Determination of the Competition Parameter for Coupling or Reduction by Use of the Rotating Disk Electrode and the Ultra-microelectrode
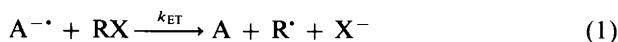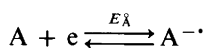
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A new technique is presented for measuring the competition between coupling and reduction in the reaction between aromatic anion radicals and alkyl radicals. By making use of the steady-state properties of, e.g., ultra-microelectrodes or rotating disk electrodes, it is possible to distinguish between the two reaction paths, thus allowing the determination of a competition parameter, q. The new method is shown to be applicable by comparing experimental results obtained in this way for the butyl radical with the corresponding ones obtained from chronoamperometric and linear sweep voltammetric measurements. The advantage of the method presented is that it is not limited by a direct electrochemical reduction of the substrate and is less limited by slow reactions and adsorption phenomena. These points are illustrated by extending previously measured q-values for the 2-norbornyl radical with new values, thus making the measurements complete. The reduction potential, self-exchange reorganization energy and standard potential calculated from the measurements of q-values are given for the 2-norbornyl radical. At the same time the method makes possible the determination of the ratio between the diffusion coefficients of the aromatic compound and its anion radical. This ratio is, for the investigated compounds, close to unity.

In recent years reduction and standard potentials have been measured by our group for a number of aliphatic and benzylic radicals with a new method.[1] The method is based on the investigation of the competition between coupling [eqn. (2)] and reduction [eqn. (3)] in the reaction between aromatic anion radicals and alkyl radicals. The anion radicals $A^{-\bullet}$ are generated by a heterogeneous electron transfer and the alkyl radicals $R^{\bullet}$ by an indirect reduction of the alkyl halide RX [eqn. (1)]. The reaction scheme has previously been thoroughly investigated.[2]

$$A + e \underset{}{\overset{E_A^{\circ}}{\rightleftharpoons}} A^{-\bullet}$$

$$A^{-\bullet} + RX \xrightarrow{k_{ET}} A + R^{\bullet} + X^{-} \tag{1}$$

$$A^{-\bullet} + R^{\bullet} \xrightarrow{k_2} AR^{-} \tag{2}$$

$$A^{-\bullet} + R^{\bullet} \xrightarrow{k_3} A + R^{-} \tag{3}$$

The products AR^{-} and R^{-} will either be protonated or react with the alkyl halide in a nucleophilic substitution. Dimerization and H-atom disproportionation of the alkyl radicals and H-atom abstraction from the solvent are assumed to be negligible.

The competition between reactions (2) and (3) can be expressed by a dimensionless parameter q defined by eqn. (4). The parameter q is equal to 0 for pure coupling

$$q = \frac{k_3}{k_2 + k_3} \tag{4}$$

and to 1 for pure reduction. The competition parameter q has, until now, been determined by linear sweep voltammetry (LSV),[1] chronoamperometry[3] and coulometry[1] in the case of coupling. A diagram of q vs. standard potentials of different anion radicals gives an S-shaped curve from which it is possible to find the reduction potential $E_{1/2}^{q}$ of the radical (the potential at which $q = 0.5$), the reorganization energy λ for reaction (3), the ratio k_2/k_d, where k_d is the diffusion-controlled rate constant ($\approx 10^{10}$ M^{-1} s^{-1}), and the standard potential $E_{R\cdot}^{\circ}$ of the radical.[1] The uncertainty in the determination of $E_{R\cdot}^{\circ}$ is estimated to be ± 150 mV, which is mainly due to a rather uncertain determination of λ, especially in the cases where measurements of q in the whole range from 0 to 1 have not been possible because of limitations in the techniques we have used until now. One of the drawbacks of LSV and chronoamperometry is that they demand rather a high rate constant ($k_{ET} > 10$ M^{-1} s^{-1}) of the first electron transfer to RX [eqn. (1)] in order to make the measurement of the competition between reactions (2) and (3)

possible. Furthermore the determination of q can be limited by the influence of the direct reduction of the RX compound.

In this paper we report on the use of the steady-state properties of ultra-microelectrodes and rotating disk electrodes in the measurement of q-values in the whole range, thus making possible a more reliable determination of reduction and standard potentials of radicals. Previously these properties have been used for monitoring homogeneous kinetics.[4,5] The steady-state current i for an ultra-micro disk electrode is given by eqn. (5), where n is the number of electrons, F is Faradays constant, D the diffusion coefficient, C the substrate concentration and r the radius of the electrode. The analogous equation for the number of electrons, F is the Faraday constant, D the diffusion coefficient, C the substrate concentration and r the radius of the electrode. The analogous equation for the

$$i = 4nFDCr \qquad (5)$$

rotating disk electrode (RDE) is given by eqn. (6), where ω is the angular velocity and ν the kinematic viscosity.[6] In

$$i = 0.620nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C \qquad (6)$$

both cases the current i is proportional to the concentration C.

From reaction scheme (1) to (3) it follows, that the increase in the concentration of the aromatic compound A (ΔC_A) in the final stage is given by expression (7), where C_{RX} is the concentration of the alkyl halide. This

$$\Delta C_A = C_{RX}(1 + q) \qquad (7)$$

formula is valid only when C_{RX} is not higher than half of the concentration of $A^{-\bullet}$ ($C_{A^{-\bullet}}$). With the ultra-microelectrode or RDE, ΔC_A and thus q can be found in the following way. For a given concentration of the aromatic compound A (C_A) the height of the wave i_A in a steady-state voltammogram is measured. The aromatic compound is then reduced electrochemically to $A^{-\bullet}$, the alkyl halide is added ($C_{RX} \leqslant 1/2C_{A^{-\bullet}}$) and the increase in reduction current Δi_A due to the production of A in reaction (1) and (3) is found from steady-state voltammograms. According to eqn. (5) or (6) ΔC_A is equal to $(\Delta i_A/i_A)C_A$ leading to the following expression for q [eqn. (8)]. With the knowledge of q it is possible, using

$$q = \frac{\Delta i_A C_A}{i_A C_{RX}} - 1 \qquad (8)$$

eqn. (5) or (6), to determine the ratio between the diffusion coefficients $D_A/D_{A^{-\bullet}}$ of the aromatic compound A and $A^{-\bullet}$. For the ultramicroelectrode the relation is given in eqn. (9) and the analogous relation for the RDE is

$$\frac{D_A}{D_{A^{-\bullet}}} = \frac{\Delta C_{A^{-\bullet}}}{\Delta C_A} \frac{\Delta i_A}{\Delta i_{A^{-\bullet}}} = \frac{2}{1+q} \frac{\Delta i_A}{\Delta i_{A^{-\bullet}}} \qquad (9)$$

given in eqn. (10). The parameters $\Delta C_{A^{-\bullet}}$ and $\Delta i_{A^{-\bullet}}$ are

$$\frac{D_A}{D_{A^{-\bullet}}} = \left(\frac{2}{1+q} \frac{\Delta i_A}{\Delta i_{A^{-\bullet}}}\right)^{3/2} \qquad (10)$$

the decreases in the concentration of $A^{-\bullet}$ and oxidation current due to the removal of $A^{-\bullet}$ in reaction (1) to (3). Once the ratio $D_A/D_{A^{-\bullet}}$ is determined, eqns. (9) and (10) can also be used to find the competition parameter q.

The determination of the q-value using eqn. (8) requires nucleophilic substitution reactions involving the alkyl halide RX and the products AR^- and R^- from reactions (2) and (3) to be negligible. However, in some cases, e.g., in the reaction between anthracene anion radical and benzyl chloride it is well known that side products such as stilbene, dibenzyl ether and bibenzyl can be isolated.[7] The q-value in this case cannot be determined from eqn. (8), but can from eqn. (9) or (10), if the ratio $D_A/D_{A^{-\bullet}}$ is already known. The ratio $D_A/D_{A^{-\bullet}}$ can be found using the technique described here or in other ways.[8]

The main advantage of the new technique compared with LSV and chronoamperometry is that it is not restricted by direct electrochemical reduction of the substrate RX, since the latter can be added in less than stoichiometric amount, and less restricted by slow reactions. The lower limit for the magnitude of the rate constant k_{ET} can be found from the differential equation for RX [eqn. (11)].

$$\frac{d[RX]}{dt} = -k_{ET}[RX][A^{-\bullet}] \qquad (11)$$

Reactions (2) and (3) are fast compared with eqn. (1), thus $[A^{-\bullet}]_0 - [A^{-\bullet}] = 2([RX]_0 - [RX])$, where $[A^{-\bullet}]_0$ and $[RX]_0$ are the initial concentrations of $A^{-\bullet}$ and RX. Entering this expression into eqn. (11) gives eqn. (12).

$$\frac{d[RX]}{dt} = -k_{ET}[RX](2[RX] + [A^{-\bullet}]_0 - 2[RX]_0) \qquad (12)$$

Introducing the two dimensionless parameters $\alpha = [RX]/[RX]_0$ and $\beta = [A^{-\bullet}]_0/[RX]_0$ into eqn. (12) gives eqn. (13).

$$\frac{d\alpha}{dt} = -k_{ET}\alpha[RX]_0(2\alpha + \beta - 2) \qquad (13)$$

Rearrangement and integration gives eqn. (14).

$$k_{ET}t = \frac{1}{[RX]_0(\beta - 2)} \ln\left(\frac{2\alpha + \beta - 2}{\alpha\beta}\right) \qquad (14)$$

Typical initial concentrations of $A^{-\bullet}$ and RX when RX is added in less than stoichiometric amount are 0.010 M and 0.004 M, respectively, giving $\beta = 2.5$. Assuming the anion radicals to be highly stable and the reaction between $A^{-\bullet}$ and RX to be 95 % complete ($\alpha = 0.05$) after, e.g., 2 min gives $k_{ET} \approx 7 \text{ M}^{-1} \text{ s}^{-1}$. If the stability of the anion radicals is very high the measurements may be

possible for smaller rate constants. In cases where the direct reduction of RX is not a problem, thus allowing an excess of RX to be used, the measurements of q-values from eqn. (9) or (10) for reactions with rate constants as low as $10^{-3}\,M^{-1}\,s^{-1}$ should be attainable. Compared with LSV and chronoamperometry the time window of this technique is considerably broader.

In Fig. 1 is shown an example of the determination of the q-value with the RDE for the reaction between m-toluonitrile anion radical and butyl chloride. Voltammograms are recorded before and after reduction of a given concentration of m-toluonitrile (curves a and b) and after addition of a known amount of butyl chloride (curve c). From the curves and eqn. (8) and (10) the q-value and the ratio between the diffusion coefficients D_A/D_{A^-} can be found equal to 0.50 and 1.13, respectively.

In Table 1 q-values measured in this way for reactions between different anion radicals and butyl chloride are compared with the corresponding ones previously obtained with LSV[1b] and chronoamperometry.[3] The results are, in most cases, in accordance with each other taking into account that the uncertainty in the determination of q with the new method is estimated to be 0.05, the same as in chronoamperometry and half as much as in LSV. With the last two techniques measurements of q with pyrene and anthracene were not possible owing to the reactions being too slow, however, coulometry has shown that q is zero in the case of anthracene,[1b] which is in agreement with the new results. The technique presented here thus seems to be a useful supplement to LSV and chronoamperometry.

Table 2 lists the ratio D_A/D_{A^-} determined either from eqn. (9) or (10). The ratio is for each mediator obtained as an average value from several experiments. As expected

Table 1. Competition parameter (q) for butyl chloride in DMF/0.1 M TBABF$_4$ measured by RDE or ultra-microelectrode.

Mediator	$-E_A^c/V$[a]	q	$q(LSV)$[b]	$q(chrono)$[c]
Anthracene	1.890	0.00	—	—
Pyrene	2.018	0.05	—	—
Quinoline	2.075	0.15	—	0.00
(E)-Stilbene	2.136	0.30	—	0.30
Benzonitrile	2.230	0.45	0.6	0.45
m-Toluonitrile	2.264	0.50	0.6	0.50
o-Toluonitrile	2.277	0.60	0.7	0.60
p-Toluonitrile	2.337	0.80	0.8	0.75
Naphthalene	2.457	0.80	0.9	0.80
Biphenyl	2.519	0.90	0.9	0.90

[a] Vs. SCE. [b] Taken from Ref. 1(b). [c] Taken from Ref. 3 or measured by the same method.

and normally assumed this ratio is near one. The conversion from parent to radical anion involves only minor changes in structure and in the weak interaction with the solvent. The ratio D_A/D_{A^-} is not given for benzonitrile and o-toluonitrile, since it is unexpectedly higher and not very reproducible ($D_A/D_{A^-} > 1.5$). Even though the measured q-values with these two mediators seem to be well in accordance with the other results (including those with m-toluonitrile and p-toluonitrile) the reaction mechanism may be more complicated in these two cases. The influence on the reaction mechanism, e.g., from the strong bases AR^- and R^- produced in reactions (2) and (3) and from the slow decay of the anion radicals to cyanide and benzene or toluene is still under investigation.[9,10] The uncertainty in the determination of the D_A/D_{A^-} ratio is estimated to be 5% for most of the compounds owing to the relatively high uncertainty in the determination of q. However, for the mediators pyrene and anthracene the uncertainty in the determination is less, since these mediators are involved in pure coupling reactions. For mediators with standard potentials less negative than pyrene this method outlines an especially simple way of determining D_A/D_{A^-} ratios.

Table 3 lists the previously measured q-values by LSV for the reaction between different anion radicals and exonorbornyl chloride. No q-value below 0.4 could be measured owing to the reactions being too slow leading to
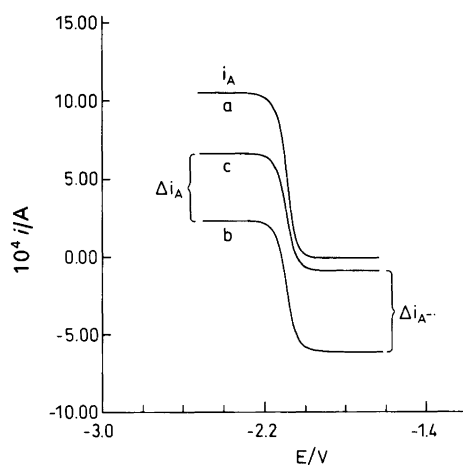

Fig. 1. Steady-state voltammograms at the RDE of 15.00 mM m-toluonitrile before (curve a) and after preparative reduction (curve b) and after addition of butyl chloride in a concentration of 4.00 mM (curve c) in DMF/0.1 M TBABF$_4$ at 0.3 V/s and $\omega = 200\,s^{-1}$. The steady-state reduction current i_A in curve a is 10.72×10^{-4} A. The changes in the reduction and oxidation currents Δi_A and Δi_{A^-} are 4.30×10^{-4} A and 5.30×10^{-4} A, respectively.

Table 2. The ratio between the diffusion coefficients of the aromatic compound A and its anion radical A$^-$ (D_A/D_{A^-}) measured in DMF/0.1 M TBABF$_4$.

Mediator	D_A/D_{A^-}
Anthracene	1.21
Pyrene	1.13
Quinoline	1.26
(E)-Stilbene	1.06
m-Toluonitrile	1.12
p-Toluonitrile	1.20
Naphthalene	1.25
Biphenyl	1.18

Table 3. Competition parameter (q) for exo-norbornyl chloride/bromide in DMF/0.1 M TBABF$_4$ measured by RDE or ultra-microelectrode.

Mediator	$-E_A^{\circ}/V^a$	q	$q(LSV)^b$
Anthracene	1.890	0.00	—
Pyrene	2.018	0.00	—
Quinoline	2.075	0.05	—
(E)-Stilbene	2.136	0.15	—
Methyl benzoate	2.183	0.20	—
Benzonitrile	2.230	0.25	0.4
m-Toluonitrile	2.264	0.35	0.4
o-Toluonitrile	2.277	0.45	0.5
p-Toluonitrile	2.337	0.65	0.7
Phenanthrene	2.388	0.80	0.8
Naphthalene	2.457	0.80	0.8
Biphenyl	2.519	0.85	0.9
1-Methoxynaphthalene	2.537	—	0.9

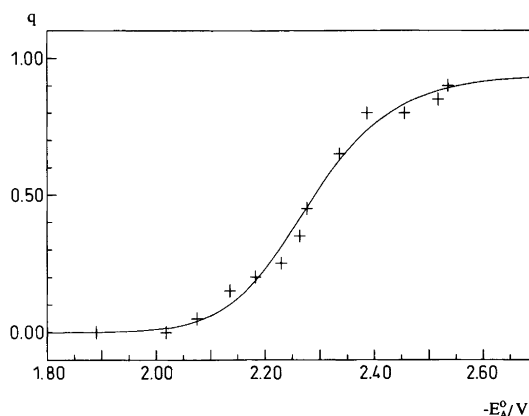^{a} Vs. SCE. ^{b} Taken from Ref. 1(c) or measured by the same method.

Fig. 2. q-Values of the norbornyl radical vs. the redox potential E_A° (vs. SCE) of some aromatic anion radicals. The curve is calculated using $E_{1/2}^q = -2.29$ V, $\lambda = 25$ kcal mol^{-1} and $k_2/k_d = 0.05$.

a high uncertainty in the determination of λ. However with the new technique it is now possible to make the measurements complete, using not only exo-norbornyl chloride as the substrate but also exo-norbornyl bromide, since its direct reduction is not a problem as in LSV. According to reaction scheme (1)–(3) the nature of the leaving group should not have any influence on the determination of q, since a free radical R• is generated independently of X. The experimental results clearly confirm this, since exactly the same values of q are found over the whole range with the two norbornyl substrates (Table 3). The new method thus, in most cases, gives one freedom to choose the leaving group.

The q-values were mostly determined from eqn. (8), except in the slow reactions between exo-norbornyl chloride and the anion radicals of pyrene and anthracene. The rate constant for the reaction between pyrene anion radical and exo-norbornyl chloride is 0.2 M^{-1}s^{-1} at 20°C measured by a potentiostatic method.[4] In these cases exo-norbornyl chloride was added in excess and q was determined from eqn. (9) or (10) applying the known ratios between the diffusion coefficients given in Table 2. Quinoline and methyl benzoate anion radicals were relatively unstable and measurements were only performed for the fast reactions with exo-norbornyl bromide. The anion radicals of 1-methoxynaphthalene were too unstable for this new technique to be applied at all and in this case LSV and chronoamperometry are the methods of choice, since they are less restricted by such a problem.

In Fig. 2 is shown a new q vs. E_A° plot for the 2-norbornyl radical. The crosses are the experimental results and the solid line is the best fit of a simulated curve to the results. The simulation gives $E_{1/2}^q = -2.29$ V vs. SCE, $\lambda = 25$ kcal mol^{-1}, $k_2/k_d = 0.05$ and $E_{R•}^{\circ} = -1.92$ V vs. SCE. These values are believed to be more accurate, than those based only on LSV measurement.[1c] According to the Marcus cross-relation[11] the reorganization energy λ can be expressed as the average value of the self-

exchange reorganization energy of the electron donor $\lambda_{A^-}(0)$ and electron acceptor $\lambda_{R•}(0)$. The reorganization energy for the self-exchange reaction of aromatic anion radicals has been measured by means of EPR spectroscopy in DMF[12] as being approximately 10 kcal mol^{-1}, thus giving $\lambda_{R•}(0) = 40$ kcal mol^{-1} for the norbornyl radical. A reasonable explanation for the smaller $\lambda_{R•}(0)$ value for the norbornyl radical compared other with other alkyl radicals [$\lambda_{R•}(0) = 50$ kcal mol^{-1}][1b,1c] is that the 2-norbornyl radical, having a bent structure,[13] does not need a large inner reorganization energy to be reduced to the corresponding anion.

Until now only reduction and standard potentials of aliphatic and benzylic radicals have been investigated. An extension of the method to the investigation of aryl radicals would be interesting. The reaction scheme for aryl halides (ArX) reaction with anion radicals is more complicated, since reaction (1) has to be replaced by (15) and (16).

$$A^{-•} + ArX \rightleftarrows A + ArX^{-•} \tag{15}$$

$$ArX^{-•} \rightarrow Ar• + X^- \tag{16}$$

The aryl radicals may be involved in side reactions such as arylation of the mediator and H-atom abstraction from the solvent. The electron transfer in reaction (15) is reversible and not concerted with the bond breakage as in the case of the alkyl halides. The anion radical ArX$^{-•}$ is a detectable species with a certain lifetime depending on the nature of X and Ar.[14] Unfortunately, bond breakage will in most cases be so slow that measurements of reliable q-values will not be possible, even with the new technique. A solution to this problem could be to use a better leaving group than halides, e.g., the diazonium group. Even though diazonium compounds are adsorbed on conventional electrodes making chronoamperometric measurements impossible this is not a problem with the new technique, since the diazonium compound can be added in less than stoichiometric amount. These points are under investigation.

Summary. The method outlined introduces a new way of estimating the competition parameter q for the reaction between aromatic anion radicals and alkyl radicals and at the same time makes possible the determination of the ratio between the diffusion coefficients of the aromatic compound and its anion radical. The uncertainty in the measurements of q is 0.05, the same as in chronoamperometry but smaller than in LSV. The method is more time consuming than chronoamperometry and demands a higher stability of the anion radicals but has no limitations concerning direct electrochemical reduction of the alkyl halide. Furthermore it can be used for much slower reactions and it does not have problems due to adsorption of the substrate. However, the method must still be used with some care and on a well-known mechanism, since it detects only the final stage of the reaction and does not reveal, e.g., a change in mechanism as chronoamperometry or LSV would do.

Experimental

Materials. The mediators were the same as used previously.[1] Butyl chloride was obtained commercially and distilled before use. *exo*-Norbornyl bromide and chloride were prepared using the procedure in Ref. 15. The supporting electrolyte, Bu_4NBF_4, and the solvent N,N-dimethylformamide (DMF) were purified by standard procedures.

Instrumentation. The cell used was an H-cell and the electrodes an ultra-microelectrode or rotating disk electrode, a platinum net, a carbon electrode and a reference electrode with a silver wire in DMF/0.1 M TBABF$_4$. The platinum disk ultra-microelectrode ($r = 5 \ \mu m$) was manufactured according to instructions in Ref. 16 and was polished with diamond paste (0.25 μm). The RDE system (Metrohm 628-10, gold electrode with $\phi = 3$ mm) was obtained commercially. The potentiostat used for the potentiostatic measurements has been described elsewhere.[17] The current from the ultra-microelectrode was connected to this potentiostat through an electrometer amplifier (AD 505). The signals from the potentiostat were recorded using a Nicolet 4094c/4570 digital oscilloscope. The equipments were controlled by means of a PC. The preparative reductions were carried out with a 200 W home-built three-electrode potentiostat.

Procedure. The aromatic compound was added to a 30 ml DMF/0.1 M TBABF$_4$ solution in a 0.015 M concentration and the solution was deaerated with argon. A steady-state voltammogram using the ultra-microelectrode or rotating disk electrode as working electrode and the platinum net as counter electrode was recorded. The aromatic compound was subsequently reduced to A$^{-\bullet}$ at a constant potential at the platinum net using the carbon electrode in the anodic chamber of the H-cell as counter electrode. Afterwards voltammograms were recorded at intervals of 2 min to control the stability of the generated anion radicals. The alkyl halide was then added with stirring in such an amount that its initial concentration became 0.004 M, and voltammograms were recorded until no further changes were observed. All experiments were repeated three times.

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