

the first reduction peak, the voltammogram is unaltered.

Controlled potential electrolysis have been carried out for the 4-picolyphenylthioether in DMF/ Bu_4NBF_4 at just 50 mV after the first reduction peak.

A plot of the current *versus* charge passed during the electrolysis was linear and the number of electrons involved per molecule of starting material was equal to 2.

In this case, thiophenol was identified as a product with a yield of the the order of 85%.

Almost identical data was obtained in DMF/ $\text{NaClO}_4 \cdot \text{H}_2\text{O}$. This medium has the advantages that the water will mediate the strongly basic conditions created during the electrolysis and that the sodium salt is readily separated from products by water extraction.

Thus, the cleavage by cathodic reduction of the picolyl group occurs in high yields and in a convenient potential range, which may well make it a very suitable protecting group of the thiol function.

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THE EFFECT OF ELECTROLYTE CONCENTRATION ON THE BEHAVIOUR OF ELECTROCHEMICAL SYSTEMS

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The electrochemical techniques usually employ high concentrations of electrolyte because i) it lowers the solution resistance, which is particularly high in many organic solvents, ii) its presence supresses the migration current. This is, however, a disadvantage of electrochemistry when compared with spectroscopic techniques, such as NMR, ESR, etc., whose measurements have no equivalent requirement for addition of electrolyte. In fact, the addition of an electrolyte limits the usefulness of voltammetric studies in thermodynamics, kinetics and analytical investigations. Therefore, it would be highly desirable if electrochemical studies could be carried out in the absence of electrolyte.

Recent developments in microelectrodes design, instrumentation and theory have shown that many new possibilities are open for electrochemical science. In particular, this has been demonstrated by voltammetric studies in solutions containing low concentrations of electrolyte[1], in the absence of electrolyte[2], in glasses[3] and in solvents with very low dielectric constant[4].

In this work we report preliminary results of an investigation of the effect of the electrolyte concentration on the reduction of nitrotoluene in N,N-dimethylformamide at gold microdiscs.

Figure 1 shows an I-E curve for the reduction of a solution of nitrotoluene 4×10^{-4} mol dm⁻³ in N,N-dimethylformamide and Bu₄NBF₄ (TBAB) (4×10^{-2} mol dm⁻³), at a gold microdisc electrode.

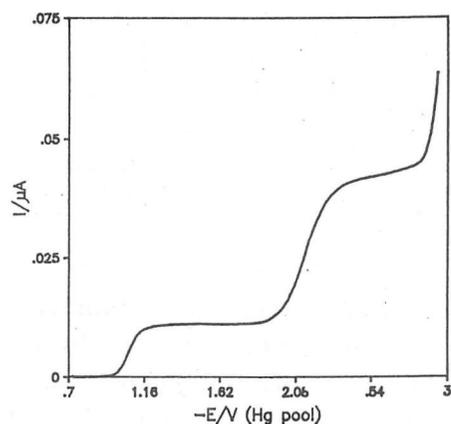


Figure 1. I-E curve for the reduction of a solution of nitrotoluene 4×10^{-3} mol dm⁻³ in N,N-dimethylformamide and Bu₄NBF₄ (TBAB) (4×10^{-2} mol dm⁻³), at a gold microdisc electrode.

Two waves are observed at approximately -1.1 V and -2.2 V vs Hg and the ratio between limiting currents is close to 3. The first process corresponds to a reversible monoelectronic reduction because $E_{3/4} - E_{1/2} \cong 60$ mV.

Under similar conditions, I-E curves of nitrotoluene were recorded using microdiscs with different radii. It was observed that a plot of the plateau current intensity of the first process as a function of the radius, r, of the microdisc was linear, (Figure 2) according to the equation

$$I_d = 4nFDcr$$

From the slope of the curve the diffusion coefficient, D, was determined to be 1.7×10^{-5} cm² s⁻¹, assuming n=1.

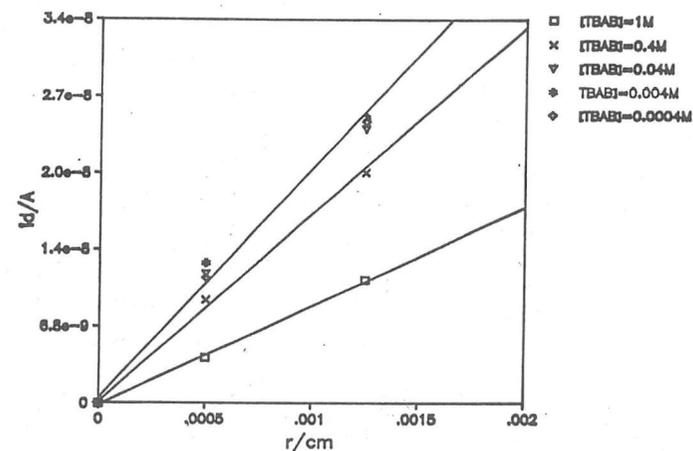


Figure 2. Variation of I_d vs r for a set of TBAB concentrations.

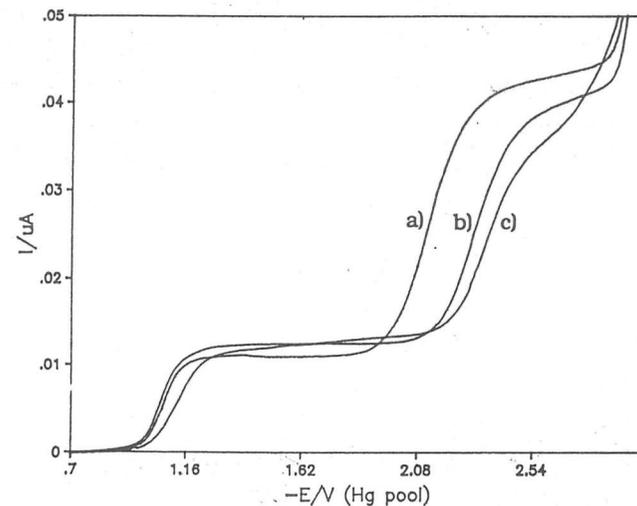


Figure 3. I-E curves for the solution of 4×10^{-3} mol dm⁻³ of nitrotoluene in DMF containing a) 4×10^{-2} mol dm⁻³; b) 4×10^{-3} mol dm⁻³; c) 4×10^{-4} mol dm⁻³ of TBAB Au microdisc, $r = 5 \times 10^{-4}$ cm.

I-E curves were recorded for other electrolyte concentrations, namely, 4×10^{-2} , 4×10^{-3} and 4×10^{-4} mol dm⁻³. The results obtained are presented in Figure 3 for three concentrations.

Table 1 shows values of D corresponding to the different electrolyte concentrations used. The decrease in the value of D with [TBAB] can be explained in terms of the increase of the viscosity of the solutions.

Table 1. Values of diffusion coefficient as a function of TBAB concentration.

[TBAB]/mol dm ⁻³	D/cm ² s ⁻¹
1	5.7×10^{-6}
0.4	1.0×10^{-5}
0.04	1.3×10^{-5}
0.004	1.3×10^{-5}
0.0004	1.3×10^{-5}

It is observed that although the wave corresponding to the first process does not show pronounced change (probably for solutions containing lower concentrations of electrolyte the wave will be less steep due to ohmic drop) the wave corresponding to the second process not only diminishes in height but also shifts to more negative potential values as the electrolyte concentration decreases. For [TBAB] \cong 0 the ratio between the two limiting currents approaches 1.

Figure 4 shows the variation of $E_{1/2}$ with log [TBAB]. The plot is linear with a slope close to 100 mV, suggesting a mechanism of the ECE type.

A possible explanation for this behaviour can be given in terms of the reduction mechanism of nitrotoluene in aprotic and moderately protic media. In aprotic medium nitrotoluene probably reduces according to the following mechanism (nitrobenzene has a similar reduction mechanism[5]):

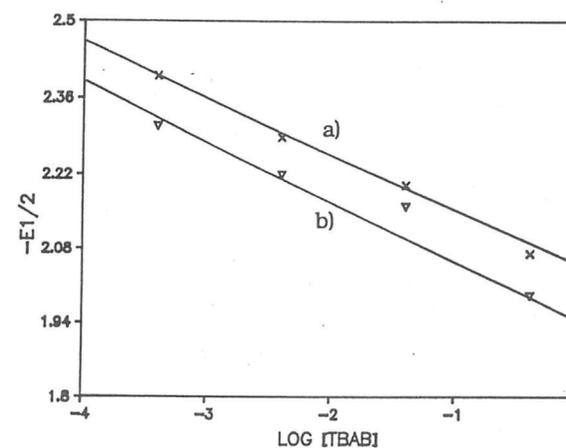
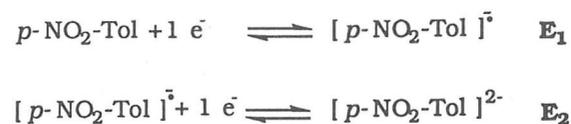
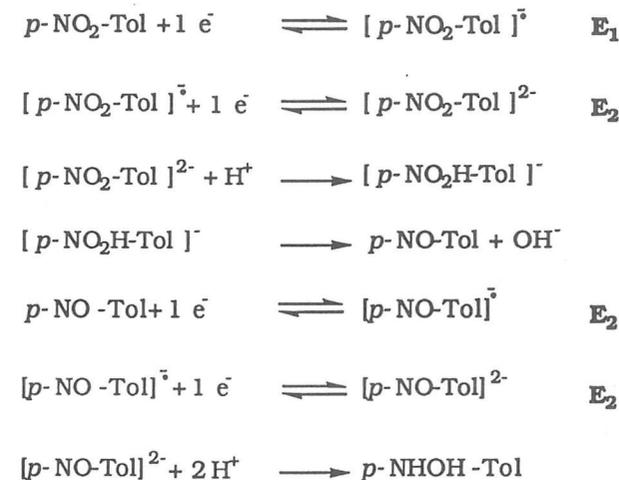


Figure 4. Variation of $E_{1/2}$ with log [TBAB], for solutions of 4×10^{-3} mol dm⁻³ of nitrotoluene in DMF and two electrode radii. a) $r=5 \times 10^{-4}$ cm; b) $r=12.5 \times 10^{-4}$ cm.

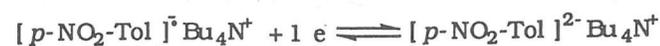
In cyclic voltammetry two reversible monoelectronic reduction processes occur at potentials E_1 and E_2 . In the presence of a weak proton donor, however, the mechanism is:



Since the experiments with microelectrodes support a mechanism involving 1+3 electrons, it is possible to assume that the medium used DMF/TBAB is sufficiently protic to yield the second mechanism presented. On the other hand, the decreasing of the height of the second plateau current with the decreasing of the concentration of TBAB seems to indicate that the electrolyte is the proton source. This hypothesis can only be confirmed when other electrolytes with different proton donor capabilities are used and these studies are now in progress.

There are, however, other possible explanations for the behaviour of nitrotoluene in the absence of electrolyte or in the presence of low concentrations of electrolyte.

After the formation of the anion radical (corresponding to the first process), this can form an ion pair with the electrolyte cation (Bu_4N^+) thus facilitating the transfer of the second electron. The removal of the electrolyte inhibits the formation of the ionic pairs and, therefore, it will difficult the formation of the dianion, rendering this reduction more negative and causing a decrease in the wave height. The mechanism suggested would be:



On the other hand, migration has also some effect on the second wave. In the absence of electrolyte mass transport of the anion radical in the direction of the electrode is inhibited by an effect of migration in the reverse direction. It is known theoretically[6], however, that the wave will diminish on maximum 20% due to this effect and thus, migration does not explain by itself, the drastic decrease in the height of the second wave.

Therefore, the results seem to support the role of the electrolyte as a proton donor, although its participation in the formation of ion pairs should not be excluded. Furthermore, the role of migration, ohmic drop and also the effects of the double layer as the concentration of electrolyte diminishes should be considered. These effects can only be completely understood after more detailed studies are carried out.

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