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Quantitative voltammetry of the reduction of methyl benzoate in THF reveals strong ion pairing of the radical anion with tetra-*n*-butyl cations

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The reduction of methyl benzoate was studied in tetrahydrofuran (THF), 0.1 M TBAP, both at platinum and glassy carbon macroelectrodes and at platinum microelectrodes. While cyclic voltammograms obtained at macroelectrodes show extensive distortion due to ohmic drop, this distortion is negligible for cyclic voltammograms obtained at microelectrodes. The system methyl benzoate/methyl benzoate radical anion was found to be chemically reversible. The fitting of chronoamperometric measurements using the Shoup and Szabo's expression obtained at microdisc electrodes allowed us to estimate the diffusion coefficient of methyl benzoate. Cyclic voltammetry was modelled allowing the determination of the formal potential, E_f^0, of the transfer coefficient, α, and of the standard heterogeneous kinetic constant for the electron transfer, k_0. Furthermore, it was found that the diffusion coefficient for the radical anion produced at the electrode surface has an apparent value of $2.1 \times 10^{-6} \pm 0.5\ cm^2\ s^{-1}$ (25 °C) which is *ca.* 10 times smaller than the value obtained for the diffusion coefficient of methyl benzoate ($2.1 \times 10^{-5} \pm 0.1\ cm^2\ s^{-1}$). Taking into account the species present in solution, this result could only be explained by a strong ion pairing between the methyl benzoate anion radical and the tetra-*n*-butylammonium cation used as an electrolyte ion in the solution. The ion pair is found to be stable on the time scale of cyclic voltammetry and no evidence of any following homogeneous chemical reaction was found. Further studies involved the performance of cyclic voltammetry and chronoamperometry at low temperatures (down up to −81 °C) and the analysis of this data allowed the determination of the activation energy, E_A, through an Arrhenius plot, both for the diffusion coefficient and for the electron transfer reaction.

Supporting information may be found in the online version of this article.

Keywords: cryoelectrochemistry; tetrahydrofuran; electrode reaction mechanisms; diffusion coefficients; single electron transfer; microelectrodes; ion pairs; TBAP

INTRODUCTION

Molecular electrochemistry, the study of electron transfers between an electrode surface and a molecule in solution (heterogeneous electron transfer), is a powerful tool to access to many physical parameters that are useful to understand how a molecule will react. Moreover, specific kinetic properties might lead to the development of useful electrosynthetic methodologies. Studies in tetrahydrofuran (THF) are of particular interest as it is a solvent that is widely used in chemical synthesis. Furthermore, the potential window available for electrochemical measurements is very wide especially towards the negative potentials; measurements at low temperature (cryoelectrochemistry) are possible because of the low freezing point of THF which extend the potential window even further.[1,2] Moreover, working at low temperature slows down both the electron transfer kinetics and reaction kinetics of any following chemical reactions thus allowing an easier insight into their mechanisms.[1–4]

Only a few studies dealing with the reduction of esters at electrode surfaces have been published.[5–17] In general, it has been accepted that the electrode reaction mechanism involves an electron transfer, and the radical anion that is produced undergoes a dissociation in a second and distinct step (Scheme 1). In some cases; however, it has been shown that the electron transfer step is fully reversible in the timescale of

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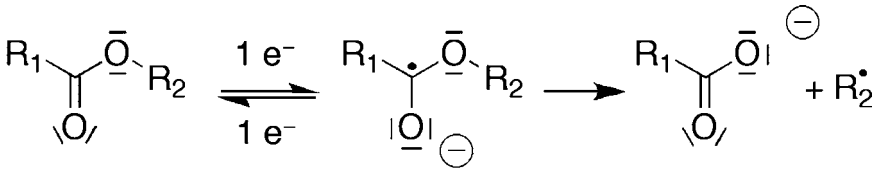


Scheme 1. Equation for the reduction of an ester at an electrode surface following a stepwise dissociative electron transfer mechanism

cyclic voltammetry, which means that the electron transfer is fast enough (electrochemical reversibility) and that the radical anion produced is stable enough and this stability has been explained by charge stabilization through electronic delocalization (chemical reversibility). It has been found that the exhaustive electrolysis of methyl benzoate in DMF and in MeCN leads respectively to benzoate and benzoylacetonitrile.[7] Methyl benzoate radical anion is thus not very stable even though it has been used as a redox mediator in DMF, 0.1 M tetra-*n*-butylammonium hexafluorophosphate, TBAF.[5] No reports on low temperature electrochemistry of esters exist to date.

As far as ion pairing is concerned, it occurs when there is an association of oppositely charged ions in electrolyte solutions to form distinct chemical species.[18] Whilst it is well known that ion pairing occurs between organic anions and alkali metals (especially for the lithium cation), the degree of ion pairing between electrochemically generated ions and supporting electrolytes is usually considered to be small enough to be neglected in most electrolyte solvents for example acetonitrile.[19] However, the large concentration of supporting electrolytes used in electrochemical studies might in some cases result in strong ion pair associations, especially in solvents with a low dielectric constant such as THF. Such phenomena will have non-negligible kinetic and mechanistic implications,[19] and recently specific efforts have been devoted to the study of ion pairs in electrochemistry.[19–27]

In the course of the last few years, a methodology has been developed in our laboratory for the study of organic molecules in THF and at low temperature. In this publication, we report the study of the reduction of methyl benzoate in THF containing TBAP. Voltammetric and chronoamperometric measurements show that the mechanism of the electrode reaction involves a fast electron transfer and that the radical anion produced is stabilized through the formation of an ion pair. Such a strong ion pair association considerably slows down the diffusion of the radical anion and also stabilizes it, so that there is no dissociation on the voltammetric time scale. To the best of our knowledge this is the first time in the literature that an ion pairing has been reported between an ester radical anion and a tetraalkylammonium cation.

EXPERIMENTAL

Chemicals

Methyl benzoate (99 wt. %) was supplied from Acros and was used without further purification. Ferrocene (purum, 98 wt. %), ferrocenium hexafluorophosphate and tetra-*n*-butylammonium hexafluorophosphate (TBAF, 98 wt. %) were obtained from Aldrich. Tetra-*n*-butylammonium perchlorate (TBAP, electrochemical grade) was purchased from Alfa Aesar (Heysham, UK) and was purified using a method given in the literature.[28] Acetonitrile (HPLC Gradient grade), acetone (99.82 wt. %) and diethyl ether (Analytical reagent grade, 99.97 wt. %) were obtained from Fisher Scientific (Loughborough, UK). THF (anhydrous) was supplied by Rathburn Chemicals Ltd. (UK); it was kept under a nitrogen atmosphere and filtrated before use through two columns of activated alumina (Alcoa, grade DD-2). Argon (impurity free) was obtained from BOC Gases (Guildford, UK).

Instrumentation and procedures

Electrochemical measurements were carried out using an Eco Chemie PGSTAT20 potentiostat (Eco-Chemie, Utrecht, Netherlands) connected to a computer. The electrochemical cell used was an airtight standard three-electrode cell. A 25 mL three-neck glass flask was used as the cell container. The working macrodisc electrodes were, respectively, a homemade 1 mm diameter platinum electrode (Pt wire obtained from Goodfellow Cambridge Ltd., Cambridge, UK, housed in Teflon) and a 3 mm diameter glassy carbon electrode (GlC, BASi, USA). The working microdisc electrode was a 10 μm diameter Pt electrode (Cypress Systems Inc., Kansas, USA). The auxiliary electrode consisted in a 0.5 mm diameter platinum wire (Goodfellow Cambridge Ltd., Cambridge, UK). A ferrocene/ferrocenium hexafluorophosphate ($Fc/Fc^+PF_6^-$) reference electrode was developed for use in THF and for cryoelectrochemical experiments.[29] It consists in a platinum wire partially immersed in a 4 mM equimolar ferrocene/ferrocenium ion hexafluorophosphate ($Fc/Fc^+PF_6^-$) and 0.1 M tetra *n*-butylammonium hexafluorophosphate, TBAF, solution in THF. The reference is housed in a distinct compartment separated from the cell solution compartment by a porous frit.

The working electrodes were all carefully polished on a clean polishing pad (Kemet, UK) using 1.0 and 0.3 μm aqueous alumina slurries (Beuhler, Lake Buff, Il, USA), and subsequently rinsed in de-ionized and doubly filtered water. The electrodes were oven-dried and cooled in a desiccator over silica gel crystals prior to use. Before carrying out electrochemical experiments in THF, the microdisc radius was electrochemically calibrated by recording a voltammogram corresponding to the ferrocene oxidation at 0.01 $V\,s^{-1}$ in a 3 mM ferrocene and 0.1 M TBAF acetonitrile solution.

Rigorous procedures have to be applied to avoid the presence of humidity in the cell. In brief, flasks containing the electrolytic salt were kept under vacuum overnight. The flasks were then filled with argon and kept under a moderate argon pressure by the use of an inflatable plastic balloon filled with argon and attached to a needle through the Suba-Seal® cap. The THF was then transferred directly from the column to the flask using a connecting needle. The electrochemical cell was similarly carefully dried under vacuum and then filled with argon. The flasks were also flame heated under argon flow to minimize the presence of humidity. The solution was then transferred to the cell using a syringe. Syringes and needles, used for the transfer of reagents or the electrolytic solution, were oven-dried and cooled

in a desiccator over silica gel crystals. The same precautions have to be taken for the preparation of the reference compartment. Typically the solutions were degassed with argon for 3 min to remove oxygen traces and an inert argon atmosphere was maintained throughout all measurements by the help of inflatable plastic balloons filled with argon. All electrochemical experiments were run within a Faraday cage in order to minimize background noise.

In the case of cryoelectrochemical experiments, the electrochemical cell was immersed in an acetone bath for which the temperature is set and controlled by a Julabo FT902 Immersion cooler equipped with a thermometer. The temperature was varied from 20 to −81 °C using this setup.

Diffusion coefficients

The diffusion coefficients assumed for ferrocene were 2.3×10^{-5} and 1.8×10^{-5} $cm^2\,s^{-1}$ [29,30], respectively in acetonitrile and THF (at 25 °C).

Fitting of experimental voltammograms and chronoamperograms

Experimental voltammograms obtained at macroelectrodes were modelled using the software Digisim®. Experimental voltammograms obtained at microelectrodes were modelled using a simulation program developed in our laboratory.[31]

Experimental chronoamperograms obtained at microelectrodes were fitted using the software Origin 7.0® and the Shoup and Szabo expression[32] following a method previously reported.[33,34] An experimental chronoamperometric measurement is made over a time scale incorporating a transition from planar diffusion (where the current is proportional to the square root of the diffusion coefficient) to steady state hemispherical diffusion (where the current is proportional to the diffusion coefficient). The deconvolution of the number of electrons transferred, *n*, and the diffusion coefficient, *D*, is then possible from a single chronoamperogram. Practically, accurate values of the concentration and electrode radius have to be entered and the software iterates through values of *D* and *n* until the fit of the experimental data is optimized.

RESULTS AND DISCUSSION

Voltammetry at macroelectrodes

The reduction of methyl benzoate at platinum or glassy carbon macrodisc electrodes provides well-defined chemically reversible cyclic voltammograms (Fig. 1) and peak potentials of −3.14 and −3.32 V/($Fc/Fc^+PF_6^-$) at 0.1 $V\,s^{-1}$ were obtained respectively at platinum and glassy carbon electrodes. Given the magnitude of the current passed and the resistive nature of the THF solution it is likely that these voltammograms are slightly distorted because of 'ohmic drop'. Accordingly attention was shifted to the use of microelectrodes to resolve this possible problem. The data extracted from the microelectrode work confirms that the cyclic voltammograms obtained at macroelectrodes are distorted through capacitive and resistive effects (see below).

Voltammetry at microelectrodes

It is possible to minimize the contribution of the ohmic drop and capacitive currents by reducing the size of the electrodes and these effects become negligible at microelectrodes when scanning at reasonably low scan rates.[34] Well-defined cyclic voltammograms were obtained at a 10 μm diameter Pt disc microelectrode between 0.01 and 20 $V\,s^{-1}$ (Fig. 2). At low scan rates a steady state wave is obtained (Fig. 2A) whereas at higher scan rates a peak is obtained (Fig. 2C) with an intermediary shaped voltammogram at (Fig. 2B). Those observations are resulting from the transition between a steady state diffusion regime (hemispherical diffusion, i.e. when $\delta \ll r$, where δ is the diffusion layer thickness and *r* the electrode radius) at low scan rates to a transitory diffusion type regime (linear diffusion, i.e. when $\delta \gg r$) at higher scan rates.[34] The plot of *I versus* $v^{1/2}$, where *I* corresponds to the limiting current, I_{lim}, or to the peak current, I_p, is presented in Fig. 3. The progressive transition towards a Randles–Ševčík behaviour with a linear dependency with $v^{1/2}$ is observed at the higher scan rates. At the lower scan rates the current tends to a limit where the limiting current is known to obey to Eqn (1).

$$I_{lim} = 4nFDCr \quad (1)$$

n is the number of electrons, *F* is the Faraday constant, *D* is the diffusion coefficient in $cm^2\,s^{-1}$, *C* is the substrate concentration in $mol\,cm^{-3}$ and *r* is the electrode radius in centimetre.

Assuming that, we have a one electron transfer the diffusion coefficient, *D*, can be obtained. An estimated value for *D* of 2.1×10^{-5} $cm^2\,s^{-1}$ was found using a measurement made at 0.01 $V\,s^{-1}$ at 20 °C. The transfer coefficient, α, can also be obtained from voltammetric measurements at low scan rates using an ordinary mass transport-corrected Tafel analysis.[35] The mass transport-corrected Tafel plot obtained, Fig. 4, has a slope of 120 mV, which gives an estimated value for α of 0.58 ± 0.01. An analysis of voltammograms obtained in a steady state diffusion regime allows as well, a rough estimation of α and of the

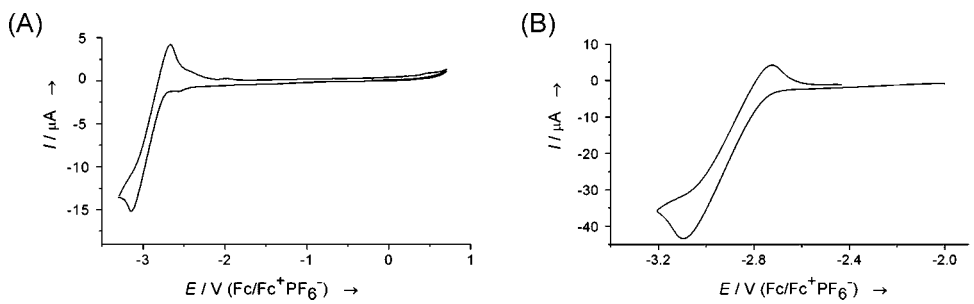


Figure 1. Cyclic voltammogram of a 5 mM methyl benzoate in THF, 0.1 M TBAP, obtained at 293 K, (A) at a 1 mm diameter Pt disc electrode at 0.1 $V\,s^{-1}$, (B) at a 3 mm diameter glassy carbon disc electrode at 0.01 $V\,s^{-1}$

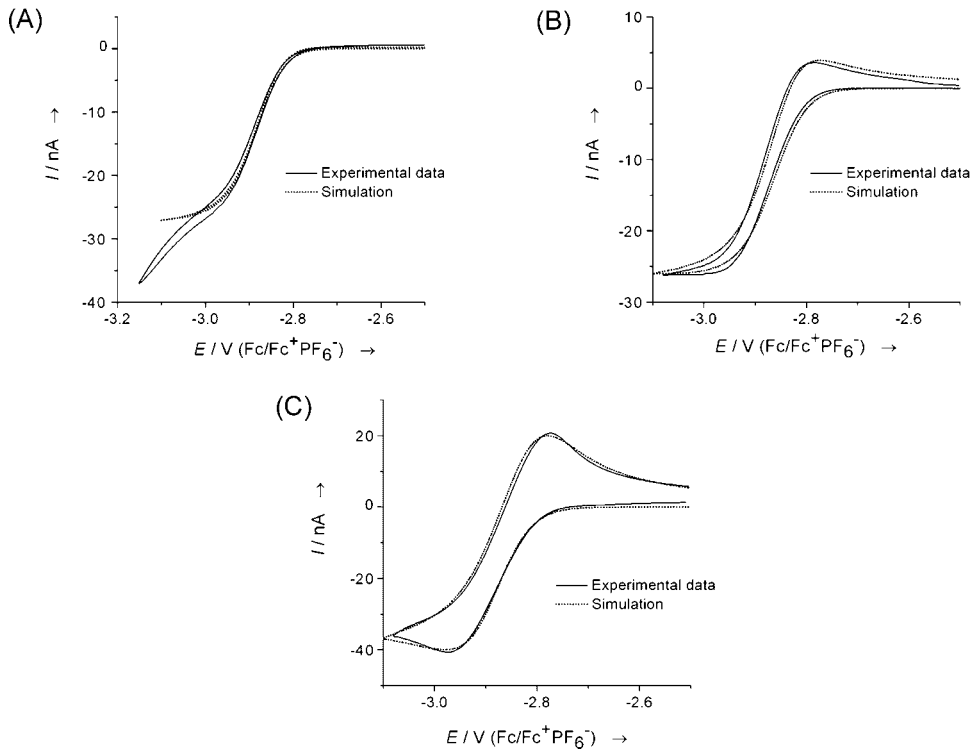


Figure 2. Experimental (solid line) and theoretical (dotted line) voltammograms for the reduction of methyl benzoate, 6 mM, in THF, 0.1 M TBAP, obtained at 293 K at a 10 μm diameter Pt disc microelectrode at various scan rates; (A) 0.01 V s^{-1}, (B) 1 V s^{-1} and (C) 20 V s^{-1}

heterogeneous electron transfer kinetic constant, k_0, using tables published by Mirkin and Bard.[36] Values for α of 0.59 and for k_0 of 0.029 cm s^{-1} were obtained by this method.

Chronoamperometry at microelectrodes

Several methods can be used for the simultaneous determination of *D* and of the number of electrons, *n*, involved in an electrode reaction on the time scale of techniques in transitory diffusion regimes.[37–40] These methods usually require the use of several electrochemical techniques and it is usually necessary to repeat the measurements many times to minimize the error the values that are extracted.[41,42] An alternative method using chronoamperometry was previously reported.[33] It consists in performing a chronoamperometric measurement at a disc microelectrode and then fitting the experimental curve using the Shoup and Szabo expression.[32] The modelling of three chronoamperograms showed that the number of electron involved, *n*, is, as expected, 1 ± 0.1. The value of n entered in the program was then considered to be a non-variable in order to get the maximum precision on the value of *D*. Using this method the values of *D* obtained at 20 °C is 2.18 ± 0.1 cm^2 s^{-1}. The value

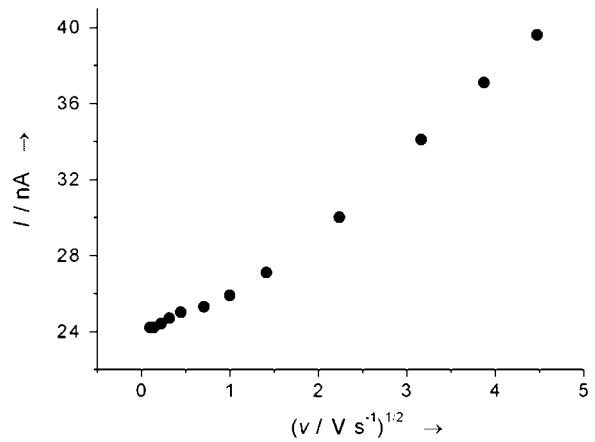


Figure 3. Plot of *I versus* $v^{1/2}$, where *I* corresponds to the limiting current, I_{lim}, or to the peak current, I_p, obtained for the reduction of methyl benzoate, 6 mM, in THF, 0.1 M TBAP, at 293 K at a 10 μm diameter Pt disc microelectrode

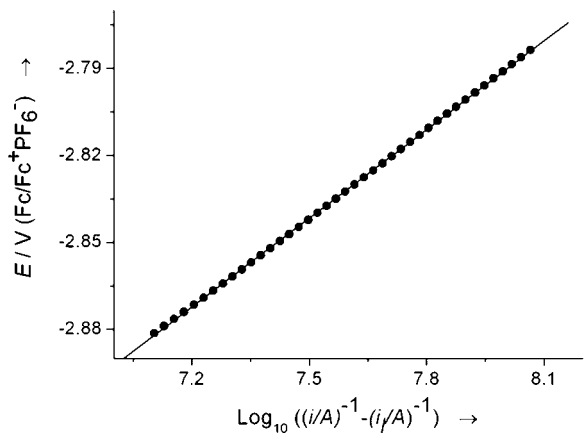


Figure 4. Mass transport-corrected Tafel plot of *E versus* $\log_{10}(I^{-1} - I_{lim}^{-1})$, where *I* corresponds to the current obtained, and I_{lim} to the limiting current, obtained for the reduction of methyl benzoate, 6 mM, in THF, 0.1 M TBAP, at 293 K at 0.01 V s^{-1} at a 10 μm diameter Pt disc microelectrode

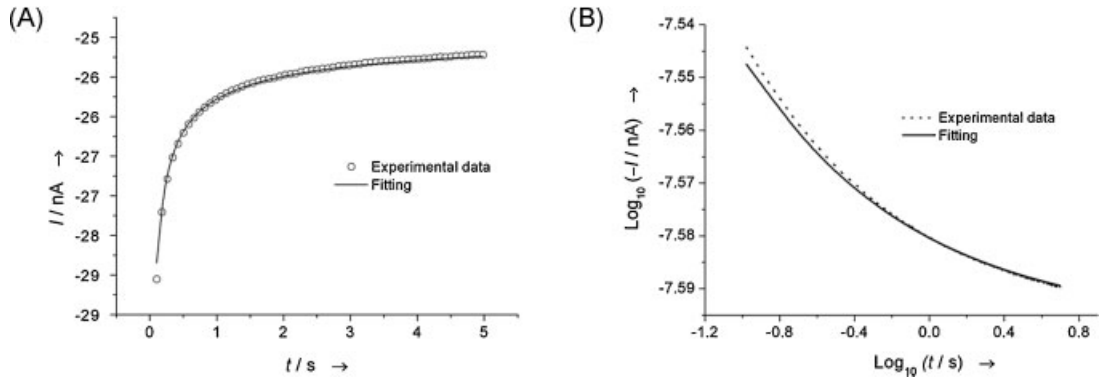


Figure 5. (A) Experimental and theoretical chronoamperometric curves and (B) corresponding logarithmic plot for the reduction of methyl benzoate, 6 mM, in THF, 0.1 M TBAP, obtained at 293 K at a 10 μm diameter Pt disc microelectrode. The potential was stepped from −2.7 to −3.03 V/($Fc/FcPF_6$)

obtained for *D* is then in good agreement with the value calculated above using Eqn (1). The experimental curve and the fitting are presented in Fig. 5A and in a logarithmic form in Fig. 5B.

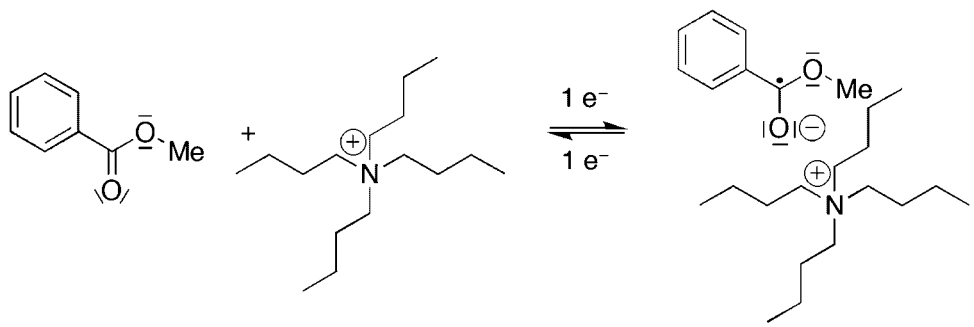
Modelling of voltammograms obtained at microelectrodes

The cyclic voltammograms obtained at 293 K at a 10 μm diameter Pt microelectrodes at 0.01, 0.1 and 20 $V\,s^{-1}$ were modelled imputing, for the precursor, the value of *D* obtained from the modelling of the chronoamperometic curves. Figure 3 shows the modelled voltammograms that were obtained. Values of 0.03 $cm\,s^{-1}$ and 0.55 were found respectively for k_0, and for α, which is in very good agreement with the value estimated above using the tables found in the literature. It can be enlightened that the same value of k_0 was used for this large scan rate range, which strengthen the validity of the estimated value. The value found for the standard potential, E^0, is −2.82 V/($Fc/Fc^+PF_6^-$). An acceptable fitting of the experimental curves can only be obtained when a very low value of the diffusion coefficient corresponding to the radical anion generated is entered in the program; the best fitting having been obtained for a value of $2.1 \times 10^{-6} \pm 0.5\ cm^2\,s^{-1}$, that is to say a value ten fold lower than the value of the corresponding neutral molecule. The radical ion anion diffuses from the electrode surface in a way that would correspond to a much bigger molecule. Taking into account the species that are in presence in the electrochemical cell and the reversibility of the voltammograms recorded, we conclude that the exceptionally low value of the diffusion coefficient of the generated radical anion can only be explained by the association of the methyl benzoate radical anion with the tetra-*n*-butylammonium cation by a strong ion pairing. Furthermore, in regard to the chemical reversibility observed on the time scale of techniques with a transitory diffusion regime, no evidence of any following chemical reaction was found. The proposed equation for the reaction at the electrode then involves a reversible electron transfer with an ion pair association (Scheme 2).

It was reported in the literature that the methyl benzoate radical anion is not chemically stable on the time scale of exhaustive electrolysis in both DMF, 0.1 M TBAP and MeCN, 0.1 M TBAP and that compounds of a similar structure such as *tert*-butyl benzoate show chemical irreversibility on the time scale of voltammetric measurements in DMF, 0.1 M TBAP.[7] It is then likely that the methyl benzoate radical anion is stabilized by the ion pairing with the electrolyte cations in THF as such ion pair associations are favoured in solvent with a low dielectric constant ($\varepsilon_{DMF} = 38$, $\varepsilon_{MeCN} = 37$ and $\varepsilon_{THF} = 7.5$).

Cryoelectrochemistry

Cryoelectrochemical measurements were performed in order to investigate further this system. Chronoamperometric measurements and further modelling were undertaken at various values of the temperature. The values of *D* obtained are reported in Table 1. Figure 6 shows the Arrhenius plot obtained using those values. The linearity of the plot confirms the values of the data obtained. Furthermore, the value of the activation energy for the diffusion, E_A, extracted from the slope is 5.7 $kJ\,mol^{-1}$. Cyclic voltammograms at microelectrodes were also recorded at various values of the temperature and further modelled; an example is given in Fig. 7A. The values of k_0 obtained are reported in Table 1 and the corresponding Arrhenius plot is presented in Fig. 7B. A good linearity was obtained and the value of the



Scheme 2. Equation of the reversible reduction of methyl benzoate at an electrode surface in presence of tetra-*n*-butylammonium cations

Table 1. Values of the diffusion coefficient, D, of the heterogeneous kinetic constant, k_0, and of the formal potential, E_f^0, for methyl benzoate at various temperatures, obtained respectively from the modelling of the chronoamperograms and from the modelling of the cyclic voltammograms obtained at a 10 μm disc platinum microelectrode in THF, 0.1 M TBAP

T/C	D ($cm^2\,s^{-1}$)	k_0 ($cm\,s^{-1}$)	E_f^0
20	2.18	0.030	−2.81
2	2.29	0.018	−2.79
−18	1.87	0.012	−2.78
−38	1.43	0.008	−2.75
−58	1.02	0.0035	−2.73
−81	0.71	0.0020	−2.72

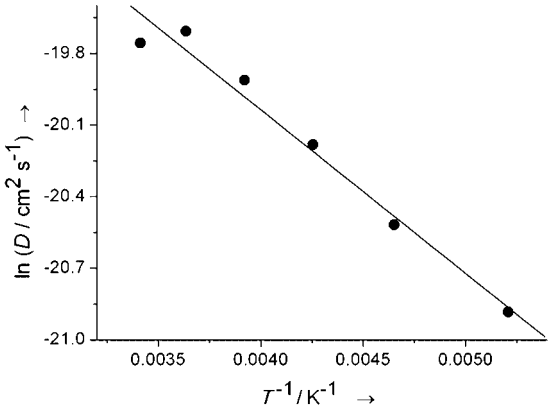


Figure 6. Arrhenius plot of ln D *versus* T^{-1} using the values of D obtained by fitting the chronoamperometric curves obtained for the reduction of methyl benzoate, 6 mM, in THF, 0.1 M TBAP, at a 10 μm diameter Pt disc microelectrode. The potential was stepped from −2.7 to −3.03 V/($Fc/FcPF_6^-$)

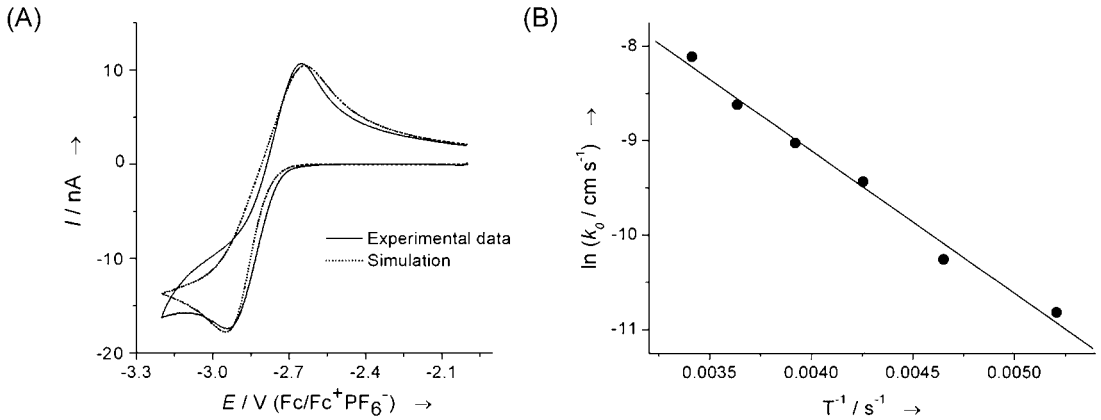


Figure 7. (A) Experimental (solid line) and theoretical (dotted line) voltammograms for the reduction of methyl benzoate, 6 mM, in THF, 0.1 M TBAP, obtained at 192 K at a 10 μm diameter Pt disc microelectrode at a scan rate of 20 $V\,s^{-1}$. (B) Arrhenius plot of ln k_0 *versus* T^{-1} using the values of k_0 obtained by fitting the voltammograms obtained for various values of T in the experimental conditions specified in (A)

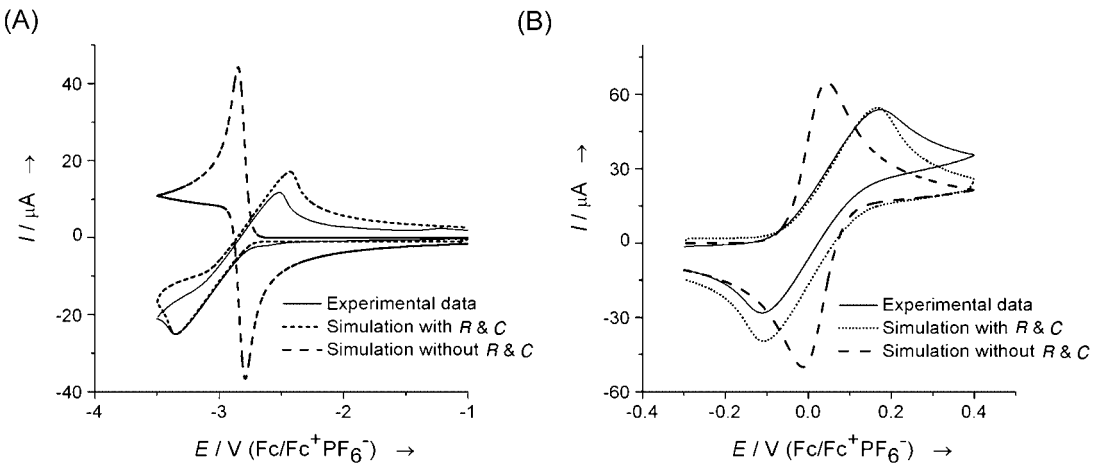


Figure 8. (A) Experimental and simulated cyclic voltammetry with and without resistance, R, and capacitance, C, parameters at a 1 mm Pt disc electrode at 0.1 $V\,s^{-1}$ and at 293 K of a THF, 0.1 M TBAP, solution containing; (A) 5 mM methyl benzoate and (B) 5 mM ferrocene

activation energy for the heterogeneous electron transfer, E_A, extracted is 12.5 kJ mol^{-1}.

Modelling of voltammograms obtained at macroelectrodes

In order to analyse further the voltammograms obtained at macroelectrodes, we used the software Digisim®. Using the parameters derived from the microelectrode experiments the inclusion of significant resistance ($R = 1.8 \times 10^4\,\Omega$) and capacitance ($C = 2 \times 10^{-6}$ F) was required to simulate the voltammograms. Figure 8 corresponds to the fit with and without the R and C effects confirming the significant distortion of the macroelectrode data.

CONCLUSION

The study of the reduction of methyl benzoate both at microelectrodes in THF reveals that the methyl benzoate radical anion created is stable on the timescale of voltammetric experiments. The careful modelling of the cyclic voltammograms obtained at moderately fast scan rates up to 20 V s^{-1} at microelectrodes suggests that the methyl benzoate radical anion forms an ion pair with the tetra-*n*-butylammonium cation used as an electrolyte ion in the solution. No evidence of a following up homogeneous reaction was found in THF, 0.1 M TBAP, as the ion pairing association with the electrolyte cation tetra-*n*-butylammonium stabilizes the methyl benzoate radical anion generated.

Acknowledgements

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REFERENCES

[1] N. Fietkau, C. A. Paddon, F. L. Bhatti, T. J. Donohoe, R. G. Compton, *J. Electroanal. Chem.* **2006**, *593*, 131–141.
[2] C. A. Paddon, F. L. Bhatti, T. J. Donohoe, R. G. Compton, *J. Electroanal. Chem.* **2006**, *589*, 187–194.
[3] C. A. Paddon, F. L. Bhatti, T. J. Donohoe, R. G. Compton, *Chem. Commun.* **2006**, 3402–3404.
[4] N. C. L. Wood, C. A. Paddon, F. L. Bhatti, T. J. Donohoe, R. G. Compton, *J. Phys. Org. Chem.* **2007**, *20*, 732–742.
[5] C. Amatore, C. Pebay, O. Scialdone, S. Szunerits, L. Thouin, *Chem. Eur. J.* **2001**, *7*, 2933–2939.
[6] C. P. Andrieux, C. Blocman, J. M. Dumas-Bouchiat, J. M. Savéant, *J. Am. Chem. Soc.* **1979**, *101*, 3431–3441.
[7] J. H. Wagenknecht, R. D. Goodin, P. J. Kinlen, F. E. Woodard, *J. Electrochem. Soc.* **1984**, *131*, 1559–1565.
[8] R. D. Webster, A. M. Bond, R. G. Compton, *J. Phys. Chem.* **1996**, *100*, 10288–10297.
[9] D. Fleury, J. Moiroux, *Electrochim. Acta* **1975**, *20*, 369–375.
[10] M. Heintz, M. Devaud, H. Hebri, E. Dunach, M. Troupel, *Tetrahedron* **1993**, *49*, 2249–2252.
[11] A. Inesi, L. Rampazzo, *J. Electroanal. Chem.* **1973**, *44*, 25–35.
[12] S. Kashimura, Y. Murai, M. Ishifune, H. Masuda, H. Murase, T. Shono, *Tetrahedron Lett.* **1995**, *36*, 4805–4808.
[13] T. Shono, M. Ishifune, H. Kinugasa, S. Kashimura, *J. Org. Chem.* **1992**, *57*, 5561–5563.
[14] T. Shono, H. Masuda, H. Murase, M. Shimomura, S. Kashimura, *J. Org. Chem.* **1992**, *57*, 1061–1063.
[15] R. D. Webster, A. M. Bond, *J. Chem. Soc. Perk. Trans. 2* **1997**, 1075–1079.
[16] R. D. Webster, A. M. Bond, *J. Org. Chem.* **1997**, *62*, 1779–1787.
[17] R. D. Webster, A. M. Bond, T. Schmidt, *J. Chem. Soc. Perk. Trans. 2* **1995**, 1365–1374.
[18] Y. Marcus, G. Hefter, *Chem. Rev.* **2006**, *106*, 4585–4621.
[19] J.-M. Savéant, *J. Phys. Chem. B* **2001**, *105*, 8995–9001.
[20] H. Cruz, I. Gallardo, G. Guirado, *Electrochim. Acta* **2008**, *53*, 5968–5976.
[21] J.-M. Savéant, *J. Am. Chem. Soc.* **2008**, *130*, 4732–4741.
[22] M. M. Islam, T. Ohsaka, *J. Phys. Chem. C* **2008**, *112*, 1269–1275.
[23] K. Miyoshi, M. Oyama, S. Okazaki, *Electroanalysis* **2001**, *13*, 917–922.
[24] K. B. Oldham, T. J. Cardwell, J. H. Santos, A. M. Bond, *J. Electroanal. Chem.* **1997**, *430*, 39–46.
[25] A. J. Wain, G. G. Wildgoose, C. G. R. Heald, L. Jiang, T. G. J. Jones, R. G. Compton, *J. Phys. Chem. B* **2005**, *109*, 3971–3978.
[26] J. J. Watkins, H. S. White, *Langmuir* **2004**, *20*, 5474–5483.
[27] J. J. Watkins, H. S. White, *J. Electroanal. Chem.* **2005**, *582*, 57–63.
[28] R. B. Morris, K. F. Fischer, H. S. White, *J. Phys. Chem. C* **1988**, *92*, 5306–5313.
[29] C. A. Paddon, R. G. Compton, *Electroanalysis* **2005**, *17*, 1919–1923.
[30] M. Sharp, *Electrochim. Acta* **1983**, *28*, 301–308.
[31] N. V. Rees, O. V. Klymenko, R. G. Compton, M. Oyama, *J. Electroanal. Chem.* **2002**, *531*, 33–42.
[32] D. Shoup, A. Szabo, *J. Electroanal. Chem.* **1982**, *140*, 237–245.
[33] C. A. Paddon, D. S. Silvester, F. L. Bhatti, T. J. Donohoe, R. G. Compton, *Electroanalysis* **2007**, *19*, 11–22.
[34] R. G. Compton, C. E. Banks, *Understanding Voltammetry*, World Scientific Publishing Co. Pte. Ltd., Singapore, **2007**.
[35] W. J. Albery, *Electrode Kinetics*, Oxford University Press, Oxford, **1975**.
[36] M. V. Mirkin, A. J. Bard, *Anal. Chem.* **1992**, *64*, 2293–2302.
[37] C. Amatore, M. Azzabi, P. Calas, A. Jutand, C. Lefrou, Y. Rollin, *J. Electroanal. Chem.* **1990**, *288*, 45–63.
[38] C. Amatore, A. Jutand, L. Thouin, J.-N. Verpeaux, *Actual. Chim.* **1998**, 43–63.
[39] S. Daniele, P. Ugo, G. A. Mazzocchin, G. Bontempelli, *Anal. Chim. Acta* **1988**, *211*, 325–331.
[40] M. Kakihana, H. Ikeuchi, G. P. Sato, K. Tokuda, *J. Electroanal. Chem.* **1981**, *117*, 201–211.
[41] R. Baron, A. Darchen, D. Hauchard, *Electrochim. Acta* **2006**, *51*, 1336–1341.
[42] R. Baron, A. Darchen, D. Hauchard, *Electrochim. Acta* **2004**, *49*, 4841–4847.