the case of a second-order homogeneous elec-

tron transfer which is followed by a fast and irreversible coupling reaction between the reduced form of the mediator and the product of the electron transfer. We found that the rate constant, k_1 , for the SET reaction could be measured easily and accurately by linear sweep voltammetry (LSV), cyclic voltammetry (CV) and double potential step chronoamperometry (DPSC).

The purpose of the present work has been to find simple methods for determination of the rate constant, k_1 , for the case in which the homogeneous electron transfer between the mediator and

the substrate is followed by two competing second-order processes; one of these processes is coupling of the reduced form of the substrate and the electrogenerated mediator, and the other process is homogeneous electron transfer from the mediator to the reduced form of the substrate.



The product of the first SET reaction is often cleaved before further reactions take place. However, the simulated data presented here cover both situations as long as the cleavage reaction is much faster than the SET reaction.

Methods employing data obtained using the most popular electrochemical techniques, viz. LSV, CV and DPSC, are described here. Savéant *et al.*^{2,3} have previously described the LSV method.

The competition between the coupling reaction and the second SET reaction, given by the competition parameter $q = k_3/(k_2+k_3)$, can be determined by the LSV method.^{2,3} We have re-simulated the data and plotted them in a different manner which, in our opinion, is more useful.

It is known that the indirect reduction of alkyl halides using aromatic catalysts leads predominantly to coupling products, the latter being entirely dominant for tertiary alkyl halides and less dominant for secondary alkyl halides.⁵ It is believed that the mechanism can be described by reactions (1), (1b), (2) and (4).

Recent investigations⁶ have shown that the indirect reduction of benzyl chloride by anthracene or perylene produces mainly toluene, which is believed to be formed in two SET reactions. The mechanism is described by reactions (1), (1b), (3) and (5).

In between these two extremes is the indirect reduction of *n*-butyl bromide by methyl benzoate, for which analysis of the distribution of

products of preparative electrolysis has shown coupling products and two-electron reduction products.

Savéant *et al.*^{2,3} have investigated the reaction sequence, where the first solution electron transfer is followed by competition between a coupling reaction and a second solution electron transfer. The description of this mechanism requires measurement of the competition parameter and of the absolute value of the rate constant k_1 . Ref. 3 describes the use of LSV to determine both of these characteristic quantities by measuring the dimensionless current i_k/i_R , where i_R is the peak current for a reversible one-electron nernstian wave corresponding to the same electrode surface area, concentration, diffusion coefficient and sweep rate.

Kinetic description

The indirect reduction of alkyl halides and benzyl halides by aromatic or heteroaromatic systems in dry aprotic media is in many cases adequately described by the former reaction scheme in which Ar/Ar^- is the mediator and RX is the substrate, i.e. the alkyl halide or the benzyl halide. SH is a proton donor, e.g. the solvent.

ArR^- and R^- may be protonated by the solvent or by another proton donor, or they may attack other substrate molecules in nucleophilic-type reactions. In most cases, however, it is not necessary to analyse in further detail the different follow-up reactions of ArR^- or R^- because they generally are much slower than the reactions (1)–(3).

Product analysis⁵ has shown that alkyl halides normally react faster by the coupling reaction (2) than by the second SET reaction (3). This is particularly significant for tertiary or secondary alkyl halides. This type of reaction is thus characterized by $k_2 \gg k_3$.

Product analysis in the case of the indirect reduction of benzyl chloride by aromatics in aprotic media⁶ has shown that the more negative the reduction potential of the catalyst/aromatic the less non-coupling product is formed. This is because the rate of reaction (3) increases with increasing difference between the reduction potentials of Ar and R^\cdot . The indirect reduction of benzyl chloride by anthracene has been found to produce no detectable coupling products.⁶ This type of reaction is characterized by $k_3 \gg k_2$.

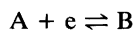
In between these two extremes are cases where it is impossible to disregard any of the competing reactions. This type of reaction is characterized by k_2 and k_3 being of the same magnitude.

In the treatment described here, the following assumptions have been made: Firstly, the rate-determining step in the reaction scheme is the forward homogeneous electron transfer (1), whereas (1b), (2) and (3) are much faster. The steady-state approximation can then be applied to RX^- and R^{\cdot} ; secondly, the diffusion coefficients of all the species in reactions (1)–(5) are equal; thirdly, the heterogeneous electron transfer Ar/Ar^- is fast and thus governed by Nernst's law. Follow-up reactions of ArR^- and R^- are assumed to be much slower than (1).

The steady-state approximations for RX^- and R^{\cdot} result in the following equality:

$$k_1[Ar^-][RX] = k_{1b}[RX^-] = (k_2 + k_3)[Ar^-][R^{\cdot}]$$

In this situation reactions (1)–(5) can be simplified to reactions (1)–(3), which can be written in general terms as:



We can describe this scheme mathematically by the following differential equations:

$$dc_A/dt = Dd^2c_A/dx^2 + k_1c_Bc_C + k_3c_Bc_D \quad (6)$$

$$dc_B/dt = Dd^2c_B/dx^2 - k_1c_Bc_C - k_2c_Bc_D - k_3c_Bc_D \quad (7)$$

$$dc_C/dt = Dd^2c_C/dx^2 - k_1c_Bc_C \quad (8)$$

$$t = 0, x \geq 0; x = \infty, t \geq 0:$$

$$c_A = c_A^0, c_B = 0, c_C = c_C^0$$

$$x = 0, t \geq 0:$$

$$\text{LSV, CV: } c_A/c_B = \exp[F/RT(E - E_{A/B}^0)]$$

$$\text{DPSC: } 0 < t \leq \tau, c_A = 0; \tau < t \leq 2\tau, c_B = 0;$$

$$i = FDA(dc_A/dx).$$

The steady-state approximation for D results in

$$k_1c_Bc_C = k_2c_Bc_D + k_3c_Bc_D$$

$$c_Bc_D = \frac{1}{k_2 + k_3} (k_1c_Bc_C)$$

and we can rearrange (6)–(8) as follows:

$$dc_A/dt = Dd^2c_A/dx^2 + \left(1 + \frac{k_3}{k_2 + k_3}\right) k_1c_Bc_C \quad (9)$$

$$dc_B/dt = Dd^2c_B/dx^2 - 2k_1c_Bc_C \quad (10)$$

$$dc_C/dt = Dd^2c_C/dx^2 - k_1c_Bc_C \quad (11)$$

The following dimensionless parameters are introduced:

$$a = c_A/c_A^0, b = c_B/c_A^0, c = c_C/c_A^0, c^0 = c_C^0/c_A^0$$

$$q = \frac{k_3}{k_2 + k_3}$$

$$\text{LSV, CV: } \theta = \left(\frac{F}{RT}\right) t, \xi = -\frac{F}{RT} (E - E_{A/B}^0)$$

$$y = \left(\frac{F}{DRT}\right)^{1/2} x, \lambda_1 = \left(\frac{RT}{F}\right) \left(\frac{k_1c_A^0}{v}\right)$$

$$\text{DPSC: } \theta = \frac{t}{\tau}, y = \frac{x}{(\tau \cdot D)^{1/2}}$$

$$\lambda_1 = k_1c_A^0 \cdot \tau$$

$$\psi = \frac{i}{FDA}$$

The differential equations and the boundary conditions can now be written in dimensionless form:

$$da/d\theta = d^2a/dy^2 + (1 + q)\lambda_1bc \quad (12)$$

$$db/d\theta = d^2b/dy^2 - 2\lambda_1bc \quad (13)$$

$$dc/\theta = d^2c/dy^2 - \lambda_1bc \quad (14)$$

$$\theta = 0, y \geq 0; y = \infty, \theta \geq 0:$$

$$a = 1, b = 0, c = c^0;$$

$$y = 0, \theta \geq 0:$$

$$\text{LSV, CV: } a/b = \exp(-\zeta);$$

$$\text{DPSC: } 0 \leq 1, a_{y=0} = 0; 1 < \theta \leq 2, b_{y=0} = 0;$$

$$\psi = (da/dy)_{y=0} = -(db/dy)_{y=0}.$$

Experimental

Reagents. The supporting electrolyte, Bu_4NBF_4 , and the solvent, DMF, were purified and dried by standard procedures. Anthracene, perylene, methyl benzoate, *n*-butyl bromide, *sec*-butyl bromide and benzyl chloride were all used as received, and no electroactive impurities could be detected.

The electrochemical cell. The measurements were made on DMF solutions containing 0.1 M Bu_4NBF_4 . The reference electrode was Ag/Ag^+ in DMF, constructed in the manner described by Moe.⁹ We used a modified cylindrical tube (25 ml volume) with a joint to accommodate a Teflon plug which served as a holder for the three electrodes. 10 ml volumes of solutions were used in all experiments. The temperature sensor and nitrogen flow entered the cell through two separate attached to the cylindrical tube.

Simulations. The simulations were performed partly on an Olivetti M24 personal computer and partly on a VAX 11/780 computer system from Digital. All programs were written in TURBO PASCAL. The figures were plotted with a HP 7475 plotter.

Instrumentation and data handling procedures were the same as described recently.¹

Results and discussion

The explicit point method,^{10,11} which has been described in detail by Britz¹² was used in the digital simulations. The stability factor $\lambda = (\text{D}\Delta t / \Delta x^2)$ was kept equal to 0.45 in all cases. Integration of the kinetic contributions to the differential equations was performed by a 4th-order classical Runge-Kutta method,¹³ although analytical integration is possible. For application of Runge-Kutta methods to electrochemistry, see Refs. 14 and 15.

In all CV and DPSC simulations a 6-point approximation of the flux near the electrode surface was applied.¹⁶ This approximation is based on the assumption that the concentration profiles near the electrode surface can be described more correctly by a third-degree polynomial than by the normal linear approximation. The equation for the flux is:

$$\left(\frac{da}{dx}\right)_{x=0} = [-137a_1 + 300(a_2 - a_3) + 200a_4 - 75a_5 + 12a_6] / 60\Delta x.$$

In the simulations of the LSV experiments an expanding grid explicit point method was used in order to save CPU time in the simulations at high xk values, and the normal linear approximation (2-point) for the flux was applied.

The LSV and CV experiments were all simulated with $E_{\text{start}} = E_{\text{A/B}}^{\circ} + 200$ mV, and the CV experiments with $E_{\text{switch}} = E_{\text{A/B}}^{\circ} - 200$ mV. Additional simulations have shown that the absolute peak current ratio measured in CV is not very sensitive (less than 1%) to moderate changes in the switching potential (± 10 mV). The simulations of the CV experiments were divided into 1600 time-steps, corresponding to 0.5 mV per time-step, whereas the LSV experiments were simulated with down to 0.02 mV per timestep, which was necessary at high xk values. The DPSC experiments were all simulated with a total of 2000 time-steps.

LSV simulations. The method is indirect, i.e. involved two experiments, the first in order to measure the reversible reduction peak current, i_{R} , when only the mediator is present, and the second to measure the peak current after the substrate has been added. The dimensionless ratio $i_{\text{k}}/i_{\text{R}}$ shows directly the catalytic efficiency.

$\log(i_{\text{k}}/i_{\text{R}})$ is plotted versus $\log(xk)$ for several values of $c_{\text{C}}^{\circ}/c_{\text{A}}^{\circ}$ and q in Figs. 1a-e. The kinetic parameter xk is given here by:

$$xk = \left(\frac{RT}{F}\right) \cdot \left(\frac{k_1 c_{\text{A}}^{\circ}}{v}\right)$$

CV simulations. In Fig. 2, the absolute ratio of $i_{\text{p,a}}/i_{\text{p,c}}$ is plotted versus $\log(xk)$ for q equal to 0.0, 0.5 and 1.0 for three values of $c_{\text{C}}^{\circ}/c_{\text{A}}^{\circ}$. Experimentally, it was found that the most accurate results were obtained with $0.10 \leq -i_{\text{p,a}}/i_{\text{p,c}} \leq 0.36$. The kinetic parameter xk is given by

$$xk = \frac{RT}{F} \frac{k_1 C_{\text{A}}^{\circ}}{v}$$

It is seen that changes in the value of q cause a shift of the curves, but not enough to make the CV technique appropriate for measuring the competition parameter, q .

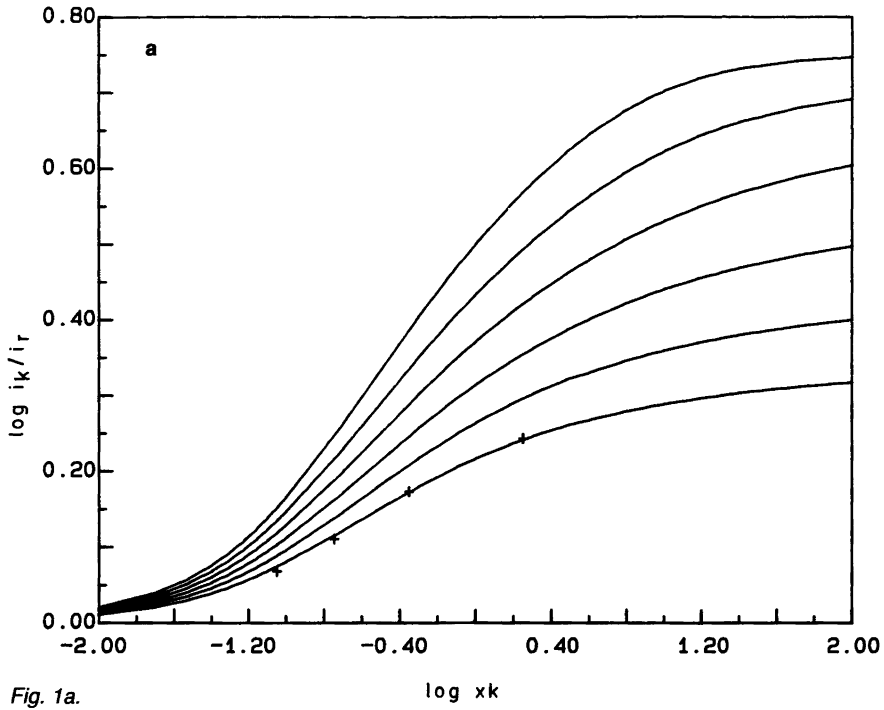


Fig. 1a.

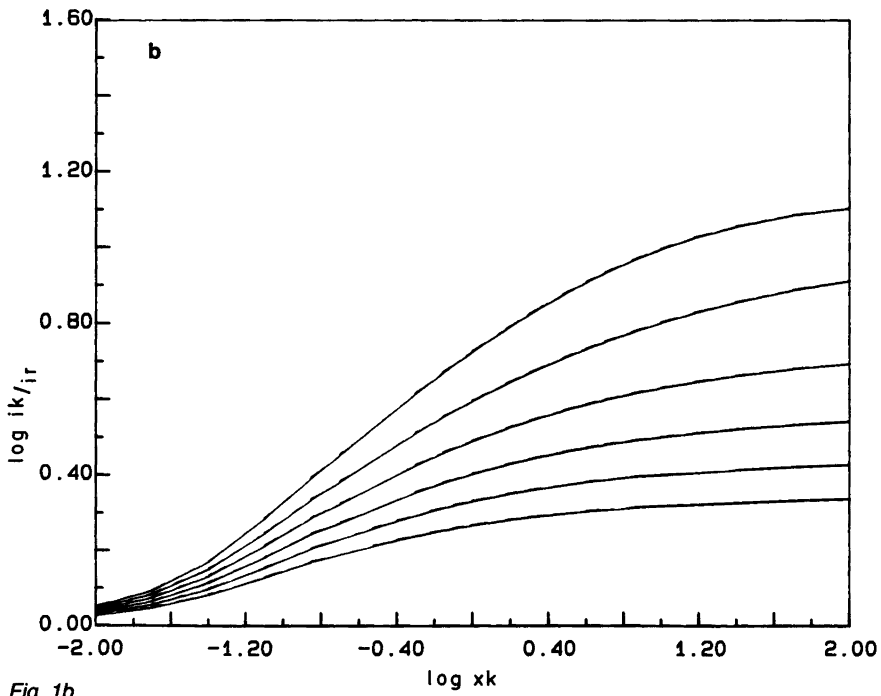


Fig. 1b.

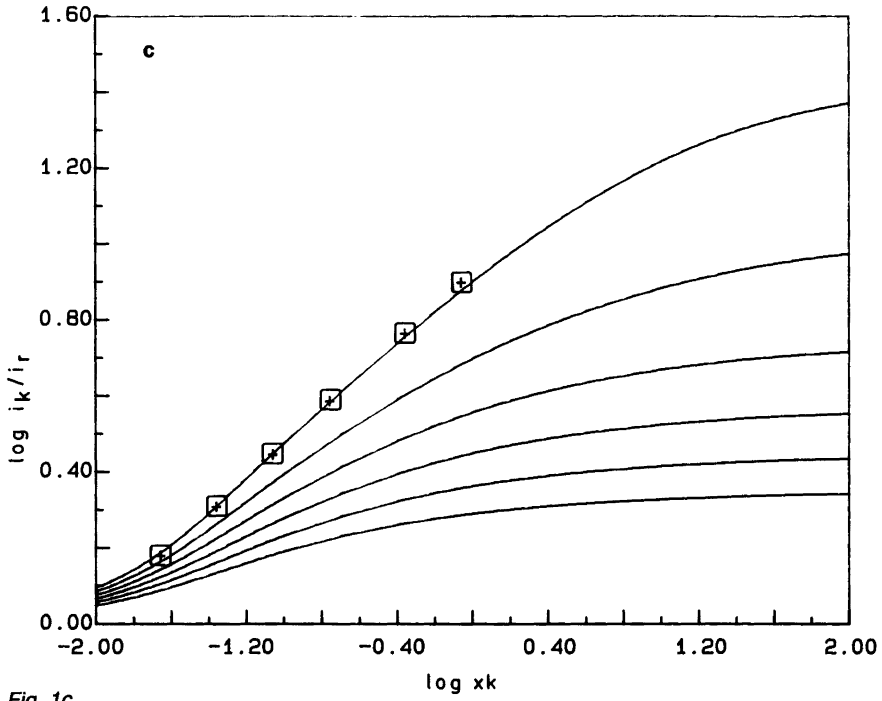


Fig. 1c.

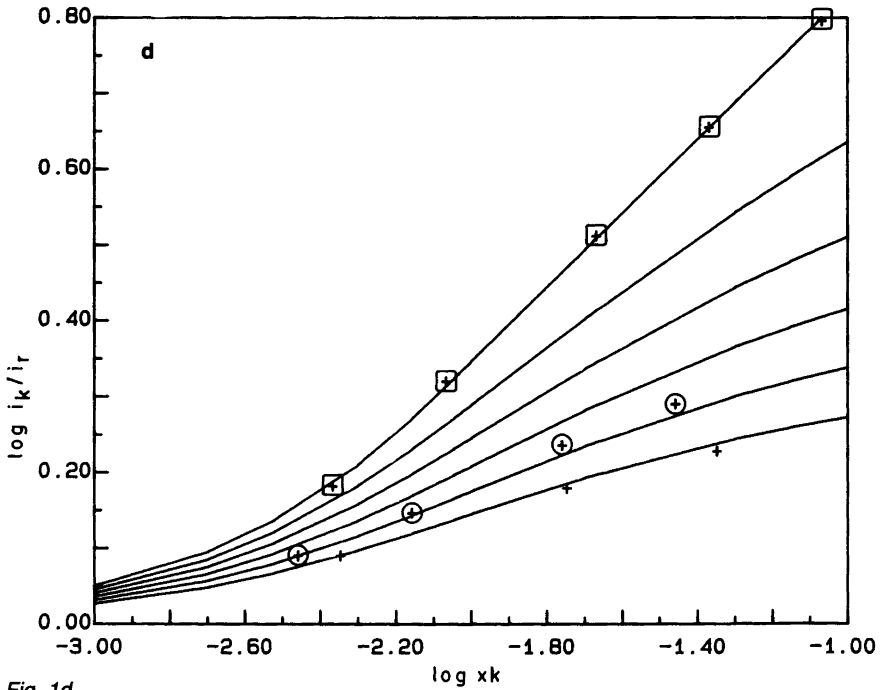


Fig. 1d.

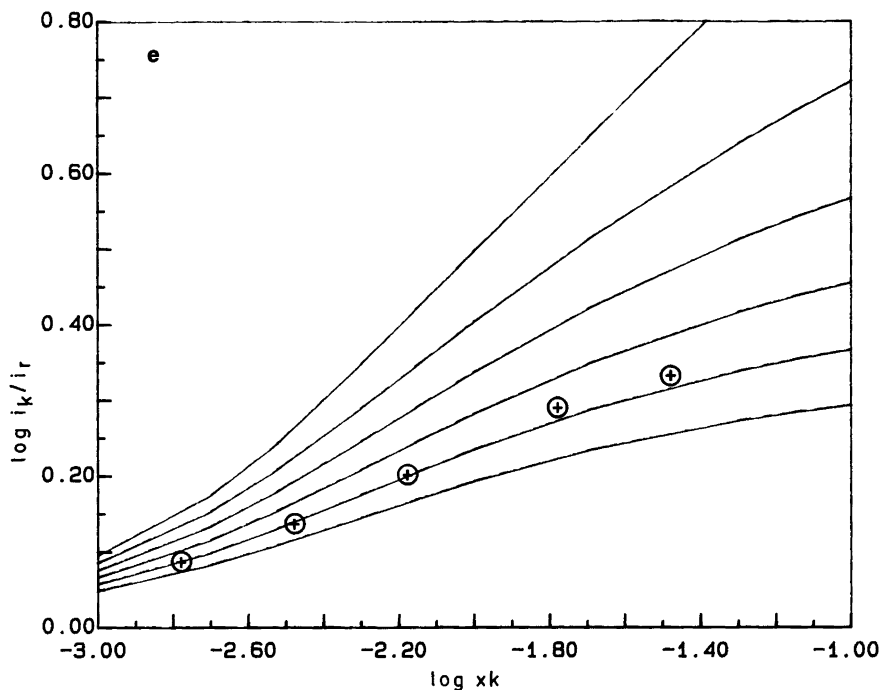


Fig. 1. The dependence of the logarithm of the current ratio i_k/i_r on $\log xk$ for the LSV method. i_r is the reversible peak current when only the mediator is present and i_k is the peak current after the substrate has been added. xk is the dimensionless kinetic parameter $xk = k_1 c_A^o RT/Fv$ and q is the competition parameter $q = k_3/(k_2 + k_3)$. All figures are plotted for $q = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 (the lowest curve is always $q = 0.0$) and the following values of c_0^o/c_A^o : (a) 2.0 (b) 5.0, (c) 10.0, (d) 50.0 and (e) 100.0. Experimental points: + anthracene/sec-butyl bromide, \oplus methyl benzoate/n-butyl bromide and \boxplus perylene/benzyl chloride.

In the interval $0.10 < -i_{p,a}/i_{p,c} < 0.36$, a 6th-degree polynomial was fitted to $i_{p,a}/i_{p,c}$ for q equal to 0.5. The effect of q is linearized around $q = 0.5$, and the q -coefficients, C_q , have been calculated. All coefficients are given in Table 1. The error in the presented data when the q depend-

ence is included and the q factor is known to an accuracy of ± 0.1 is typically less than 5%. For inexpedient combinations of c_0^o/c_A^o and $i_{p,a}/i_{p,c}$ the error may be larger; the maximum error (27%) occurs for $c_0^o/c_A^o = 1.0$. Thus, the xk value can now be calculated from the experimental dimen-

Table 1. 6th-order polynomial fit for CV simulations with included linearization of q -dependence.

c_0^o/c_A^o	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_q
1.0	0.0	9.713	57.67	273.8	797.6	1284	866.0	0.170
2.0	0.0	25.40	262.3	1573	5237	9104	6440	0.130
5.0	0.0	40.82	461.2	2859	9711	17110	12220	0.115
10.0	0.0	50.09	569.2	3510	11870	20850	14870	0.111
20.0	0.0	58.73	668.8	4118	13950	24630	17710	0.111
50.0	0.0	71.76	834.2	5181	17630	31150	22350	0.107
100.0	0.0	81.19	951.9	5937	20270	35920	25840	0.107

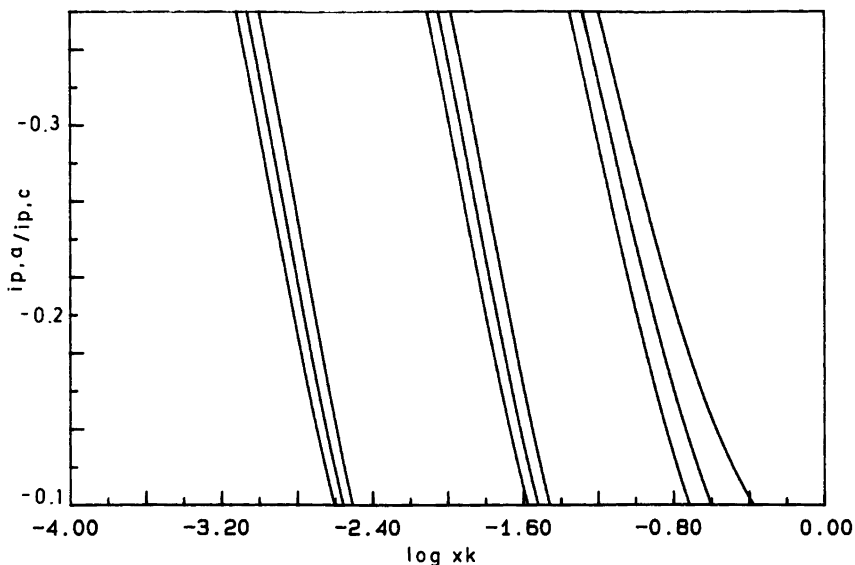


Fig. 2. The dependence of the current ratio $i_{p,a}/i_{p,c}$ on $\log (RT/F) \cdot (k_1 c_a^0/v)$ for different values of $q = k_3/(k_2+k_3)$. $i_{p,c}$ and $i_{p,a}$ are the absolute cathodic and anodic peak current when the switch potential is set to $E_{\text{switch}} = E_{AB}^0 - 200$ mV. The curves are simulated for the following values of c_c^0/c_a^0 and q (from right to left): $c_c^0/c_a^0 = 1.0$: $q = 1.0, 0.5, 0.0$; $c_c^0/c_a^0 = 5.0$: $q = 1.0, 0.5, 0.0$; $c_c^0/c_a^0 = 50.0$: $q = 1.0, 0.5, 0.0$.

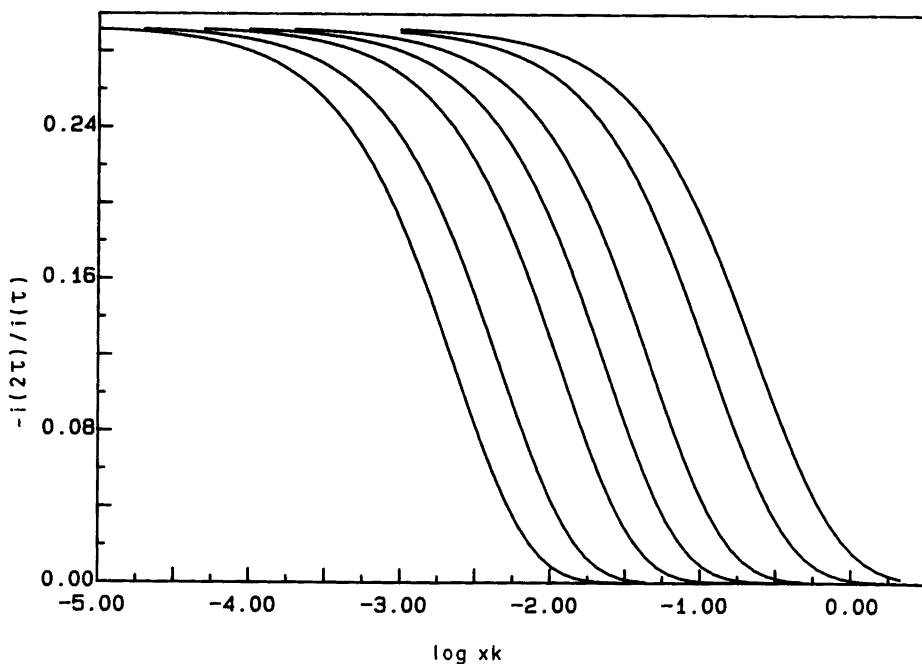


Fig. 3. The dependence of the current ratio $-i(2\tau)/i(\tau)$ on $\log k_1 c_a^0$ for $q = k_3/(k_2+k_3) = 0.5$ and different values of c_c^0/c_a^0 . The curves are simulated for the following values of c_c^0/c_a^0 (from right to left): 1.0, 2.0, 5.0, 10.0, 20.0, 50.0 and 100.0.

Table 2. The coefficients $C_{0.5}$ for the DPSC-2 method.

	q					
	0.0	0.2	0.4	0.6	0.8	1.0
$C_{0.5}$	0.179	0.174	0.169	0.164	0.160	0.156

sionless current ratios, $r = i_{p,a}/i_{p,c}$, and the competition parameter, q :

$$\log(xk) = C_6r^6 + C_5r^5 + C_4r^4 + C_3r^3 + C_2r^2 + C_1r + C_0 + C_q(q-0.5)$$

If q can be determined with an accuracy of ± 0.1 , then the accuracy in the rate constant k_1 is better than 5%. The rate constant is given by:

$$k_1 = \left(\frac{F}{RT}\right) \left(\frac{xk \cdot v}{c_A^0}\right)$$

The DPSC experiments were simulated with the assumption that the reduction of A is diffusion controlled during the first potential step ($c_{,x=0} = 0$) and that the oxidation of B is diffusion controlled during the second potential step ($c_{B,x=0} = 0$). This is the case when the potential is stepped 300 mV more negative and 300 mV more positive than $E_{\lambda B}^0$, respectively.

Method DPSC-1. In Fig. 3, the ratio $-i(2\tau)/i(\tau)$ is plotted versus $\log(xk)$ for q equal to 0.5 for several values of c_C^0/c_A^0 . The kinetic parameter is given here by:

$$xk = k_1 c_A^0 \tau$$

Simulations showed that the curves depend only very little on q . If a deviation of $\pm 8\%$ is acceptable, the curves for q equal to 0.5 can be used in all cases. When xk has been determined from the curves, the rate constant k_1 can be calculated according to:

$$k_1 = xk/(c_A^0 \tau)$$

Method DPSC-2. The fourth and last method for determining the rate constant is to use the approach of Bard *et al.*,¹⁷ where the pulse time, τ , is

varied experimentally until the normalized current ratio, $-i(2\tau)/[i(\tau) 0.2928]$, is equal to 0.5 for $c_C^0/c_A^0 > 10$. The coefficient $C_{0.5}$ is calculated for q equal to 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, and is given in Table 2. The rate constant is then given by:

$$k_1 = 0.5/(c_C^0 \tau)$$

Experimentally, we have studied the electron transfer reaction in dry media between anthracene/*sec*-butyl bromide, methyl benzoate/*n*-butyl bromide and perylene/benzyl chloride. The experimental curves of $\log i_k/i_R$ vs. $-\log v$ (Figs. 1a-e) have been shifted along the x -axis until the simulated and experimental curves match. The shift value, $k_{\text{shift}} = \log xk + \log v = \log k_1 c_A^0 RT/F$, is readily used to calculate k_1 . It is also possible to determine the respective competition parameters for the three mediator/acceptor systems by comparing the experimental curves with the simulated, and it is found that anthracene/*sec*-butyl bromide is non-catalytic with $q = 0.0$, whereas perylene/benzyl chloride is totally catalytic with $q = 1.0$. Methyl benzoate/*n*-butyl bromide is only partly catalytic with $q = 0.2$.

We have measured the rate constant k_1 by the three different experimental techniques and the results are given in Tables 3-5.

Conclusion

The measured competition parameters for the three investigated systems are in accordance with previous reported values for SET reactions between aromatic mediators and alkyl or aryl halides.

The simulations can only be said to describe the experiments acceptably if the calculated rate constant, k_1 , is found to be constant after changing the scan rate, the pulse time or c_A^0/c_A^0 . All the cases dealt with here give quite constant values of

Table 3. Rate constants calculated from simulated data for electron transfer from anthracene to *sec*-butyl bromide in 0.1 M TBABF₄/DMF at 25 °C.

Method LSV ($q = 0.0$)

c_A^0/mM	c_D^0/c_A^0	v/Vs^{-1}	i_k/i_R	k_{shift}	$k_1/10^3\text{M}^{-1}$
1.98	2.0	0.050	1.75		
1.98	2.0	0.200	1.49		
1.98	2.0	0.497	1.29	-1.05	1.75
1.98	2.0	0.996	1.17		
1.60	50	0.497	1.87		
1.60	50	1.99	1.69		
1.60	50	4.98	1.51	-1.05	2.17
1.60	50	19.8	1.23		

Method CV ($q = 0.0$)

c_A^0/mM	c_D^0/c_A^0	v/Vs^{-1}	$-i_{p,a}/i_{p,c}$	$k_1/10^3\text{M}^{-1}$	$\langle k_1 \rangle / 10^3\text{M}^{-1}\text{s}^{-1}$
1.98	2.0	1.99	0.170	1.98	
1.98	2.0	2.98	0.262	1.88	1.91(0.04)
1.98	2.0	3.98	0.322	1.98	
1.95	5.0	4.97	0.149	2.01	
1.95	5.0	7.95	0.237	2.14	2.09(0.06)
1.95	5.0	10.94	0.313	2.11	
1.90	10.0	10.94	0.163	2.06	
1.90	10.0	16.80	0.261	2.04	2.06(0.02)
1.90	10.0	22.8	0.327	2.08	
1.60	50	59.4	0.189	2.31	
1.60	50	79.4	0.244	2.42	2.43(0.13)
1.60	50	119.0	0.326	2.55	

Method DPSC-1 ($q = 0.0$)

c_A^0/mM	c_D^0/c_A^0	τ/ms	$-i(2\tau)/i(\tau)$	$\langle k_1 \rangle / 10^3\text{M}^{-1}\text{s}^{-1}$
1.98	2.0	20.0	0.143	
1.98	2.0	18.4	0.148	2.49(0.08)
1.98	2.0	16.0	0.152	
1.95	5.0	10.3	0.120	
1.95	5.0	7.37	0.149	2.35(0.09)
1.95	5.0	6.03	0.170	
1.90	10.0	5.00	0.131	
1.90	10.0	3.99	0.148	2.31(0.10)
1.90	10.0	2.99	0.170	

k_1 . Another check of the simulations is to compare the results obtained with different electrochemical techniques. Also here the results are concordant.

The experiments show that the competition factor q , as well as the absolute value of the rate constant for the first SET reaction, can be determined by use of LSV, CV or DPSC. While the

Table 4. Rate constants calculated from simulated data for electron transfer from methyl benzoate to *n*-butyl bromide in 0.1 M TBABF₄/DMF at 25 °C.
Method LSV ($q = 0.2$)

Method LSV ($q = 0.2$)					
c_A^0/mM	c_C^0/c_A^0	v/Vs^{-1}	i_k/i_R	K_{shift}	$k_1/\text{M}^{-1}\text{s}^{-1}$
2.0	50.0	0.05	1.95		
2.0	50.0	0.10	1.72		
2.0	50.0	0.25	1.40	-2.76	33.8
2.0	50.0	0.50	1.23		
1.96	100.0	0.05	2.15		
1.96	100.0	0.10	1.95		
1.96	100.0	0.25	1.59	-2.78	33.0
1.96	100.0	0.50	1.37		
1.96	100.0	1.00	1.22		

Method CV						
c_A^0/mM	c_C^0/c_A^0	v/Vs^{-1}	$-i_{p,a}/i_{p,c}$	$k/\text{M}^{-1}\text{s}^{-1}$		
				$q = 0.1$	$q = 0.2$	$q = 0.3$
2.0	50	1.0	0.113	45.7	46.9	48.1
2.0	50	1.5	0.207	44.0	45.1	46.2
2.0	50	2.0	0.271	44.8	46.0	47.1
2.0	50	3.0	0.357	46.9	48.0	49.2
1.96	100	2.0	0.142	40.0	41.0	42.0
1.96	100	2.5	0.196	39.3	40.2	41.2
1.96	100	3.0	0.237	39.3	40.3	41.3
1.96	100	4.0	0.300	40.5	41.5	42.5

Table 5. Rate constants calculated from simulated data for electron transfer from perylene to benzyl chloride in 0.1 M TBABF₄/DMF at 25 °C.
Method LSV ($q = 1.0$)

c_A^0/mM	c_C^0/c_A^0	v/Vs^{-1}	i_k/i_R	K_{shift}	$k_1/\text{M}^{-1}\text{s}^{-1}$
2.0	10.0	0.05	7.90		
2.0	10.0	0.10	5.79		
2.0	10.0	0.25	3.84		
2.0	10.0	0.50	2.78	-1.36	830
2.0	10.0	1.00	2.03		
2.0	10.0	1.99	1.51		
2.0	10.0	4.98	1.20		
1.98	50.0	0.05	18.7		
1.98	50.0	0.10	13.3		
1.98	50.0	0.25	8.64		
1.98	50.0	0.50	6.25	-1.37	839
1.98	50.0	1.00	4.52		
1.98	50.0	1.99	3.25		
1.98	50.0	4.98	2.09		
1.98	50.0	9.94	1.52		

LSV method is indirect and is better the faster reactions are (or the slower the scan rate), the other methods are direct methods where a certain degree of reversibility has to be reached.

The direct methods are generally preferable, but they cannot be used in the measurement of the competition parameter because the working curves are nearly independent of q . In LSV, where the time-window is different, the chemical reactions are allowed to run further and the difference in catalytic efficiency becomes much clearer.

In LSV experiments, the competition parameter can be measured with an accuracy of ± 0.1 if reaction (1) is reasonably fast and/or very slow scan rates can be used.

If the competition parameter is unknown, the rate constant k_1 can be estimated by CV and DPSC. The CV experiments are more dependent on the q factor than the DPSC experiments. The CV experiments have a q -dependence on k_1 up to 65%, but typically 15%, and the DPSC experiments 8%.

When the competition parameter is known, all the reversal techniques can be used; however, the CV and DPSC-2 approaches are very convenient because no fitting to working curves is necessary. Especially the polynomial data presentation is convenient when combined with computerized data acquisition systems. LSV should not be used for rate constant measurements for non-catalytic systems ($q = 0.0$) unless reversible voltammograms cannot be measured at reasonable scan rates. In the non-catalytic case the experimental parameter i_k/i_R only changes from 1.00 to 2.22, which makes the matching procedure more difficult.

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