

Direct Digital Simulation of the Steady-State Limiting Current at a Rotating Disk Electrode for a Complex Mechanism

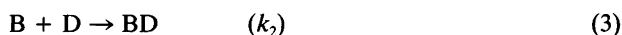
Henrik Balslev* and Dieter Britz†

Kemisk Institut, Aarhus Universitet, DK-8000 Aarhus C, Denmark

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The steady-state limiting current at a rotating disk electrode was simulated for a complex mechanism involving homogeneous electron transfer from a mediator to an alkyl halide leading to a short-lived radical that either couples with the anion radical of the mediator or is reduced by it. The simulations consisted of the iterative solutions of the linearised form of the nonlinear system of equations resulting from the formulation. The working curves derived from the simulation were compared with experimental curves, and the competition parameter and the rate constant for homogeneous electron transfer were measured. The results were compared with results obtained by other electrochemical techniques, and generally good agreement was found.

Ongoing work in our laboratory on the indirect catalysed reduction of organic halides has led to the formulation of the mechanism shown by reactions (1)–(4). In our case with



the indirect reduction of organic halides, A is a large aromatic compound like anthracene or perylene, and B is the corresponding anion radical. In the initial homogeneous electron transfer [reaction (2)], B acts solely as a mediator that transfers an electron to the substrate C, typically an alkyl halide. This anion radical cleaves immediately to the halide anion (not shown in the equations) and a radical (D) in a reaction that in most cases is believed to be concerted with the initial homogeneous electron transfer.¹ D is a short-lived radical that reacts with another anion radical B either by coupling [reaction (3)] or by a single electron transfer [reaction (4)]. The products BD and E are non-electroactive anions that react further by abstracting a proton from the solvent or another proton donor. This mechanism has previously been investigated by cyclic voltammetry (CV), linear sweep voltammetry (LSV),^{2,3} and most recently also by double potential step chronoamperometry.⁴ Nolan and Plambeck⁵ have used orthogonal collocation⁶

to simulate the steady-state limiting current at the rotating disk electrode (RDE) for a similar catalytic mechanism in the special case when $k_2 = 0$. This paper reports a convenient way to simulate the steady-state limiting current for the mechanism at the RDE, by iteratively solving the linearised form of the nonlinear equations resulting from the formulation.

Assuming Nernstian equilibrium for reaction (1) we have eqns. (5)–(7) for the concentrations c_x of species X, (X=A, B, C) at the RDE, in which the diffusion coefficients D

$$\frac{\partial c_a}{\partial t} = D \frac{\partial^2 c_a}{\partial x^2} + k_1 c_b c_c + k_3 c_b c_d - v_x \frac{\partial c_a}{\partial x} \quad (5)$$

$$\frac{\partial c_b}{\partial t} = D \frac{\partial^2 c_b}{\partial x^2} - k_1 c_b c_c - k_2 c_b c_d - k_3 c_b c_d - v_x \frac{\partial c_b}{\partial x} \quad (6)$$

$$\frac{\partial c_c}{\partial t} = D \frac{\partial^2 c_c}{\partial x^2} - k_1 c_b c_c - v_x \frac{\partial c_c}{\partial x} \quad (7)$$

have been taken to be equal. The symbol t stands for time, x for the distance normal to the disk from the disk surface, and v_x is the velocity of the liquid in the x -direction. As substance D is assumed to be a short-lived radical, we can now apply the chemical steady-state approximation for the concentration of substance D at any point in space [eqn. (8)]. Using eqn. (8) and defining the dimensionless

$$\frac{\partial c_d}{\partial t} = 0, \text{ i.e. } k_1 c_b c_c - (k_2 + k_3) c_b c_d = 0 \text{ or}$$

$$c_b c_d = \left(\frac{k_1}{k_2 + k_3} \right) c_b c_c \quad (8)$$

* To whom correspondence should be addressed. E-mail address: bal@kemi.aau.dk.

† E-mail address: britz@kemi.aau.dk.

parameter $q = k_3/(k_2+k_3)$, eqns. (5)–(7) become eqns. (9)–(11).

$$\frac{\partial c_a}{\partial t} = D \frac{\partial^2 c_a}{\partial x^2} + k_1(1+q)c_b c_c - v_x \frac{\partial c_a}{\partial x} \quad (9)$$

$$\frac{\partial c_b}{\partial t} = D \frac{\partial^2 c_b}{\partial x^2} - 2k_1 c_b c_c - v_x \frac{\partial c_b}{\partial x} \quad (10)$$

$$\frac{\partial c_c}{\partial t} = D \frac{\partial^2 c_c}{\partial x^2} - k_1 c_b c_c - v_x \frac{\partial c_c}{\partial x} \quad (11)$$

The thickness of the diffusion layer at an RDE is given by eqn. (12),⁷ where ν is the kinematic viscosity coefficient of

$$\delta = 1.61166 D^{1/3} \nu^{1/6} \omega^{-1/2} \quad (12)$$

the liquid and ω is the angular velocity of the RDE. The velocity in the x -direction (perpendicular to the electrode) is⁷ given by eqn. (13).

$$v_x = -0.510 \nu^{-1/2} \omega^{3/2} x^2 \quad (13)$$

Let the observation time be $\tau = \delta^2/D$. Normalizing as usual by τ , δ and c_a^* (bulk concentration of species A) we have eqns. (14)–(16), and defining the kinetic parameter $\lambda = \tau c_a^* k_1$, eqns. (9)–(11) become eqns. (17)–(19).

$$C_x = c_x/c_a^* \quad (14)$$

$$T = t/\tau = tD/\delta^2 \quad (15)$$

$$Z = x/\delta \quad (16)$$

$$\frac{\partial C_a}{\partial T} = \frac{\partial^2 C_a}{\partial Z^2} + \lambda(1+q)C_b C_c + 2.135 Z^2 \frac{\partial C_a}{\partial Z} \quad (17)$$

$$\frac{\partial C_b}{\partial T} = \frac{\partial^2 C_b}{\partial Z^2} - 2\lambda C_b C_c + 2.135 Z^2 \frac{\partial C_b}{\partial Z} \quad (18)$$

$$\frac{\partial C_c}{\partial T} = \frac{\partial^2 C_c}{\partial Z^2} - \lambda C_b C_c + 2.135 Z^2 \frac{\partial C_c}{\partial Z} \quad (19)$$

In order to have as few points as possible in the concentration profile for each species, we transform Z to Y using Feldberg's exponentially expanding function,^{8,9} eqn. (20) or (21),

$$Y = \ln(1+aZ) \quad (20)$$

$$Z = \frac{1}{a}(e^Y - 1) \quad (21)$$

where a is a real number chosen in the interval between 1 and 3.

With this transformation (for details see Ref. 9) and now setting all $\partial C/\partial T$ to zero (steady state at the RDE), we finally have the non-linear system comprising eqns. (22)–(24).

$$\left\{ \begin{aligned} & \frac{\partial^2 C_a}{\partial Y^2} - \frac{\partial C_a}{\partial Y} + \lambda(1+q)a^{-2}e^{2Y}C_b C_c \\ & + 2.135(e^Y-1)^2 a^{-3}e^Y \frac{\partial C_a}{\partial Y} = 0 \end{aligned} \right. \quad (22)$$

$$\left\{ \begin{aligned} & \frac{\partial^2 C_b}{\partial Y^2} - \frac{\partial C_b}{\partial Y} - 2\lambda a^{-2}e^{2Y}C_b C_c \\ & + 2.135(e^Y-1)^2 a^{-3}e^Y \frac{\partial C_b}{\partial Y} = 0 \end{aligned} \right. \quad (23)$$

$$\left\{ \begin{aligned} & \frac{\partial^2 C_c}{\partial Y^2} - \frac{\partial C_c}{\partial Y} - \lambda a^{-2}e^{2Y}C_b C_c \\ & + 2.135(e^Y-1)^2 a^{-3}e^Y \frac{\partial C_c}{\partial Y} = 0 \end{aligned} \right. \quad (24)$$

These equations are now discretized,⁹ and after rearrangement and substitution with eqns. (25) and (26),

$$s_i = 1.0675(e^{iH}-1)^2 a^{-3} H e^{iH} \quad (25)$$

$$p_i = a^{-2} H^2 e^{2iH} \quad (26)$$

where H is the length of one interval in Y -space, eqns. (22)–(24) become eqns. (27)–(29) (for $i \dots m$).

$$\left\{ \begin{aligned} & C_{a,i-1} \left(1 + \frac{H}{2} - s_i \right) - 2C_{a,i} + C_{a,i+1} \left(1 - \frac{H}{2} + s_i \right) \\ & + \lambda(1+q)p_i C_{b,i} C_{c,i} = 0 \end{aligned} \right. \quad (27)$$

$$\left\{ \begin{aligned} & C_{b,i-1} \left(1 + \frac{H}{2} - s_i \right) - C_{b,i} (2 + 2\lambda p_i C_{c,i}) \\ & + C_{b,i+1} \left(1 - \frac{H}{2} + s_i \right) = 0 \end{aligned} \right. \quad (28)$$

$$\left\{ \begin{aligned} & C_{c,i-1} \left(1 + \frac{H}{2} - s_i \right) - C_{c,i} (2 + \lambda p_i C_{b,i}) \\ & + C_{c,i+1} \left(1 - \frac{H}{2} + s_i \right) = 0 \end{aligned} \right. \quad (29)$$

Applying the boundary conditions of eqns. (30a–d), the remaining equations are provided.

$$\left\{ \begin{array}{l} C_{a,m+1} = 1, C_{b,m+1} = 0, C_{c,m+1} = C_c^* = \lambda \\ \text{(semi-infinite conditions)} \\ C_{a,0} = 0 \text{ (transport limited current)} \\ \left(\frac{\partial C_a}{\partial Y} \right)_{Y=0} = - \left(\frac{\partial C_b}{\partial Y} \right)_{Y=0} \text{ (flux equality)} \\ \left(\frac{\partial C_c}{\partial Y} \right)_{Y=0} = 0 \\ \text{(C is electroinactive at the working potential)} \end{array} \right. \quad (30a) \quad (30b) \quad (30c) \quad (30d)$$

To eliminate the awkward nonlinear terms $C_{b,i}C_{c,i}$ in this system of equations, the Newton-Raphson method is convenient.¹⁰ Let $f_{A,i}$, $f_{B,i}$ and $f_{C,i}$ be the left-hand sides of eqns. (27)–(29), respectively. A first-order Taylor approximation of the $f_{A,i}$, $f_{B,i}$ and $f_{C,i}$ is applied, resulting in the system of linear equations in the approximate error terms δX_i (for $i = 1 \dots m$) given by eqns. (31)–(33).

$$f_{A,i} + \left(1 + \frac{H}{2} - s_i \right) \delta A_{i-1} - 2\delta A_i + \left(1 - \frac{H}{2} + s_i \right) \delta A_{i+1} + \lambda(1+q)p_i C_{c,i} \delta B_i + \lambda(1+q)p_i C_{b,i} \delta C_i = 0 \quad (31)$$

$$f_{B,i} + \left(1 + \frac{H}{2} - s_i \right) \delta B_{i-1} - 2(1+\lambda p_i C_{c,i}) \delta B_i + \left(1 - \frac{H}{2} + s_i \right) \delta B_{i+1} - 2\lambda p_i C_{b,i} \delta C_i = 0 \quad (32)$$

$$f_{C,i} + \left(1 + \frac{H}{2} - s_i \right) \delta C_{i-1} + (2+\lambda p_i C_{b,i}) \delta C_i + \left(1 - \frac{H}{2} + s_i \right) \delta C_{i+1} - \lambda p_i C_{c,i} \delta B_i = 0 \quad (33)$$

It remains to implement the boundary conditions [system (30)] in this new set of equations, and provided that the boundary conditions hold for the first estimate of the concentration profiles, we have that $C_{a,0}$, $C_{a,m+1}$, $C_{b,m+1}$ and $C_{c,m+1}$ all are known, so the corresponding values of δ must be zero. To evaluate δB_0 we use the flux equality condition for A and B. In the two-point approximation to the gradient this becomes eqn. (34a or b) in discrete form. Simi-

$$C_{a,1} - C_{a,0} = C_{b,0} - C_{b,1} \quad (34a)$$

$$\delta A_1 - \delta A_0 = \delta B_0 - \delta B_1 \Rightarrow \delta B_0 = \delta A_1 + \delta B_1 \quad (34b)$$

larly, from the boundary condition for species C we have eqn. (35a or b). In the actual implementation a five-point

$$C_{c,1} - c_{c,0} = 0 \quad (35a)$$

$$\delta C_0 = \delta C_1 \quad (35b)$$

approximation was used,⁹ which gives somewhat more complicated expressions, but the principle is the same.

Now if we have a reasonable estimate of the concentration profiles (see below under Results and discussion), we can evaluate the $f_{A,i}$, $f_{B,i}$ and the $f_{C,i}$ and solve the new system of equations with respect to the δ values. The new system of equations in corrective terms δ , all linear, can now be solved simply by using any available computer routine for the purpose. The δ terms are correction terms for the concentration profiles, so one adds these to the corresponding concentrations in order to obtain the corrected profiles. As the first estimate to the profiles is an approximation, the procedure must be repeated with the corrected profiles, until the δ terms are sufficiently small. Experience shows that about three or four iterations suffice. Note that the system of equations (31)–(33) contains many constant terms that can be precalculated and stored.

Implementation

Programming was done in FORTRAN, and the programs were run on a Digital Equipment Corporation VAX 6210 computer under VMS.

There are three basic parameters in the simulations, the first being the bulk concentration of component C. In the normalised case this is a pure number, here called γ (the excess factor). Next is the kinetic parameter λ , which contains information about the rate constant k_1 , the angular velocity ω of the RDE, the kinematic viscosity coefficient ν of the liquid and the diffusion coefficient D of the species (assumed common to all species). Last we have the q -value, which is a pure number between 0 and 1. This number contains information about the rate of coupling towards the catalytic effect (pure coupling when $q=0$ and a pure catalytic effect when $q=1$). These are the variables that must be changed over a (wide) range in order to fit the simulations to experimental results.

There are also a few parameters that only concern the simulation itself: the integer m (there are $m+2$ points in each concentration profile), the number a connected with the unequal intervals [eqn. (20)], and the number Z_{lim} , which sets the distance out in the solution to which the calculations should be made. Z_{lim} is given in units of the thickness of the diffusion layer, and its determination has been described⁹ (about 3 units suffice).

Since the procedure as described was unknown territory for the present authors, it was clear that it needed checking. The method adopted was to write an additional independent program, directly simulating the normalised form of eqns. (17)–(19). For simplicity, the explicit point method⁹ was used. The simulated current (using a five-

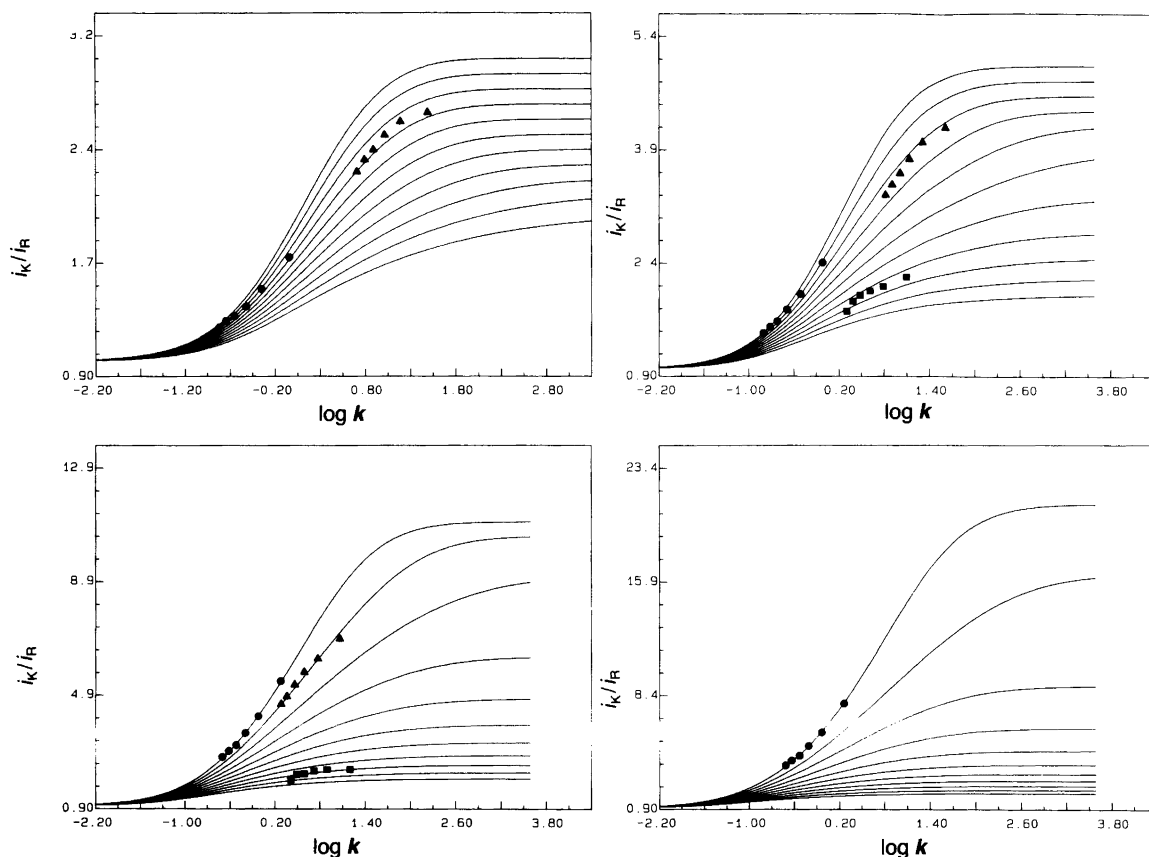


Fig. 1. Working curves showing the kinetic current increase i_k/i_R as a function of $\log k$. The working curves are shown for $q=0.0$ to $q=1.0$ with a spacing of 0.1 between the curves. In all cases $q=0.0$ corresponds to the bottom line and $q=1.0$ to the top line. Curves are shown for four different values of γ , $\gamma=1$ (top left), $\gamma=2$ (top right), $\gamma=5$ (bottom left) and $\gamma=10$ (bottom right). Examples of fits to working curves are also shown for different mediators and alkyl halides. The symbols on the curves stand for: (●) 9,10-diphenylanthracene and benzyl chloride, (▲) anthracene and 1-chloro-1-phenylethane and (■) pyrene and ethyl bromide.

point approximation) came to a steady state in about two T -units and, for a set of quite widely varying simulation parameters, matched results from the present method within computational precision. After this check, the present direct method was used to compute the working curves.

Application to experiments

The simulations were carried out for different values of γ , q and λ in order to make working curves to be used for fitting with experimental curves. Working curves were made for $\gamma=1, 2, 5, 10, 20, 50$ and 100, and for each value of γ curves were made for $q=0.0, 0.1, 0.2 \dots 1.0$. Four of the working curves are shown in Fig. 1. The curves show the normalised current function, which is identical to the catalytic current increase, versus the logarithm of k as defined by Nolan and Plambeck⁵ in eqn. (36). k is equal to λ as defined above,

$$k = (\nu/D)^{1/3} k_1 c_a^* / \omega \quad (36)$$

except for the constant 1.61166 squared. We used k in order to compare our results with the results of Nolan and Plambeck. For all values of γ the curve corresponding to $q=0.0$

is the lowest, and the curve corresponding to $q=1.0$ is the highest. Our results for $q=1.0$, seem to be in good accord with the working curves published by Nolan and Plambeck.⁵

The lowest uncertainty in the measurements will be encountered in the region of k , where there is the largest change in i_k/i_R per unit change of k , and from the working curves we find that this roughly corresponds to a region of k where $-0.7 < \log k < 2.5$. With $\nu = 8.43 \times 10^{-3}$ St ($= 7.96 \times 10^{-3}$ poise, DMF at 25°C),¹¹ $D = 1.0 \times 10^{-5}$ cm² s⁻¹ and normal experimental conditions $c_a^* = 1.0 \times 10^{-3}$ M and $50 < \omega < 300$ s⁻¹ ($500 < f < 3000$ r.p.m., where f is the rotation rate of the RDE) this corresponds to a region of k_1 ranging from 10^3 to 10^7 dm³ mol⁻¹ s⁻¹, so the reactions that can be studied by the method have a rather high secondary rate constant for the homogenous electron transfer.

The method described in this paper is an indirect method, i.e. involves two experiments. In this respect the method is similar to the LSV method described by Pedersen.³ In the first experiment the reduction current plateau i_R , when only the mediator A is present, is measured at different rotation rates of the RDE, and in the second experiment the current plateau i_k is measured after the substrate C has been added. The dimensionless ratio i_k/i_R

Table 1. q -Values and rate constants for some alkyl halides and mediators determined by RDE and by other electrochemical techniques.

Mediator	Alkyl halide	γ	q^{RDE}	$k_1^{RDE}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	q^{SV}	$k_1^{CV}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
9,10-Diphenyl-anthracene	Benzyl chloride	1	0.7–0.8	1.6×10^4	1.0 ^a	15 350 ^b
		2	0.9	8.1×10^3	—	
		5	1.0	1.8×10^4	—	
		10	1.0	1.3×10^4	—	
Pyrene	Ethyl bromide	2	0.0–0.2	1.3×10^3	0.1 ^c	Not measured
		5	0.2	1.6×10^3	—	
		10	0.2	2.1×10^3	—	
		2	0.0–0.1	1.1×10^3	—	
		5	0.0–0.1	1.3×10^3	—	
		10	0.0–0.1	1.1×10^3	—	
		2	0.0–0.2	8.9×10^2	—	
		5	0.1	1.1×10^3	—	
		10	0.0–0.2	1.3×10^3	—	
		<i>trans</i> -Stilbene	Ethyl bromide	2	0.2	1.9×10^4
5	0.2			1.8×10^4	—	
2	0.2–0.3			5.4×10^4	—	
5	0.2			5.2×10^4	—	
10	0.2			2.6×10^4	—	
Anthracene	1-Chloro-1-phenylethane	1	0.6–0.7	7.1×10^4	1.0 ^d	90 500 ^e
		2	0.4	10.8×10^4	—	
		5	0.9	8.6×10^4	—	
		1	0.7–0.8	1.2×10^5	—	
		2	0.8	1.1×10^5	—	

^aIn Ref. 12 the q -value for benzyl chloride was measured with anthracene and with tetracene, with $q=1.0$ and $q=0.9$, respectively. As the standard potential of 9,10-diphenylanthracene is between the standard potentials of anthracene and tetracene, the q -value measured here should be 1.0 ^bDaasbjerg, K., unpublished result. ^cFrom Ref. 13. ^dIn Ref. 12 the q -value for 1-chloro-1-phenylethane and perylene is measured to be 0.9, and as the redox potential of anthracene is substantially more negative than that of perylene, the q -value here should be 1.0. ^eFrom Ref. 14.

then directly shows the catalytic current increase. When i_k/i_R is plotted against $-\log f$ the parameters q and k_1 can be determined by fitting the experimental curves to the simulated one.

Results and discussion

Simulation. In the simulations the parameter set $m = 50$, $a = 2$, $Z_{lim} = 3$ and $\epsilon = 10^{-5}$ (the convergence criterion) was used. Some care must be exercised in the choice of the first estimate of the steady-state concentration profiles for species A, B and C. It was found that the fastest convergence was attained by the following: C_a was taken to increase linearly from 0 to 1 in the first $(m/2)+1$ points (in Y -space). For the remainder the concentration of A was taken to be unity (bulk concentration). All C_b were taken to be $1 - C_a$. C_c was set at a constant value of γ (bulk concentration). These approximations were chosen as they gave quite fast convergence for any values of λ , γ and q and were easy to implement. Also they satisfy the boundary conditions. Unlike the method used by Nolan and Plambeck⁵ no problems of instability were encountered here.

The solution of one set of $3m$ equations required about 10 s CPU time (with $m = 50$) and with the starting values cited above 3 iterations were sufficient on average. So the

solution for one set of λ , γ and q -values takes about 30 s CPU time. As most of this time is spent on solving the equations, efforts to lower the CPU time should be concentrated on making this process faster. Some measures towards this are as follows:

- (1) The number m can be lowered. As the time spent on solving a set of equations is proportional to m^3 a small change of m could give considerable changes in the charged CPU time. Some experiments show that even $m = 40$ is satisfactory.
- (2) The Gauss–Jordan subroutine used for solving the equations did not take into account the special form of the matrix, which has many zeroes, always in the same places, so a subroutine could be developed to make use of this fact. The estimated lowering of CPU time would be about a factor of 2, and does not appear worth the effort. Using this method to simulate the steady-state current for a rotating disk electrode, a large amount of time was spent with pen and paper and on programming. However, this is an initial investment only, and there are some decided advantages in this method: (1) once the program is implemented the CPU use is lower than with other methods; (b) small errors in implementation cause unmistakable instabilities, so one always knows if the program is faulty.
- (3) The program is adaptable to other mechanisms without

too much trouble (this has been done). (4) The method is numerically stable.

Measurements

A number of experiments were carried out with different mediators and different alkyl halides in order to compare the results obtained by the RDE method described in this paper and results obtained by other electrochemical techniques. The results of these experiments are shown in Table 1, together with the corresponding results obtained by other methods. Generally the fits were quite good, and the q -value could usually be determined unambiguously with an uncertainty of ± 0.1 , which is also encountered with the LSV method. Usually $\log k$ could be determined with an uncertainty of 0.1 on a logarithmic scale, which corresponds to an uncertainty of k_1 of about 25%, which is comparable to the uncertainty encountered with other electrochemical methods when applied to systems with the rather large rate constants discussed here. Some examples of the fits are shown in Fig. 1. Generally the fits are better for higher q -values, especially when γ is 5 or 10, as the change of i_k/i_R per unit change of k is then larger than with lower q - or γ -values. With most of the compounds studied here, the q -value determined by the RDE method is in good accord with the q -value measured by other methods.¹²⁻¹⁴ It is also seen that the determination of the q -value is generally better when γ is 5 or 10 than when γ is 1 or 2. The rate constants determined by the RDE method are in good agreement with the rate constants measured by cyclic voltammetry (CV). Both for 9,10-diphenylanthracene and benzyl chloride and for anthracene and 1-chloro-1-phenylethane the rate constants obtained by this method are within 10% of those measured by CV,¹⁴ when the mean value is used. This is as good as one might expect, when the uncertainty in the determination of $\log k$ is considered.

Some experimental difficulties were encountered, and these might limit the usefulness of this method. The quite large rate constants of the homogenous electron transfer that can be studied by this method are usually found in systems where the redox potential of the mediator is quite close to the potential of the direct reduction of the alkyl halide, at least in the systems we have investigated. However, in order to use the RDE method described here, a well defined plateau is needed, and the direct reduction of the substrate often masks this plateau, especially with large values of γ (this was the problem with anthracene and 1-chloro-1-phenylethane, which is why we could not take measurements with $\gamma = 10$). LSV is not as sensitive to this problem, so whenever the plateau is ill defined owing to this difficulty, one will often choose the LSV method.

We therefore conclude that the RDE method, with the above limitations, is an alternative to the methods previously described, e.g. LSV and double potential step chronoamperometry,²⁻⁴ when one wishes to determine the competition parameter q and/or the rate constant for homogenous electron transfer.

Experimental

All the RDE measurements were carried out with a Metrohm 628-10 RDE with a gold electrode ($\varphi = 3.0$ mm). Currents were sampled and monitored using a Olivetti M24 personal computer, and attendant sampling hardware.

The mediators were used as received. Benzyl chloride and ethyl bromide were distilled prior to the experiments. 1-Chloro-1-phenylethane was prepared from 1-phenylethanol and dry HCl and distilled at 10 mmHg, b.p. 64°C.

The experiments were carried out in an H-cell designed for the RDE. The solvent was in all cases DMF containing 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) as a supporting electrolyte. The solvent with the supporting electrolyte was dried in an alumina column prior to use. The cathode chamber of the cell contained 40 ml of solution, so about 70 ml of solvent were used for each experiment. This amount can, however, be lowered considerably (to about 30 ml), if a one-chamber cell is used.

A typical experiment was carried out in the following way: 38 ml of DMF with TBABF₄ were poured into the cathode chamber, and the other two chambers of the cell were filled with the appropriate amount of solvent. The solvent was purged with nitrogen for 10–15 min, and the baseline was checked by a slow potential scan at the RDE in order to be sure that no electroactive impurities were present. 2 ml of standard solution of the mediator were then added to the solution, and a table was made of the steady-state limiting current (i_R), measured by a slow potential scan, at six different frequencies of the RDE. Also $i_R/f^{A/2}$ was tabulated to check that this quantity was constant, which it usually was within 2%. Now the alkyl halide was added, the steady-state limiting current i_k was measured by a potential scan, and the catalytic current efficiency i_k/i_R was calculated for the different rotation rates of the RDE. A plot of i_k/i_R vs. $-\log f$ was made and fitted to the simulated working curves from which the competition parameter q and the kinetic parameter k could be found. The rate constant k_1 was computed using eqn. (36).

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