Electrochemical Methods for Determination of Rate Constants. III. Homogeneous Electron Transfer Followed by Elimination Induced by the Substrate Anion

Norberto Gatti, Steen Uttrup Pedersen and Henning Lund

Department of Organic Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

The indirect elecrochemical reduction of 1-bromo-1,2-diphenylethene yields a mixture of 50 % stilbene and 50 % diphenylacetylene, the latter being formed by an elimination induced by the electrogenerated vinyl anion. The kinetic equations for single electron transfer (SET) followed by an elimination reaction between the reduced form of the substrate and the substrate have been solved by digital simulation for linear sweep voltammetry (LSV) and cyclic voltammetry (CV). The rate constant for the SET reaction has been determined for the indirect reduction of E and Z 1-bromo-1,2-diphenylethene by a number of mediators. The rate constant of the elimination step has also been estimated.

The indirect reduction of alkyl halides,[1] benzyl halides[2] and vicinal dihalides[3] by organic mediators, aromatic or heteroaromatic systems has been treated in several publications recently. The first step in the indirect reductions or oxidations is the single electron transfer (SET) between the mediator (Ar) and the substrate (RX).

Several mechanisms with different follow-up reactions have been analysed (Ref. 4 and references therein). Recently, the case where the SET step is followed by a coupling reaction competing with another electron transfer reaction has been analysed.[5] In some cases the mediator acts solely as an electron-carrier, while in other reactions the mediator also forms a chemical bond to the substrate. The first kind of system the process is a purely catalytic reduction of RX, as the mediator is completely regenerated. The catalytic efficiency (i_k/i_R) is taken as the ratio between the peak currents measured in LSV in a mixture of mediator and substrate (i_k) and the peak current for the mediator alone (i_R).

When the scan rates are low compared to the rate of the catalytic reaction then the catalytic efficiency is limited to a plateau value, which for the catalytic case is dependent on the substrate concentration. In the second kind of system (non-catalytic) the "catalytic efficiency" is also limited and is a function of the mediator concentration.

It was recently found[6] that the indirect reduction of vinyl halides having a β-hydrogen was complicated by elimination of HX, induced by the substrate anion, from the substrate.

This paper discusses the measurement of rate constants for the SET reaction between the mediator and substrate in the cases where such an elimination takes place. An estimation of the rate of the elimination reaction between substrate and substrate anion is also attempted.

Methods using data from LSV and CV are discussed. The LSV technique is the method of choice for these kinds of systems because the mechanism here is catalytic, so that the increase in the catalytic efficiency (i_k/i_R) will be substantial. In cases where the mediator couples with a reduced form of the substrate,[4] the peak height can only increase from 1 to 2.22, which is the same as going from a reversible one-electron reduction to a two-electron irreversible reduction of the mediator.

CV is not appropriate if the potential for the direct reduction of the substrate is too close to the reduction potential of the mediator. This is the case for compounds **1** and **2**.
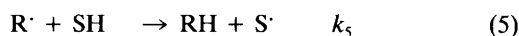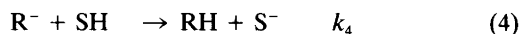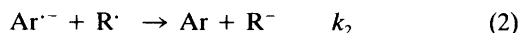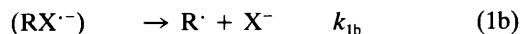
$$R^1 \qquad R^2$$
$$C=C$$
$$X \qquad R^3$$
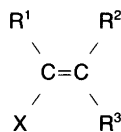
1: $R^1 = C_6H_5$, $R^2 = C_6H_5$, $R^3 = H$, $X = Br$

2: $R^1 = C_6H_5$, $R^2 = H$, $R^3 = C_6H_5$, $X = Br$

3: $R^1 = C_6H_5$, $R^2 = C_6H_5$, $R^3 = C_6H_5$, $X = Br$

4: $R^1 = NO_2$, $R^2 = H$, $R^3 = C_6H_5$, $X = Br$

5: $R^1 = C_6H_5$, $R^2 = C_6H_5$, $R^3 = H$, $X = H$

6: $R^1 = C_6H_5$, $R^2 = H$, $R^3 = C_6H_5$, $X = H$

Kinetic description

Recent results from preparative reduction of **1** in aprotic media showed that equal amounts of *trans*-stilbene (**6**) and diphenylacetylene (**7**) were formed. The product distribution seems to be due to a base-catalyzed step involving the substrate and probably the substrate anion (Scheme 1).

Formation of a small amount of *cis*-stilbene (**5**) (3–4%) was also observed in the preparative reduction of **1** and **2**; the ratio of *cis*- to *trans*-stilbene was independent of whether **1** or **2** were the substrate. This indicates that either the intermediate radical R· or the anion R⁻ can isomerize.

The indirect reduction followed by an elimination reaction is adequately described by eqns. (1)–(5), in which Ar/Ar·⁻ is the mediator and RX is **1** or **2**.

$$Ar + e \quad \rightleftharpoons Ar^{\cdot-}$$

$$Ar^{\cdot-} + RX \rightleftharpoons Ar + (RX^{\cdot-}) \quad k_1/k_{-1} \qquad (1)$$

$$(RX^{\cdot-}) \quad \rightarrow R^\cdot + X^- \qquad k_{1b} \qquad (1b)$$

$$Ar^{\cdot-} + R^\cdot \rightarrow Ar + R^- \qquad k_2 \qquad (2)$$

$$R^- + RX \rightarrow products \qquad k_3 \qquad (3)$$

$$R^- + SH \rightarrow RH + S^- \qquad k_4 \qquad (4)$$

$$R^\cdot + SH \rightarrow RH + S^\cdot \qquad k_5 \qquad (5)$$
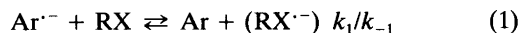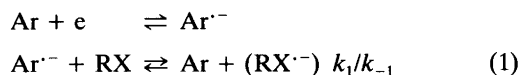
CV of **1** at scan rates up to 1000 V s⁻¹ did not show any sign of reversibility. Even 2-bromo-1,1,2-triphenylethene (**3**) did not exhibit reversibility. Reduction of 2-bromo-2-nitrostyrene (**4**) becomes reversible at a scan rate of approximately 100 V s⁻¹, but this compound is reduced at a potential 0.8 V more positive than that of **1**. It can thus be anticipated that the rate of dissociation of the anion radicals of **1** and **2** is much faster than that of **4**.

In Table 1 are collected rate constants measured by LSV at different concentrations, but using a constant ratio between concentrations of substrate and mediator. If the back-reaction (k_{-1}) played a role in the mechanism then the calculated values for the rate constants should be a function of the concentration of the mediator at constant excess $([RX]/[A])$.[7] When the dissociation reaction (eqn. 1b) is much faster than the back reaction (eqn. 1), i.e.:

$$k_{1b} \gg k_{-1}[Ar] \gg k_1[Ar] \qquad (6)$$

the back reaction will play no role in the kinetics and the values obtained for rate constants will not be dependent on the concentration of the mediator.

The dissociation (eqn. 1b) and the second SET reaction (eqn. 2) are assumed to be much faster than the first SET reaction (eqn. 1). The elimination step (eqn. 3) cannot, however, generally be assumed to be much faster than reaction (1), and this makes it necessary to work with two kinetic variables, k_1 and k_3, in the digital simulations. When $k_3 \leq 100 \, k_1$, the steady state approximation applies only to $(RX^{\cdot-})$ and R· [eqn. (7)], and when $k_3 \geq 100 \, k_1$ the steady-state ap-

$$k_1[Ar^{\cdot-}][RX] = k_{1b}[(RX^{\cdot-})][A] = k_2[Ar^{\cdot-}][R^\cdot] \quad (7)$$

Scheme 1.

12
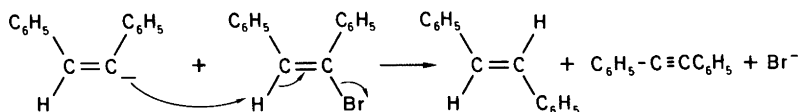
Table 1. Dependence of k_1 on mediator concentration (c_A°) at constant excess (c_C°/c_A°); c_A° is the concentration of the mediator, 2-benzoylpyridine, and c_C° is the concentration of the substrate, 1.
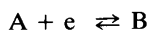
c_C°/c_A°	c_A°/mM	$k_1/10^{-3} M^{-1} s^{-1}$
2	0.493	2.80
2	0.971	2.25
2	2.326	2.08
2	4.721	2.07

proximation applies for $RX^{\cdot-}$, $R^\cdot$ and R^- [eqn. (8)]. It is furthermore assumed that the hetero-

$$k_1[Ar^{\cdot-}][RX] = k_{1b}[(RX^{\cdot-})][A] = k_2[Ar^{\cdot-}][R^\cdot]$$
$$= k_3[R^-][RX] \qquad (8)$$

geneous electron transfer $Ar/Ar^{\cdot-}$ is fast and thus governed by Nernst's law.

The mechanistic scheme can now be simplified, as shown in eqns. (9)–(11), and we can describe

$$A + e \rightleftarrows B$$

$$B + C \rightarrow A + D \quad k_1 \qquad (9)$$

$$B + D \rightarrow A + E \quad k_2 \qquad (10)$$

$$E + C \rightarrow products \ k_3 \qquad (11)$$
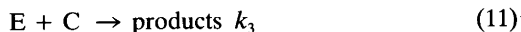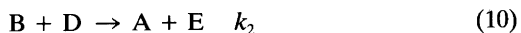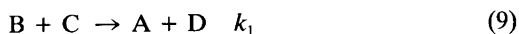
the scheme mathematically by the differential eqns. (12)–(16) shown below. D (diffusion coefficient) is assumed equal for species A–E.

$$dc_A/dt = Dd^2c_A/dx^2 + k_1c_Bc_C + k_2c_Bc_D \qquad (12)$$

$$dc_B/dt = Dd^2c_B/dx^2 - k_1c_Bc_C - k_2c_Bc_D \qquad (13)$$

$$dc_C/dt = Dd^2c_C/dx^2 - k_1c_Bc_C - k_3c_Ec_C \qquad (14)$$

$$dc_D/dt = Dd^2c_D/dx^2 + k_1c_Bc_C + k_2c_Bc_D \qquad (15)$$

$$dc_E/dt = Dd^2c_E/dx^2 + k_2c_Bc_D + k_3c_Ec_C \qquad (16)$$

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

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

$x = 0, t \geq 0$:

$$c_A/c_B = \exp(F/RT(E - E_{A/B}^\circ))$$

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

The steady-state approximation for D results in the equality:

$$k_1c_Bc_C = k_2c_Bc_D \qquad (17)$$

whereas the steady-state approximation for E gives the equality:

$$k_2c_Bc_D = k_3c_Ec_D \qquad (18)$$

The following dimensionless parameters are introduced:

$$a = c_A/c_A^\circ, \ b = c_B/c_A^\circ, \ c = c_C/c_A^\circ, \ c^\circ = c_C^\circ/c_A^\circ,$$

$$d = c_D/c_A^\circ, \ e = c_E/c_A^\circ, \ q = k_3/k_1$$

$$\Theta = \left(\frac{F}{RT}\right)t, \ \zeta = -\frac{F}{RT}(E - E_{A/B}^\circ)$$

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

where v is the scan rate (V s^{-1}).

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

$$da/d\theta = d^2a/dy^2 + 2\lambda_1bc \qquad (19)$$

$$db/d\theta = d^2b/dy^2 - 2\lambda_1bc \qquad (20)$$

$$dc/d\theta = d^2c/dy^2 - \lambda_1bc - q\lambda_1ec \qquad (21)$$

$$de/d\theta = d^2e/dy^2 + \lambda_1bc - q\lambda_1ec \qquad (22)$$

and if steady-state also applies for E, eqns. (21) and (22) are replaced by

$$dc/d\theta = d^2c/dy^2 - 2\lambda_1bc \qquad (23)$$

$$de/d\theta = d^2e/dy^2 \qquad (24)$$

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

$$a = 1, b = 0, c = c^\circ, e = 0$$

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

$$a/b = \exp(-\zeta);$$

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

Results

The explicit point method,[8,9] which is described in detail by Britz,[10] has been used in the digital

simulations. The stability factor $D\Delta t(\Delta x)^{-2}$ was kept equal to 0.45 in all cases. The integration of the kinetics for $q = k_3/k_1 = \infty$ was performed by a 4th-order classical Runge-Kutta method[11] (for application of the Runge-Kutta method in electrochemistry see Refs. 12 and 13).

In all the simulations a 6-point approximation to the flux near the electrode surface was applied [(eqn. (25)]:[4]

$$(da/dx)_{x=0} = (-137a_1 + 300(a_2 - a_3)$$
$$+ 200a_4 - 75a_5 + 112a_6)/60dx \qquad (25)$$

The LSV experiments were simulated from $E_{A/B}^\circ$ + 100 mV to the peak value, whereas the CV experiments were simulated from $E_{A/B}^\circ$ + 200 mV to $E_{A/B}^\circ$ − 200 mV. Previously reported results had shown that the absolute peak-current ratio is not very sensitive to moderate changes (+/− 10 mV) in the switch potential.

The number of time-steps in both LSV and in CV were calculated by the algorithm in eqn. (26):

$$nt = int\ 2^{[5 + \log(c_C^\circ xk/5)]}\ (E_{switch} - E_{start}) \qquad (26)$$

LSV simulation. This method always requires two separate measurements of the peak current. The first measurement is made with only the mediator in the solution (i_R), and the second is made with the mixture of mediator and substrate (i_k). The i_R is measured at 4–5 different scan-rates covering the used range.

The function $i_R/\sqrt{v}$ can then be found by linear regression and the slope can be used to find $i_R(v)$. When $i_k(v)$ is measured, the $i_k/i_R(v)$ can readily be calculated.

In Figs. 1a–g, i_k/i_R is plotted vs. log (xk) for several values of q and c_C°/c_A°. The q-values are equal to k_3/k_1 and the kinetic parameter is given by eqn. (27). The case with q equal to zero has already been treated in Ref. 5.

$$xk = \frac{RT}{F}\ \frac{k_1 c_A^\circ}{v} \qquad (27)$$

$$(k_1/M^{-1}\ s^{-1};\ c_A^\circ/M;\ T/^\circ K) \qquad (28)$$

CV simulation. It was found previously that absolute current ratios at constant $E_{switch} - E_{A/B}^\circ$ could

be used to measure the rate constant for the SET reaction in CV. As previously, the interval 0.10 $\leq -i_{p,a}/i_{p,c} \leq 0.36$ has been used and the function log(xk) versus $i_{p,a}/i_{p,c}$ has been fitted by a 6th-order polynomial. The coefficients to the polynomials at different c_C°/c_A° and q values are given in Table 2. Experimentally, the xk value is found from the absolute current ratio, r $= i_{p,a}/i_{p,c}$ [eqn. (29)]. The rate constant k_1 can then be found from the xk value and the experimentally known parameters by using eqn. (30):

$$\log\ (xk) = C_6 r^6 + C_5 r^5 + C_4 r^4 + C_3 r^3$$
$$+ C_2 r^2 + C_1 r + C_0 \qquad (29)$$

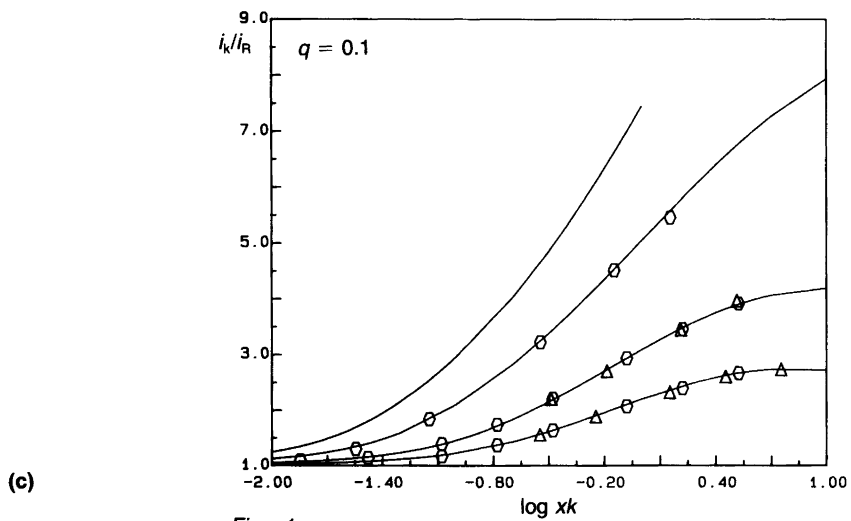$$k_1 = \frac{F}{RT}\ \frac{xk v}{c_A^\circ}\ M^{-1}\ s^{-1} \qquad (30)$$

Results for **1** *and* **2**. We have studied experimentally the indirect reduction followed by elimination for *E*- (**2**) and *Z*-1-bromo-1,2-diphenylethene (**1**). A range of compounds with different $E_{A/B}^\circ$ have been used as mediators.

In the previous investigations CV has been the favoured technique rather than LSV. However, the foot of the direct reduction wave for **1** and **2** is less than 200 mV cathodic to the chosen mediators; this is clearly unacceptable, as demonstrated by preliminary results. When mediators with less negative redox potential were chosen, the SET reaction was too slow; this is a consequence of the relatively small solvent and reorganization energy, λ, of vinyl halides.[6] These problems are not unique to CV, but are to be expected in all reversal techniques. LSV yields acceptable rate constants because of the substantial increase in the cathodic peak current due to the catalytic effect observed when **1** or **2** are added to the mediator; the ratio i_k/i_R is not seriously influenced by the direct reduction current for **1** or **2**.

In Figs. 1a–g the experimental points are plotted together with the relevant simulated curves. From the shift-values:

$$(\log xk + \log v) = \log k_1 + 1.59 - \log c_A^\circ \qquad (31)$$

the rate constant k_1 is found and by curve-fitting the q value and thus the rate constant for elimination can be estimated. The results are given in Table 3.

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(a)

i_k/i_R $q = 0.001$

log xk

(b)

i_k/i_R $q = 0.01$

log xk

(c)

i_k/i_R $q = 0.1$

log xk

Figs. 1a–c.

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(d)

(e)

(f)

Figs. 1d–f.

(g)

Fig. 1g.
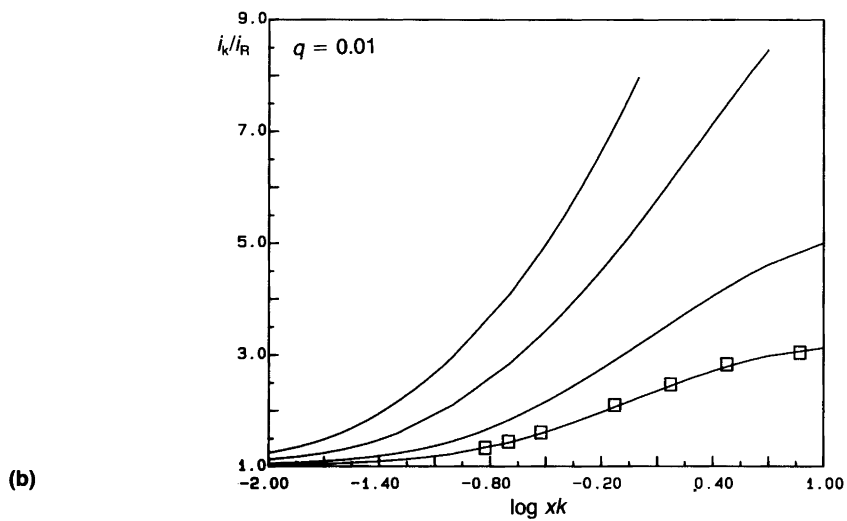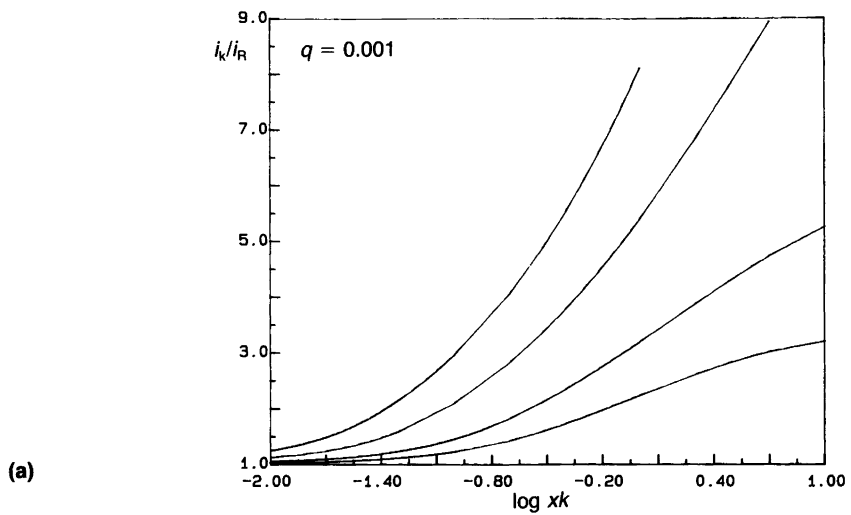
Figs. 1a–1g. The dependence of the current ratio i_k/i_R on
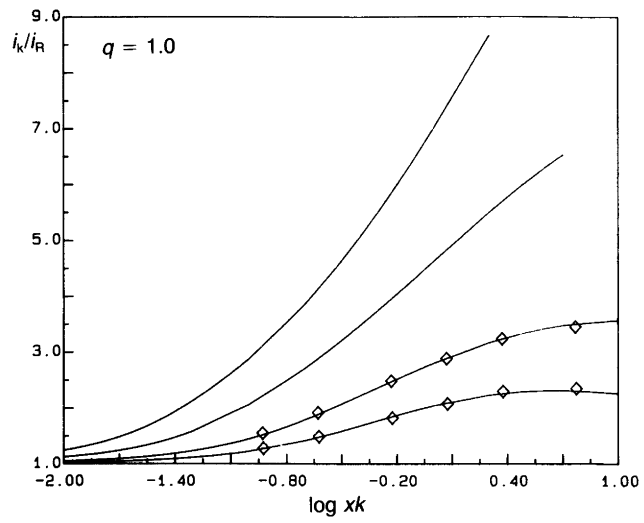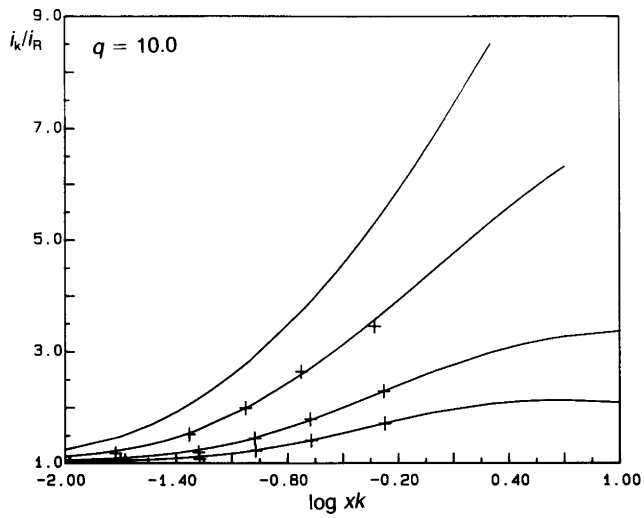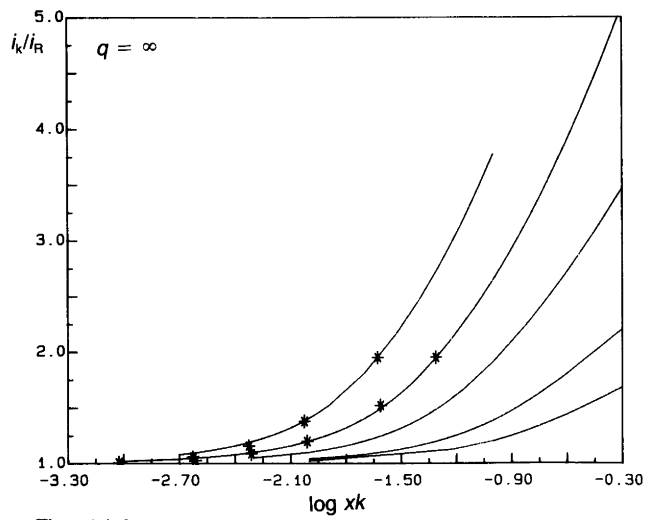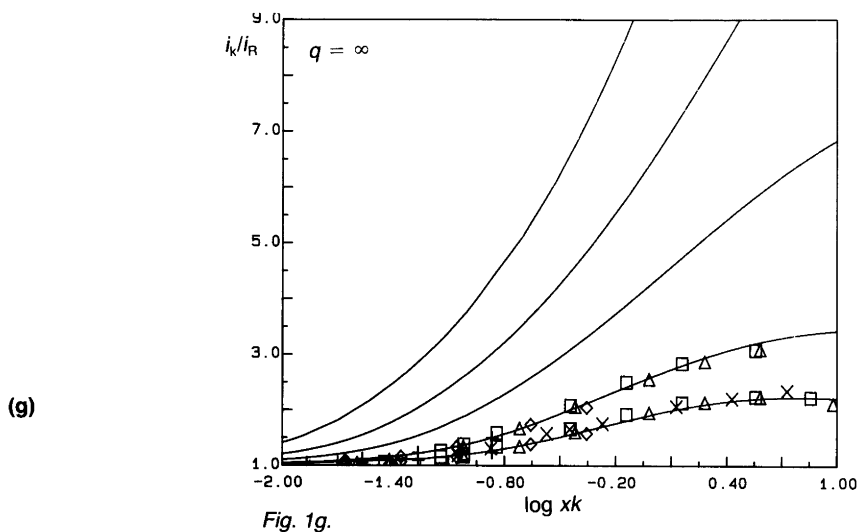
$$\log\left(\frac{RT}{F}\,\frac{k_1\,c_A^o}{v}\right)$$

for different values of k_3/k_1. All figures are plotted for c_C^o/c_A^o equal to 1.0, 2.0, 5.0 and 10.0, but Figs. 1f and 1g include also c_C^o/c_A^o equal to 20 (the lowest curve is always $c_C^o/c_A^o = 1.0$). The experimental use of the simulated curves is illustrated by plotting experimental points: The points are marked by □ for perylene, △ for dimethyl terephthalate, ◯ for 3-benzoylpyridine, ◇ for 2-benzoylpyridine, + for 2,4'-dimethoxyazobenzene, × for benzophenone, and finally ✳ for 2-methoxyazobenzene. The substrate **1** has been used in all experimental points on Figs. 1a–1f, whereas substrate **2** is used in Fig. 1g.

Preparative experiments have been carried out by mediated and direct electrolysis of **1** and **2** under aprotic conditions and in the presence of proton donors such as phenol. The results are provided in Table 4.

A possible isomerization of the starting material during the reduction was checked by reducing **1** under aprotic conditions and stopping after one-third of the calculated amount of charge had passed. The presence of **2** could not be detected. Similarly an isomerization of the product **6** was checked by reduction of dimethyl phthalate in the presence of **6**, and no **5** could be detected.

The preparative electrolysis performed under aprotic conditions showed that both the direct and mediated reductions of **1** or **2** gave approximately the same product distribution, i.e. **7** (50 %), **5** (47 %) and **6** (3 %).

In the presence of a proton donor such as phenol the direct protonation of the substrate anion competes with the elimination reaction. We find find that starting from **1** or **2** the percentage of **7**

is decreased and more stilbene (**5** + **6**) is produced in both cases.

Discussion

Experiments showed that the rate of the SET reaction between the mediator and the arylvinyl bromides could be measured by LSV. The SET reaction between a mediator and **2** is generally 3–4 times slower than for **1** and the same mediator. The difference is probably due to a difference in standard potentials for **1** and **2**. From the Arrhenius equation the difference can be estimated as:

$$E_1^o - E_2^o = 28\text{–}36 \text{ mV}$$

A Marcus plot is presented in Fig. 2. The reorganisation energy, λ, for the SET reaction is found to be 17.6 kcal mol^{-1} for **1** and 14.6 kcal mol^{-1} for **2**, which is close to those for other vinyl bromides[6] and aryl halides.[4,14]

2*

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Table 2. The coefficients for the 6th-order polynomial fit for CV.

c_C^0/c_A^0	log	c_0	c_1	c_2	c_3	c_4	c_5	c_6
1	-4	0	-14.88	-191.4	-1053	-3000	-4360	-2564
	-3	0	-19.50	-285.0	-1773	-5682	-9220	-6017
	-2	0	-19.73	-286.9	-1775	-5646	-9097	-5896
	-1	0	-152.3	-3198	-26460	-106800	-210200	-161600
	0	0	-571.8	-1.0260	-73260	-259200	-454300	-315500
	∞	0	-747.0	-11920	-76450	-245700	-395100	-254100
2	-3	0	5.194	-78.92	-537.5	-1929	-3541	-2622
	-2	0	-5.250	-79.95	-545.1	-1957	-3593	-2659
	-1	0	-5.502	-83.54	-565.0	-2008	-3648	-2673
	0	0	-10.22	-174.2	-1272	-4765	-8987	-6764
	∞	0	-19.27	-347.5	-2643	-10240	-19910	-15410
5	-3	0	-1.741	-27.79	-202.3	-780.5	-1542	-1228
	-2	0	-1.741	-27.81	-202.5	-781.5	-1544	-1229
	-1	0	-1.757	-27.92	-202.1	-774.5	-1520	-1203
	0	0	-2.087	-34.83	-261.4	-1030	-2066	-1662
	$+1$	0	-2.049	-32.74	-235.4	-891.8	-1724	-1340
	∞	0	-2.358	-37.01	-262.4	984.3	-1892	-1469
10	-3	0	-0.7834	-12.28	-88.40	-338.8	-667.1	-530.8
	-2	0	-0.7860	-12.33	-88.82	-340.2	-669.3	-531.8
	-1	0	0.7900	-12.38	-89.09	-340.9	-669.7	-531.4
	0	0	0.7986	-12.35	-87.50	-330.0	-639.7	-501.7
	∞	0	-2.358	-37.01	-262.4	-984.3	-1892	-1469
20	-3	0	-0.3657	-5.616	-39.78	-150.5	-293.2	-231.3
	-2	0	-0.3665	-5.639	-40.02	-151.7	-296.4	-234.5
	-1	0	-0.3628	-5.530	-38.86	-146.0	-282.6	-221.8
	0	0	-0.3699	-5.653	-39.78	-149.5	-289.5	-227.2
	$+1$	0	-0.3947	-6.219	-44.99	-173.1	-342.2	-273.1
	∞	0	-0.4587	-7.074	-50.01	-188.0	-362.7	-282.7

Table 3. Measured rate constants for different combinations of mediator and substrates.

Mediator	$-E_p{}^a$/mV	Substrate	$c_A^0/10^{-3}$ mM	Excess[b]	k_1/M^{-1} s^{-1}	q^c	k_3/M^{-1}
2-Methoxyazobenzene	898	1	1.90	10, 20	1.0×10^1	∞	
2,4'-Dimethoxyazobenzene	991	1	1.93	1, 2	2.1×10^2	10	2100
2-Benzoylpyridine	1095	1	1.93	1, 2	2.3×10^3	1	2300
3-Benzoylpyridine	1167	1	1.90	1, 2	3.3×10^4	0.1	3300
Dimethyl terephthalate	1191	1	1.93	1, 2	6.0×10^4	0.1	2900
Perylene	1213	1	1.96	1	2.9×10^5	0.01	2900
2,4'-Dimethoxyazobenzene	991	2	1.92	1, 2, 5	5.5×10^1	∞	—
2-Benzoylpyridine	1095	2	1.95	1, 2	8.8×10^2	∞	—
Dimethyl terephthale	1191	2	1.95	1, 2	3.8×10^4	∞	—
Perylene	1213	2	1.94	1, 2	1.4×10^5	∞	—
Benzophenone	1320	2	0.98	1	1.1×10^6	∞	—

[a]Peak potential for mediator measured in mV vs. Ag/AgI. [b]Excess defined as substrate concentration divided by mediator concentration. [c]q is equal to k_3/k_1. q is set to infinity when higher than 10.
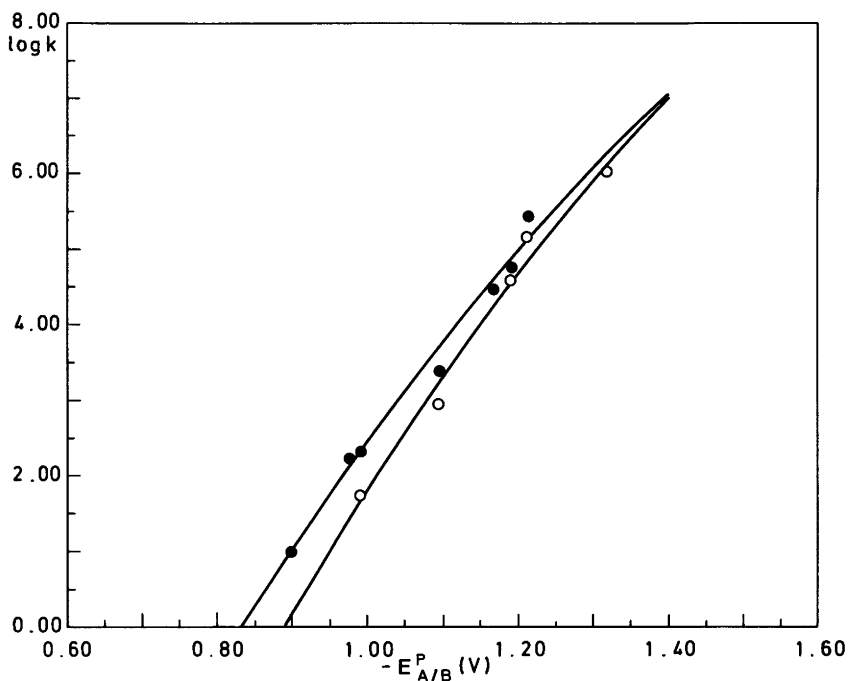
Fig. 2. Dependence of rate constants (k_1) for the SET reaction between different anion radicals A⁻ and **1** (●) and **2** (○) on the redox potential ($-E_p$) of the A compound. The plots are based on the results presented in Table 3.

The magnitude of the rate constant for the elimination reaction between the substrate and the substrate anion could also be estimated for **1** and **2**. The elimination reaction rate constant for **1** is found to be about 3000 M⁻¹ s⁻¹, and for **2** it is at least 1000 times greater. This might be expected because of the favourable stereochemistry in **2**, with H being *trans* to Br. The estimated values may be in error by a factor of 3, so when this is taken into account the rate constant (k_3) shown in Table 3 is found to be independent of the choice of mediator.

One would expect that the elimination reaction of **2**, which was found by LSV to be at least 1000 times faster than that of **1**, was able to compete more successfully with the direct protonation and would result in a higher percentage of **7** than when starting from **1**.

It can be seen from Table 4 that **2** gives more elimination product (**7**) than **1** at the same concentration of phenol, indicating a faster elimination reaction for the former; however, the dif-

ference seems to be much smaller than expected from the LSV data.

Experiments with tetrabutylammonium phenolate induced elimination of **1** resulted in formation of **7**. Phenolate is known to be a quite weak base, so that **1** must be more acidic than expected for a vinyl system.

In the simulated reaction scheme the substrate anion is assumed to react directly with the substrate:

$$R^- + RX \rightarrow products \tag{32}$$

The substrate anion might be so strong a base that the protonation step becomes unselective and the substrate anion reacts with the solvent; the deprotonated solvent molecules then induce the elimination of the substrate:

$$R^- + SH \rightarrow RH + S^- \tag{33}$$

$$S- + RX \rightarrow 7 + SH \tag{34}$$

Table 4. Product distribution in the direct and indirect reduction of E-(1) and Z-(2)-1-bromo-1,2-diphenylethene. Reaction conditions: divided cell, Hg pool cathode, C anode; solvent DMF with 0.1 M $TBABF_4$ as supporting electrolyte, 25 °C.
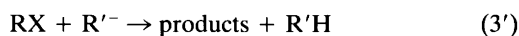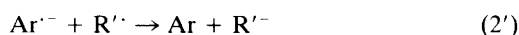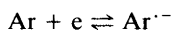
Entry	Starting material	Electrolysis	Equiv. PhOH added	5/%	6/%	7/%
1	1	Indir.	0	3.2	47.7	49.1
2	2	Indir.	0	4.9	43.3	51.8
3	2	Dir.	0	2.2	47.7	50.1
4	(75 % 1, 25 % 2)	Dir.	0	2.0	47.0	51.0
5	1	Indir.	2	13.6	80.8	5.6
6	1	Indir.	20	24.8	74.3	0.9
7	2	Indir.	2	10.5	67.4	22.1
8	2	Indir.	25	21.4	77.6	1.0
9	2	Dir.	2	6.8	74.1	19.1

An *a priori* explanation for the results in Table 4 could be either that the bulk of the starting material **1** isomerizes under the electrolysis or that the product **6** isomerizes to the more stable **5**; this was not observed, however.

The isomerization of vinyl halides has been discussed previously.[15-18] Fry *et al.*[15] found that *cis*- and *trans*-3-iodo-3-hexene isomerize at some stage during reduction in DMF. Addition of phenol did not change the isomer ratio of the product. The latter result was used to rule out the isomerization of the vinyl anion and the conclusion was that the isomerization took place in the vinyl radical.

Curtin *et al.*[16-18] have found that arylvinyllithium compounds isomerize more readily than alkylvinyllithium compounds and that the rate of the isomerization depends on the polarity of the solvent, with the highest rate in the most polar solvent. Curtin concluded that the isomerization of arylvinyllithium compounds occurs by ionization of the carbon–lithium bond, and that the resulting arylvinyl anion isomerizes through a linear transition state or intermediate in which the charge is highly delocalized into the aromatic system.

If the substrate radical as well as the substrate anion is assumed to isomerize, then the following reaction scheme can be written:

$$Ar + e \rightleftharpoons Ar^{\cdot -}$$

$$Ar^{\cdot -} + RX \rightarrow Ar + (RX^{\cdot -}) \qquad (1)$$

$$(RX^{\cdot -}) \rightarrow R^{\cdot} + X^{-} \qquad (1b)$$

$$R^{\cdot} \rightleftharpoons R'^{\cdot} \qquad (1c)$$

$$Ar^{\cdot -} + R^{\cdot} \rightarrow Ar + R^{-} \qquad (2)$$

$$Ar^{\cdot -} + R'^{\cdot} \rightarrow Ar + R'^{-} \qquad (2')$$

$$R^{-} \rightleftharpoons R'^{-} \qquad (2c)$$

$$RX + R^{-} \rightarrow products + RH \qquad (3)$$

$$RX + R'^{-} \rightarrow products + R'H \qquad (3')$$

The isomerization of the substrate radical is supposed to be a very fast equilibrium process. This accounts for the fact that equivalent results were obtained for **1** and **2**.

The isomerization of the vinyl anion is believed to be slower than the former isomerization. Vinyl anions are generally configurationally more stable than alkyl anions.

The digital simulations presented in this paper are based on the assumption that the chemical reactivity of the substrate radicals and anions of the two configurations (*Z* and *E*) are equal. The rate constants for reactions (2) and (2') and for (3) and (3') are thus assumed equal, and no effect of the change in configuration has been included in the digital simulations.

Experimental

Reagents. The supporting electrolyte, Bu_4NBF_4, and solvent, DMF, were purified and dried by standard procedures. *E*-Bromostilbene (**1**) was synthesized from *trans*-stilbene by bromination[19]

and dehydrobromination[20] in a manner analogous to the dehydrochlorination of 1,2-dichloro-1,2-diphenylethene. Z-1-Bromo-1,2-diphenylethene (2) was synthesized from cis-stilbene by bromination as for the E-isomer followed by dehydrobromination of the resulting compound by a modification of a method described by Sasson,[21] as follows: To a well stirred solution of 3.40 g (10 mmol) of d,l-1,2-dibromo-1,2-di-phenylethane (from the bromination of cis-stilbene) and 3.40 g (10 mmol) of Bu_4NHSO_4 in 20 ml of hexane and 5 ml of CH_2Cl_2, at room temperature, was added dropwise a solution of 0.60 g (15 mmol) of NaOH in 3 ml of water. The reaction was exothermic and the mixture was stirred without external heating for 2 h. After adding 20 ml of water the reaction mixture was extracted three times with hexane, which was washed twice with water and dried over magnesium sulfate. Removal of the hexane under reduced pressure gave 2.4 g of a white solid. Analysis by GLC (25 m methylsilicone capillary column, injection temperature 250 °C, 140 °C for 5 min to 220 °C at 10 °C min^{-1}) showed a purity of 85 % of Z-1-bromo-1,2-diphenylethene, the main by-product (5 %) being diphenylacetylene. The product was purified by recrystallization three times from hexane with cooling to −10 °C. 2-Bromo-1,1,2-triphenylethene was prepared by the reaction of benzophenone with benzylmagnesium chloride.[22] The resulting alcohol was dehydrated[23] and finally brominated.[24] Purity was checked by GLC.

2-Methoxyazobenzene, 2,4'-dimethoxyazobenzene, 2-benzoylpyridine, benzophenone, 3-benzoylpyridine, dimethyl terephthalate and perylene were used as received and no electroactive impurities could be detected.

The Bu_4NPhO was synthesized using a phase-transfer reagent: Equimolar amounts of phenol and Bu_4NHSO_4 were dissolved in an excess of NaOH(aq). The Bu_4NPhO was extracted from the aqueous phase with methylene chloride, and the organic phase was washed with water, dried over 4 Å molecular sieves and evaporated to dryness.

The electrochemical cell. The measurements were conducted in DMF solutions containing 0.1 M Bu_4NBF_4. The reference electrode was Ag/Ag$^+$ in DMF constructed in the manner described by Moe.[25] The cell was a cylindrical tube (25 ml volume) with a joint to accomodate a teflon plug which served as a holder for the working electrode, the counter electrode and a thermosensor. The reference electrode and the nitrogen inlet had separate entrances to the cell through two side-arms.

Instrumentation. This was the same as described in Ref. 4.

Preparative experiments. These were performed as described in Ref. 6. The product distribution was examined by injecting the catholyte directly in the GLC column. The GLC conditions were: 25 m methylsilicone capillary column, injection temperature 250 °C, 140 °C for 5 min to 220 °C at 10 °C min^{-1}.

Simulations. The simulations were performed on a VAX 11/780 from Digital Instruments, programs being written in FORTRAN. All critical parameters were used in double precision.

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