*Short Communication*

# Ultra-microelectrodes for Electrochemical Monitoring of Homogeneous Reactions

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Several authors dealing with ultra-microelectrodes have focused on the small cell time constant *RC* (*R*: solution resistance; *C*: double-layer capacitance), which allows fast transient electrochemical techniques, such as fast-sweep cyclic voltammetry,[1-6] to be used. Other papers have emphasized the small current drawn by ultra-microelectrodes and applied this to investigations in highly resistive solvents[7,8] or under conditions close to industrial practice.[9]

It is known from cyclic voltammetry that the voltammograms at small electrodes become sigmoidal at low scan rates $(D/ar^2)^{1/2} > 1$; (*D*: diffusion coefficient, *a*: $nFv/RT$ and *r*: radius of electrode).[10] Digital simulations of chronoamperometry at microdisk electrodes have shown that the current is constant within 2 % for $(r^2/Dt)^{1/2} < 0.1$. By using a 10 μm (diameter) platinum disk electrode and assuming a diffusion coefficient equal to $1.0\times10^{-9}$ m$^2$ s$^{-1}$ the former equation states that for $t > 3.0$ s the current will be constant to within 2 %.[11,12] We have used this steady-state property of ultra-microelectrodes to measure rate constants for homogeneous reactions.

The steady-state current, *i*, for an ultra-micro disk electrode is given by eqn. (1) where *n* is the number of electrons, *F* is the Faraday constant, *D* is the diffusion coefficient, *c* is the substrate concentration, and *r* is the radius of the electrode. The current is thus proportional to the concentration. For pseudo first-order kinetics eqns. (2) and (3) apply, where *t* is the time, *i* is the current, $i_0$ is the current at $t = 0$, and *k* is the pseudo first-order rate constant.

$$i = 4nFDcr \qquad (1)$$

$$i/i_0 = \exp(-kt) \qquad (2)$$

$$\ln(i) = -kt + \ln(i_0) \qquad (3)$$

This paper describes the use of ultra-microelectrodes for monitoring slow homogeneous reactions. The dropping mercury electrode[13] and the rotating disk electrode[14,15] have previously been used for following slow homogeneous reactions electrochemically. The reaction [eqns. (4)–(6)] chosen in order to exemplify such a use of ultra-microelectrodes, is the electron-transfer reaction (ET) between anion radicals of aromatic compounds such as perylene, benzophenone and quinoxaline (A) and sterically hindered alkyl halides (BX) such as 2-chloro-2-methylpropane (**1**), 1-bromoadamantane (**2**), and 1-bromo-2,2-dimethylpropane (**3**).

$$\mathrm{A^{-\bullet} + B\text{–}X \xrightarrow{k_4} A + B^{\bullet} + X^{-}} \qquad (4)$$

$$\mathrm{A^{-\bullet} + B^{\bullet} \xrightarrow{k_5} A\text{–}B^{-}} \qquad (5)$$

$$\mathrm{A^{-\bullet} + B^{\bullet} \xrightarrow{k_6} A + B^{-}} \qquad (6)$$

Reactions (5) and (6) are fast compared with (4), and the steady-state approximation can be applied to $\mathrm{B^{\bullet}}$. The kinetics are discussed in detail in Ref. 16. The differential equation for the disappearance of the anion radical is given in eqn. (7).

$$\begin{aligned}\mathrm{d(A^{-\bullet})}/\mathrm{d}t &= -k_4\mathrm{(A^{-\bullet})(BX)} - (k_5 + k_6)\mathrm{(A^{-\bullet})(B^{\bullet})} \qquad (7)\\ &= -2k_4\mathrm{(A^{-\bullet})(BX)}\end{aligned}$$

It is worth noticing that this method, unlike the LSV and CV method published before,[16] is insensitive to changes in the ratio between $k_5$ and $k_6$.

We have studied this reaction for some time, being interested in the ET/$S_N2$ transition,[13,16-22] and the rate constants have generally been measured by cyclic voltammetry. Polarography has been used only for the very slow reactions ($k_4 < 1.0$ M$^{-1}$ s$^{-1}$), i.e. reactions between mediators and sterically hindered alkyl halides such as **1**, **2** and **3**.[13]

Experimentally the aromatic compound, A, was reduced to the anion radical at a mercury pool. The potential of the ultra-microelectrode was then adjusted to a value at which the anion radical was reoxidized at a diffusion-controlled rate. The alkyl halide was then added and the decay of the oxidation current was recorded.

Reactions with a half-time less than 10 s are not mea-

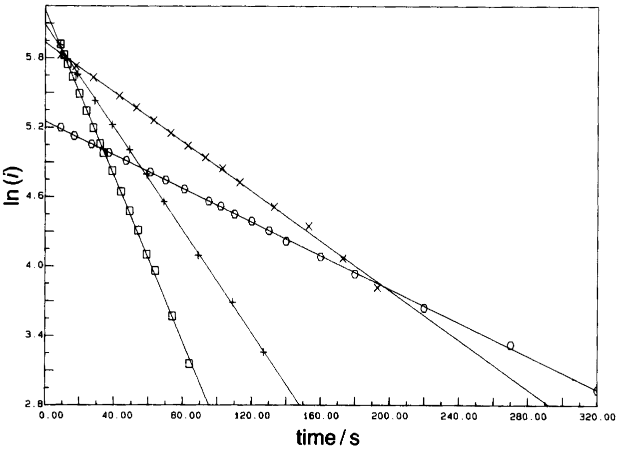

*Fig. 1.* Current decay curves: the natural logarithm of the oxidation current of the anion radical plotted against time (s) for the four combinations of A/BX: (+) benzophenone/**3**, (×) perylene/**3**, (□) perylene/**2** and (○) quinoxaline/**1**.

sureable by this technique owing to incomplete mixing or an insufficient decay curve. Ultra-microelectrodes are thus useful for the monitoring of first-order reactions with rate constants less than 0.07 $s^{-1}$. The smallest measurable rate constant depends on the stability of $A^{-\bullet}$ but this was not a problem in the present investigation. Rate constants as low as $10^{-4}$ $M^{-1}$ $s^{-1}$ should be measurable when side reactions are negligible.

The experimental results are shown in Fig. 1 where the natural logarithm of the current is plotted versus time (s) for four combinations of anion radical and alkyl halide. The straight lines were determined by linear least-square methods and the correlation coefficients were in no case smaller than 0.999. All experiments were performed with an excess of ca. 10 or more, and pseudo first-order kinetics were assumed. The slope of the lines in the ln($i$) versus time in the diagram is equal to $2k_4\,c_{BX}$. The calculated values of $k_4$ are shown in Table 1.

The rate constant $k_4$ for the reaction between perylene and **2** was measured four times in independent experiments; it varied between 0.27 and 0.34 $M^{-1}$ $s^{-1}$. The standard deviation was equal to 0.03 $M^{-1}$ $s^{-1}$ or 10%. The rate constants for perylene/**2** and benzophenone/**3** were both determined, by cyclic voltammetry, to be 0.32 and 0.19 $M^{-1}$ $s^{-1}$, respectively. The potentiostatic method with ultra-microelectrodes thus gives reproducible rate constants, which are in accordance with measurements by other techniques.

The use of ultra-microelectrodes is a good alternative to polarography and the rotating disk electrode for the electrochemical monitoring of slow homogeneous reactions. The former method requires only an electrometer preamplifier and the ultra-microelectrodes, whereas the other techniques require more specialized equipment. In cases where adsorption onto platinum is a problem, ultra-microelectrodes plated with mercury can be used.[23] Only where a fresh electrode surface is a requirement, is polarography advantageous compared with measurements with ultra-microelectrodes. Faster homogeneous chemical reactions are best monitored with a rotating disk electrode where the necessary stirring is faster and it is not necessary to wait until the solution is quiescent before measuring. Lower substrate concentrations can also be measured with these larger electrodes.

## Experimental

*Reagents.* The supporting electrolyte, $Bu_4NBF_4$, and solvent, DMF (Fluka AG), were purified by standard procedures. Perylene, benzophenone, quinoxaline, *tert*-butyl chloride, 1-adamantyl bromide and neopentyl bromide were used as received. No electroactive impurities were detected by cyclic voltammetry.

*Instrumentation.* The platinum disk electrodes were manufactured according to instructions in Ref. 24. The electrode was polished with diamond paste (0.25 μm).

The preparative reduction was carried out with a 200 W home-built three-electrode potentiostat. The potentiostatic measurements were made with a new home-constructed computer-controlled three-electrode potentiostat. 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.

*Procedure.* The aromatic compound (15–18 ml, 5 mM in 0.1 M $TBABF_4$/DMF) was reduced to $A^{-\bullet}$ in an H-cell at constant potential; the reduction was more than 95% complete within 15 min. The decay of $A^{-\bullet}$ was then followed

*Table 1.* Rate constants for electron transfer (ET) from electrochemically generated anion-radicals to some sterically hindered alkyl halides in DMF/0.1 M $TBABF_4$ measured by the potentiostatic method using ultra-microelectrodes.

| BX | A | $-e_A$/V[a] | $c_A$/mM | $c_{BX}$/mM | $k_{ET}$/$M^{-1}$ $s^{-1}$ [b] |
|---|---|---|---|---|---|
| **3** | Benzophenone | −1.320 | 5.5 | 51.2 | 0.22 |
| **3** | Perylene | −1.213 | 4.7 | 44 | 0.12, 0.01 |
| **3** | Perylene | −1.213 | 5.9 | 57 | 0.31, 0.03 |
| **1** | Quinoxaline | −1.200 | 19.4 | 525 | 0.0065 |

[a]Measured against the Ag/AgI, $I^-$ (0.1 M) reference electrode. [b]Measured at $T$ = 22 °C.

with the 10 μm platinum disk electrode using a mercury pool as a counter electrode. The potential of the ultramicroelectrode was chosen such that $A^{-\bullet}$ was oxidized at a diffusion-controlled rate to A. The anodic current of $A^{-\bullet}$ was followed for 1 min; the alkyl bromide was then added with vigorous stirring and while the reaction was bubbled with nitrogen. After some seconds the stirring and bubbling were stopped, the current was monitored, and an exponential decay of the current was observed. The measurements from the first 5 s after the stirring was stopped were always discarded. The current was followed for a minimum of 8 min.

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