PERKIN 2

In situ electrochemical-ATR-FTIR spectroscopic studies on solution phase carboxylate radical anions†

Richard D. Webster

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia.
E-mail: webster@rsc.anu.edu.au; Fax: + 61 2 6125 0750

Received (in Cambridge, UK) 24th June 2002, Accepted 2nd September 2002
First published as an Advance Article on the web 14th October 2002

Pyridine- and benzene-based *para*- and *meta*-substituted diesters (**1**) were reduced by one-electron in CH_3CN (with 0.1 M Bu_4NPF_6 as the supporting electrolyte) in a two-compartment controlled potential electrolysis cell at negative potentials [-2.0 to -2.5 V *vs.* Fc/Fc$^+$ (Fc = ferrocene)] to produce anion radicals (**2**) that subsequently decomposed to form carboxylate anions (**3**). The sequence of reactions beginning with **1** being reduced to **2**, then **2** reacting to form **3** was monitored using *in situ* FTIR spectroscopy with an attenuated total reflectance (ATR) probe containing a diamond composite sensor inserted into the working electrode compartment of the electrolysis cell. Analysis of the data obtained during the reduction of several esters allowed for the first time the identification of spectral features that can be considered typical of carboxylate radical anions (**2**). It was observed that the C=O bond stretch that occurs in the neutral esters (**1**) at 1720–1730 cm^{-1} was missing from the spectra of the anion radicals (**2**). Instead, the anion radicals (**2**) showed a strong absorbance in the range 1600–1575 cm^{-1}, which was at a slightly lower wavenumber than the asymmetric carboxylate stretch in the corresponding carboxylate anions (**3**) (1620–1600 cm^{-1}). The O–C–R stretch present in the spectra of the neutral esters at 1120–1130 cm^{-1} shifted to 1075–1085 cm^{-1} in the anion radicals (**2**), whilst the C–C(=O)–O stretch at ~1280–1250 cm^{-1} in the neutral esters shifted by only 0–10 cm^{-1} lower in the spectra of the anion radicals (**2**).

1 Introduction

In situ electrochemical-IR spectroscopic experiments are most frequently performed using an external reflectance (ER) sampling method where the IR source passes through a thin layer of solution/electrolyte and is reflected off the surface of the electrode towards the IR detector.[1] The ER method allows both adsorbed[2,3] and solution phase[3–5] species to be studied, and, when combined with potential modulation electrochemical techniques and a fast scanning FTIR spectrometer, can allow the detection of species with relatively short lifetimes. Thin-layer transmittance cells for IR spectroelectrochemistry have been employed for studying solution phase processes where the redox active species are sufficiently stable to allow generation under controlled potential electrolysis time-scales (usually ranging from minutes to hours).[6,7]

Chemically resistant and mechanically robust mid-IR ATR probes[8] have recently been developed for on-line monitoring of industrial reactions.[9–12] Heretofore, the ATR probes have not been used for monitoring electrochemical reactions but it was thought that in certain situations such devices would offer advantages over existing *in situ* electrochemical-IR cells for studying species present in the bulk solution. One advantage of using an ATR sensor is that the probe can be conveniently positioned away from the confinement of the IR spectrometer inside an electrochemically efficient two-compartment bulk electrolysis cell. A further advantage to using an ATR probe is in situations where compounds are able to exist in multiple redox states and exhaustive electrolysis is needed to exclusively generate individual species (due to comproportionation reactions favouring species in lower oxidation states). Such a situation is more difficult to achieve in ER systems that rely solely on diffusion control where the IR spectra may represent mixtures of the starting material and product(s), and which can be difficult to interpret if the individual species have overlapping vibrational bands. For this study, a conventional[13] two-compartment bulk electrolysis cell was used to exhaustively generate solutions of reactive radical anions for analysis by FTIR spectroscopy using a commercial[14] ATR diamond composite sensor.

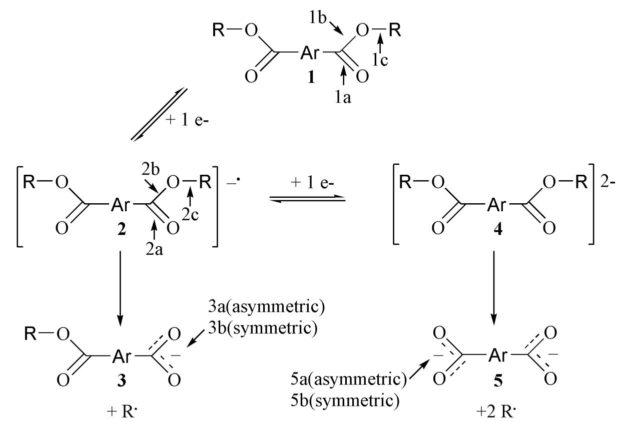
Work from these laboratories has previously characterised the voltammetric behaviour of all the mono- and disubstituted alkyl (alkyl = Pr and some Et and Me) pyridine and benzene esters,[15] as well as the identity and yields of the products obtained by bulk controlled potential electrolysis experiments in acetonitrile.[16–18] The esters can be reduced by one-electron at negative potentials (–1.9 to -2.7 V *vs.* Fc/Fc$^+$) with the *para*-substituted diesters also exhibiting a second reduction step.[15] The stability of the anion radicals formed during the first (least negative) reduction step and the electrochemical reversibility of the reduction process, as measured by cyclic voltammetry and controlled potential electrolysis, varied considerably between the compounds (from milliseconds to several hours at room temperature),[15] with EPR[15–17,19] and UV–VIS[20] spectra being obtained of the more stable radical anions, thereby confirming their existence. On the long time scale the ester anion radicals decay *via* a simple bond cleavage mechanism to form the carboxylate anions in very high yield (70–100 %) (Scheme 1).[16,17]

The mechanism in Scheme 1 was elucidated by product analysis studies after exhaustive electrochemical bulk reduction of the esters. The ^{1}H NMR spectra for the electrolyte–product mixture recorded at the completion of the electrolysis were clean in the aromatic region, which suggested that only one product was formed. The addition of an equivalent molar amount of methyl iodide to the reaction mixture at room temperature led to the immediate generation of the methyl ester.[16,17] The observation that that esterification reaction occurred readily at room temperature was used as supporting evidence

---

† Electronic supplementary information (ESI) available: first derivative EPR spectra of radical anions. See http://www.rsc.org/suppdata/p2/b2/b206087f/

DOI: 10.1039/b206087f



Scheme 1 Reduction performed in CH_3CN with 0.1 M Bu_4NPF_6 as the supporting electrolyte. Ar = benzene or pyridine. R = Me or Pr. 1a = C=O stretch; 1b = asymmetric C–C(=O)–O stretch; 1c = asymmetric O–C–R stretch; 2a = asymmetric carboxylate radical stretch; 2b = asymmetric C–C(=O)–O radical stretch; 2c = asymmetric O–C–R radical stretch; 3a = asymmetric carboxylate anion stretch; 3b = symmetric carboxylate anion stretch; 5a = asymmetric carboxylate dianion stretch; 5b = symmetric carboxylate dianion stretch (see Figs. 3–6).

that the carboxylate anions existed in their non-protonated form, ion-paired with the supporting electrolyte cation[21] (since esterification of carboxylic acids usually requires high temperatures). A possible reason why the carboxylate anions do not react with trace water or the solvent to form carboxylic acids after loss of the alkyl groups may be due to the stabilising influence of the Bu_4N^+ cation. The alkyl radical, $R^{\cdot}$, in Scheme 1 is a postulated intermediate whose existence has been proposed based on the high yield of the carboxylate anion and the number of electrons transferred in the reaction.[15–17,19,22]

The reaction mechanism shown in Scheme 1 illustrates that several species are available containing the carbonyl and carboxylate functional groups, all of which would be expected to absorb strongly in the mid-infrared region. While esters **1** and carboxylate anions **3**, **5** are well known infrared absorbers,[23] as far as we are aware there are no reports on the infrared spectra of ester radical anions **2** or dianions **4**. This is not surprising considering the very negative reduction potentials of the starting materials and the relative chemical instability of the anion radicals, which to date, have not been isolated as solid compounds. Therefore, the access to infrared data from unusual chemical intermediates that do not exist out of solution, such as the carboxylate anion radicals, is most readily achievable using an *in situ* spectroscopic approach. Infrared spectroscopy will also be useful in confirming the previous assumption[16,17] that the carboxylate anions are able to exist as stable species in dry acetonitrile, without undergoing further reaction to the carboxylic acids (by reacting with trace water or the solvent).

2 Experimental

The preparation and purification of the esters has been described previously.[17] Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), which was used as the supporting electrolyte, was prepared and purified by standard methods and dried under vacuum at 393 K for 72 h. HPLC grade acetonitrile (EM Science) was purified and dried according to a published procedure,[24] stored over calcium hydride (under nitrogen) and distilled immediately prior to use.

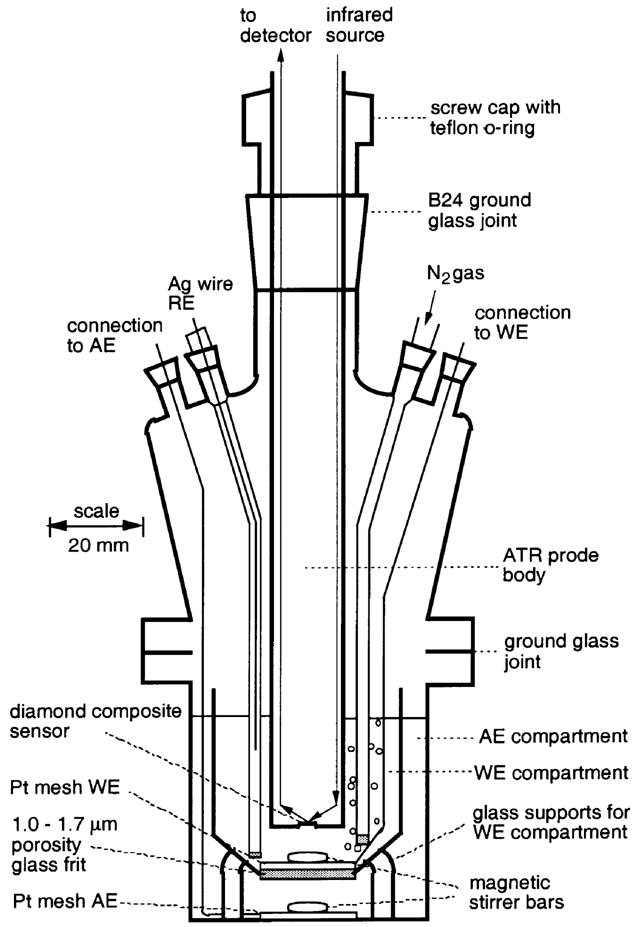


Fig. 1 Cross-section through electrochemical-ATR-FTIR cell. AE = auxiliary electrode, RE = reference electrode, WE = working electrode.

Voltammetric experiments were conducted with a PAR model 273 potentiostat/galvanostat controlled through a PC with standard PAR software. Bulk electrolysis experiments were conducted at room temperature in a two-compartment cell using platinum mesh as the working and auxiliary electrodes and a silver wire reference electrode, isolated from the test solution with a salt bridge (Fig. 1). The electrolysis potential was set at approximately 0.1 V more negative than the cathodic peak potential (E_p^{red}) which was determined by recording a cyclic voltammogram of the solution in the working electrode compartment using a 1 mm diameter planar Pt electrode. Solutions were thoroughly deoxygenated with solvent-saturated nitrogen prior to the electrolysis and nitrogen was passed over the solution during the experiments. Typical electrolysis times for a one-electron bulk reduction of 20 mM ester were 30 min for >99% conversion. The data for the fraction of electrons transferred were calculated from eqn. (1),

$$N = Q/nF \qquad (1)$$

where N = no. of moles, Q = charge, n = no. of electrons and F = the Faraday constant.

In situ infrared spectra were obtained during the electrolysis using a Mettler Toledo ReactIR™ 4000[14] with a diamond composite ATR probe situated inside the working electrode compartment (Fig. 1). Each reported spectrum represents 100 accumulated scans recorded at resolutions in the range 2–4 cm^{-1}. The diamond composite probe has a usable wavenumber range of 4000–2200 cm^{-1} and 1900–650 cm^{-1}. Preliminary experiments showed that the minimal concentration of analyte necessary to obtain acceptably intense absorption bands within a reasonable time frame was approximately 20 mM.

Continuous wave X-band EPR spectra were recorded at room temperature on Bruker ESP 300e with a rectangular TE_{102} cavity and using a silica flat cell.

3 Results and discussion

Previously performed voltammetric, EPR and UV–VIS spectroscopic experiments on aromatic esters established that diesters with carboxylate groups in the *para*-position formed the most stable anion radicals. Therefore, for the present study dipropyl pyridine-2,5-dicarboxylate and dipropyl benzene-1,4-dicarboxylate were chosen as species most likely to give detectable anion radicals *via in situ* electrochemical-FTIR spectroscopy. Fig. 2 shows cyclic voltammograms of the two compounds illustrating their two one-electron reduction processes to form first the radical anion and then at more negative potentials the dianion diamagnetic species. If the scan in the negative potential direction is reversed prior to the second reduction process (dashed line in Fig. 2), the anodic (i_p^{ox}) to cathodic (i_p^{red}) peak current ratio is equal to unity indicating that the anion radicals are stable on the time frame of the voltammetric scan. At a scan rate of 100 mV s^{-1} the second (more negative) one-electron reduction process has an i_p^{ox}/i_p^{red} ratio <1, due to chemical instability of the dicarboxylate dianions. Increasing the scan rate to 5 V s^{-1} increased the i_p^{ox}/i_p^{red} ratio associated with the second reduction process to unity.[15] Therefore, it was anticipated that only the anion radicals and not the dianions would be detectable by FTIR spectroscopy, the dianions being too unstable to generate in sufficient quantity on the bulk electrolysis time-scale.

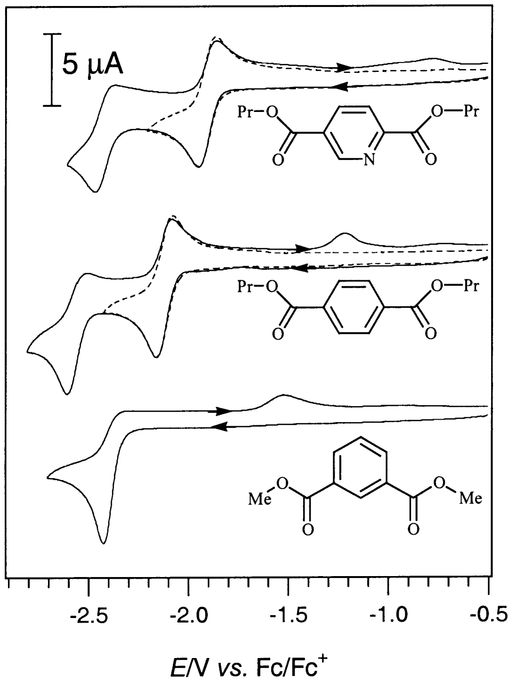


Fig. 2 Cyclic voltammograms of 2 mM analytes recorded at room temperature with a 1 mm diameter planar Pt electrode in CH_3CN with 0.1 M Bu_4NPF_6 at a scan rate of 100 mV s^{-1}.

3.1 Dipropyl benzene-1,4-dicarboxylate

Fig. 3 shows IR spectra obtained during the *in situ* electrolysis of 20 mM dipropyl benzene-1,4-dicarboxylate in CH_3CN with 0.1 M Bu_4NPF_6. The spectra were background subtracted to remove the peaks associated with the solvent and supporting electrolyte. The spectrum obtained prior to commencing the electrolysis showed three strong bands associated with the ester group: a C=O stretch at 1720 cm^{-1} (1a), and two asymmetric coupled C–O stretches for the C–C(=O)–O and O–C–R vibrations at 1275 cm^{-1} (1b) and 1120 cm^{-1} (1c), respectively. Shortly after the electrolysis had begun, two new bands appeared at 1575 cm^{-1} (2a) and 1075 cm^{-1} (2c), that reached maximum intensity after *ca.* 20 minutes, then diminished again in intensity with increasing time. Bands 2a and 2c were thus determined to be associated with the intermediate anion radical (**2**). Additional strong bands appeared during the electrolysis at 1615 cm^{-1} (3a) and 1355 cm^{-1} (3b), which persisted until the end of the experiment. Bands 3a and 3b occurred precisely where the asymmetric (3a) and symmetric (3b) stretches of carboxylate anions are expected to occur[23] and for that reason are certainly due to the carboxylate anion final product (**3**). Although the electrolysis reaction shown in Fig. 3 occurred over a period of 60 min, the measured current decreased exponentially over time indicating that 90% of the reduction was completed within the first 10–15 min.[25]

It is apparent from the data presented in Fig. 3 that the intermediate anion radical (**2**) produced during the one-electron reduction of the ester is decaying over the time-frame of the experiment (one hour) to form the carboxylate anion final product (**3**), so that many of the spectra shown in Fig. 3 represent a mixture of all the possible carboxylate-containing species, **1**, **2** and **3** (Scheme 1). The final spectrum shown in Fig. 3 (t = 60 min) displays peaks associated with the ester and carboxylate anion moieties since the stable product (**3**) contains both functional groups. The band at 1575 cm^{-1} (2a) present in the intermediate anion radical spectrum (**2**) is particularly interesting since it occurs at a very similar wavenumber to the asymmetric stretch (3a) of the carboxylate anion (**3**). The implication of this observation is that the bonding in the carbonyl region for the anion radical is very similar to that of the carboxylate anion, that is, the bond strength/length is intermediate between that of a C=O bond and a C–O bond. Clearly no symmetric carboxylate stretch would be expected to occur in the anion radical since the alkyl substituent remains bonded to the oxygen atom.

EPR spectroscopic data[15] and results from semiempirical molecular orbital calculations[20] predicted that the unpaired electron in the anion radical was delocalised over the aromatic ring and carboxylate functional groups as well as the alkyl carbons immediately adjacent to the oxygen atom. Therefore, some difference in the frequencies of the two asymmetric C–O stretches present in the radical anions compared to that observed in the ester starting materials was expected due to changes in bonding around the oxygen–alkyl and oxygen–carbonyl bonds. A shift in position of the O–C–R stretching band from 1120 cm^{-1} (1c) in the neutral ester to 1075 cm^{-1} (2c) in the anion radical was observed (Fig. 3), suggesting weakening of the oxygen–alkyl bond in the anion radical. In contrast, the C–C(=O)–O stretch in the ester (1b) at 1275 cm^{-1} showed no detectable shift in going from the ester to the anion radical (Fig. 3). It is interesting to note that decomposition of the anion radicals occurs *via* cleavage of the oxygen alkyl bonds rather than the oxygen carbonyl bond (Scheme 1), presumably due to the weakening of the O–C–R bond that is noticeable in the IR spectra.

In order to maintain charge neutrality as the controlled potential electrolysis proceeds, the supporting electrolyte ions must transfer between the two compartments in the electrolysis cell. Thus, the strong negative absorbance that occurred at 845 cm^{-1} (Fig. 3) was due to the PF_6^- anion being lost from the working electrode compartment and transferring into the auxiliary electrode compartment of the electrolysis cell. Simultaneously to this occurring, the BuN^+ cation transferred from the auxiliary electrode compartment into the working electrode compartment and the band between 2850 and 3000 cm^{-1} (data not shown) associated with the C–H stretching vibrations of the electrolyte cation increased in size. The growth of the supporting electrolyte bands at high wavenumber as the electrolysis proceeded interfered with the interpretation of the C–H stretching vibrations associated with the anion radicals. In addition, the sensitivity of the diamond composite probe is lower between 4000 and 2200 cm^{-1} than 1900–650 cm^{-1}, making interpretation in the higher wavenumber region much more difficult, such that no new bands or shifts in existing bands were detected in the spectra of the anion radicals or carboxylate anions when compared to the ester starting materials.

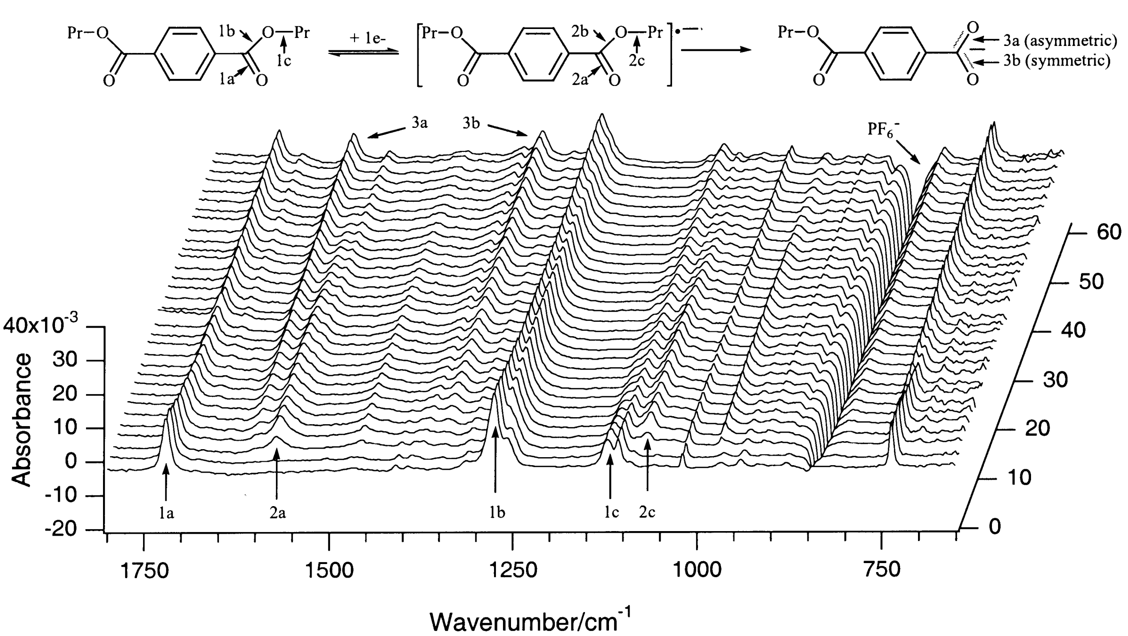


Fig. 3 Background (CH_3CN with 0.1 M Bu_4NPF_6) subtracted *in situ* FTIR spectra obtained during the one-electron bulk electrochemical reduction (applied $E = -2.2$ V *vs.* Fc/Fc$^+$) of 20 mM dipropyl benzene-1,4-dicarboxylate at room temperature.

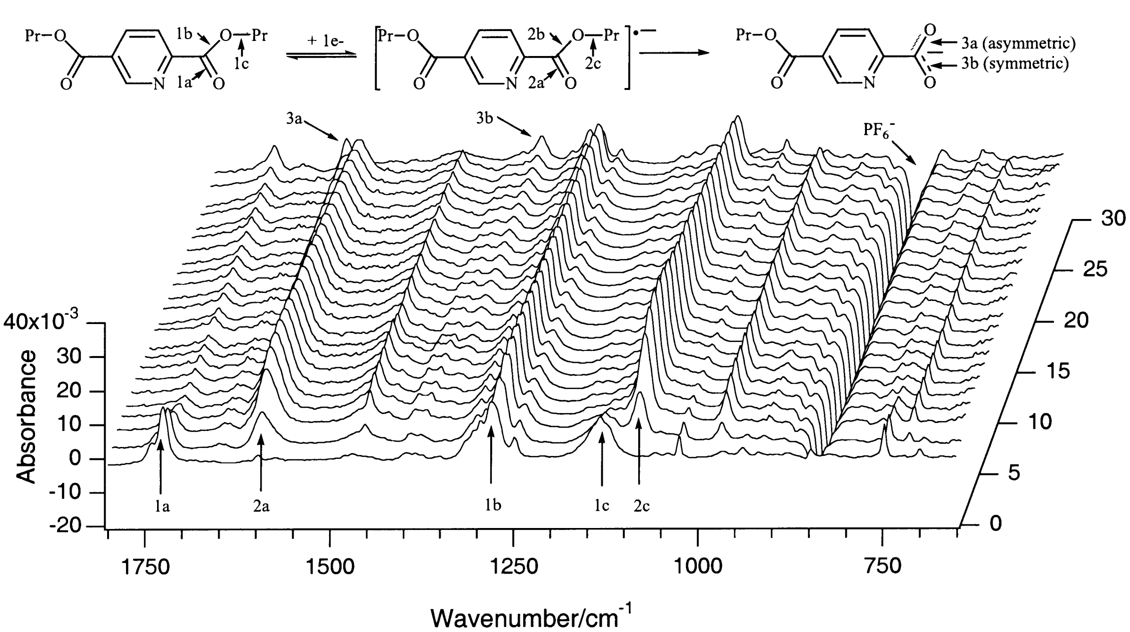


Fig. 4 Background (CH_3CN with 0.1 M Bu_4NPF_6) subtracted *in situ* FTIR spectra obtained during the one-electron bulk electrochemical reduction (applied $E = -2.0$ V *vs.* Fc/Fc$^+$) of 20 mM dipropyl pyridine-2,5-dicarboxylate at room temperature.

3.2 Dipropyl pyridine-2,5-dicarboxylate

The FTIR spectroscopic data obtained during the one-electron reduction of dipropyl pyridine-2,5-dicarboxylate (Fig. 4) were similar to the benzene analogue described above, with the exception that the reduced form was substantially more stable, which enabled a purer spectrum of the anion radical to be obtained. The lowering of molecular symmetry as a result of the N-atom in the aromatic ring did not significantly change the spectroscopic properties of the two inequivalent ester groups so that the diester starting material showed one C=O stretch at 1725 cm^{-1} (1a), a C–C(=O)–O asymmetric stretch at 1280 cm^{-1} (1b) and a O–C–R asymmetric stretch as 1130 cm^{-1} (1c). Ten minutes after the electrolysis had commenced, the C=O stretch at 1725 cm^{-1} decreased in intensity almost completely whilst simultaneously a new peak grew in at 1600 cm^{-1} (2a) due to the anion radical, thereby confirming that the anion radical has no formal C=O functional group. The reason why the band at 1725 cm^{-1} almost completely disappeared during the electrolysis in the spectra shown in Fig. 4 (compared to Fig. 3) was due to the increased stability of the pyridine-based anion radical. In the benzene-based analogue (Fig. 3) the radical anion decayed to the mixed carboxylate/ester final product (**3**) relatively quickly, hence at all times there was a substantial quantity of species containing the ester group present. Similar to the benzene ester, the O–C–R asymmetric stretch (2c) in the pyridine ester shifted to lower wavenumber (1085 cm^{-1}) in the radical anion, whilst the C–C(=O)–O stretch decreased only slightly (by approximately 10 cm^{-1}).

The final spectrum shown in Fig. 4 at t = 30 minutes was obtained after bubbling dry air through the electrolysed solution in order to speed up the decomposition of the anion radical [it was known that the anion radicals react immediately with molecular oxygen to form the ester/carboxylate anion (**3**) in 100% yield[18]]. Therefore, the increase in the peak intensity at 1725 cm^{-1} in the final spectrum (t = 30 min) was due to the

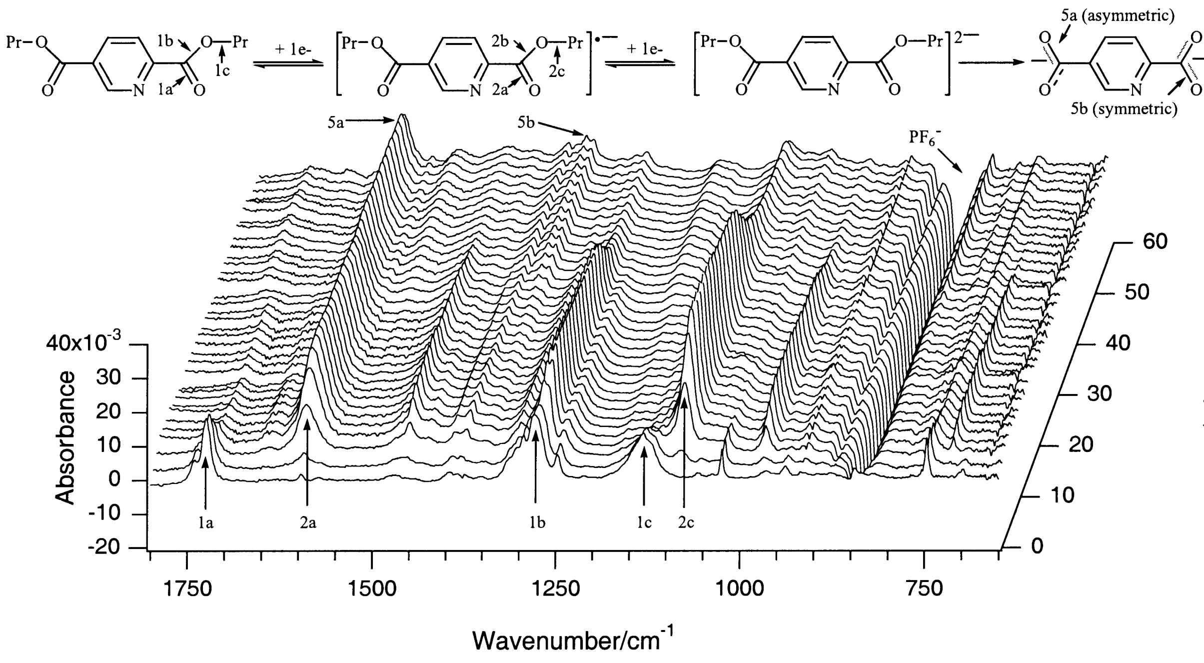


Fig. 5 Background (CH_3CN with 0.1 M Bu_4NPF_6) subtracted *in situ* FTIR spectra obtained during the one-electron (t = 0.1–30 min, applied E = −2.0 V *vs.* Fc/Fc^+) then two-electron (t = 30.1–60 min, applied E = −2.5 V *vs.* Fc/Fc^+) reduction of 20 mM dipropyl pyridine-2,5-dicarboxylate at room temperature.

increased rate of conversion to the ester/carboxylate anion product (**3**) *via* the reaction with molecular oxygen. (Synthetic scale controlled potential electrolysis experiments have shown that the two possible carboxylate anion isomers (**3**) are obtained in approximately equal yield).[17] The asymmetric carboxylate stretch present in the final product (**3**) spectrum at 1620 cm^{-1} (3a) is only 20 cm^{-1} higher than the band observed for the anion radical (2a). The symmetric carboxylate stretch (3b) occurred at the same position as the analogous benzene compound (1355 cm^{-1}).

Examination of the spectroscopic data suggested that the anion radical of dipropyl pyridine-2,5-dicarboxylate was stable for several hours at room temperature in CH_3CN. The higher stability of the anion radical of the pyridine diester did allow the opportunity to extend the reduction process by two-electrons in order to produce the dianion (**4**) (Fig. 5). The ester was first reduced to the monoanion for 30 min, then the potential was changed to a value sufficiently negative to produce the dianion (*cf.* Fig. 2) and the electrolysis continued for another 30 min (Fig. 5). It was anticipated from the cyclic voltammetry data that the diester dianion (**4**) would not be sufficiently stable to be detected by *in situ* FTIR spectroscopy (see discussion above), and would react immediately to form the dicarboxylate dianion (**5**), and this was verified by the spectroscopic data presented in Fig. 5. As soon as the potential sufficiently negative to produce the dianion was applied (t = 30 min), the peaks associated with the two asymmetric C–O stretches (1b and 2c) diminished in intensity due to the formation of the dicarboxylate dianion (**5**), which had lost both alkyl groups. The spectrum of **5** was relatively simple showing the bands associated with the asymmetric (5a) and symmetric (5b) carboxylate anion stretches at 1600 cm^{-1} and ~1350 cm^{-1}, respectively. Bands 1b and 2c present in the final spectrum in low intensity are likely to be due to residual unreacted **3** (due to the partial decay of **2** to **3** before/after the two-electron reduction had commenced). The absence of bands between 1800 and 1600 cm^{-1} in the spectrum of the dicarboxylate dianion confirmed the previous assumption[16,17] that the dianion does not react with trace water or abstract a proton from the solvent to form a carboxylic acid (or dicarboxylic diacid), since the C=O stretch in the spectra of carboxylic acids is expected to occur between 1760 and 1660 cm^{-1}.[23]

Several other bands were present that could be associated with the anion radicals of the pyridine- and benzene-based *para*-substituted diesters, such as the bands at *ca.* 1450, 970 and 720–750 cm^{-1} (Figs. 3–5), although they are more difficult to assign to particular vibrations.

3.3 Dimethyl benzene-1,3-dicarboxylate

EPR spectroscopy established that the anion radicals formed by one-electron reduction of *meta*-substituted diesters were also moderately stable, although their voltammetric behaviour was more complicated than the corresponding *para*-substituted diesters.[19] For example, a cyclic voltammogram of dimethyl benzene-1,3-dicarboxylate (Fig. 2) *appears* to show chemically irreversible behaviour at slow scan rates (in the sense that $i_p^{ox}/i_p^{red} < 1$) suggesting that the associated anion radical of this compound is relatively unstable and quickly decomposes to form the carboxylate anion. However, a detailed voltammetric and EPR spectroscopic study found that the reason for the diminished reverse i_p^{ox} value in the cyclic voltammograms at slow scan rates was due to a reversible dimerization mechanism where the anion radical (**2**) exists in equilibrium with a dianion dimer.[19]

The IR spectra of the starting material showed several strong bands in the 1350–1050 cm^{-1} region, which made it difficult to definitively assign bands associated with C–O stretching. The FTIR spectroscopic data obtained during the *in situ* one-electron reduction (Fig. 6) were also more complicated than for the *para*-substituted diesters, although one noteworthy transitory band grew in at 1600 cm^{-1} (2a) that appears to be typical of carboxylate radical anions (by comparison with the data from *para*-substituted diesters). Other bands, which were clearly associated with an intermediate species, were detected at 1510, 1200, 1155 and 1070 cm^{-1}. The broad band at ~1510 cm^{-1} is particularly interesting since it has no equivalent in the spectra of the *para*-substituted diesters. Since it is likely that the IR spectroscopic data obtained during the electrolysis of the *meta*-substituted diester were complicated by the occurrence of the dimer dianion jointly with the anion radical, the equilibrium transformation may account for the additional band at 1510 cm^{-1}, and possibly other bands present. Such a situation is in marked contrast to the relatively straightforward reduction

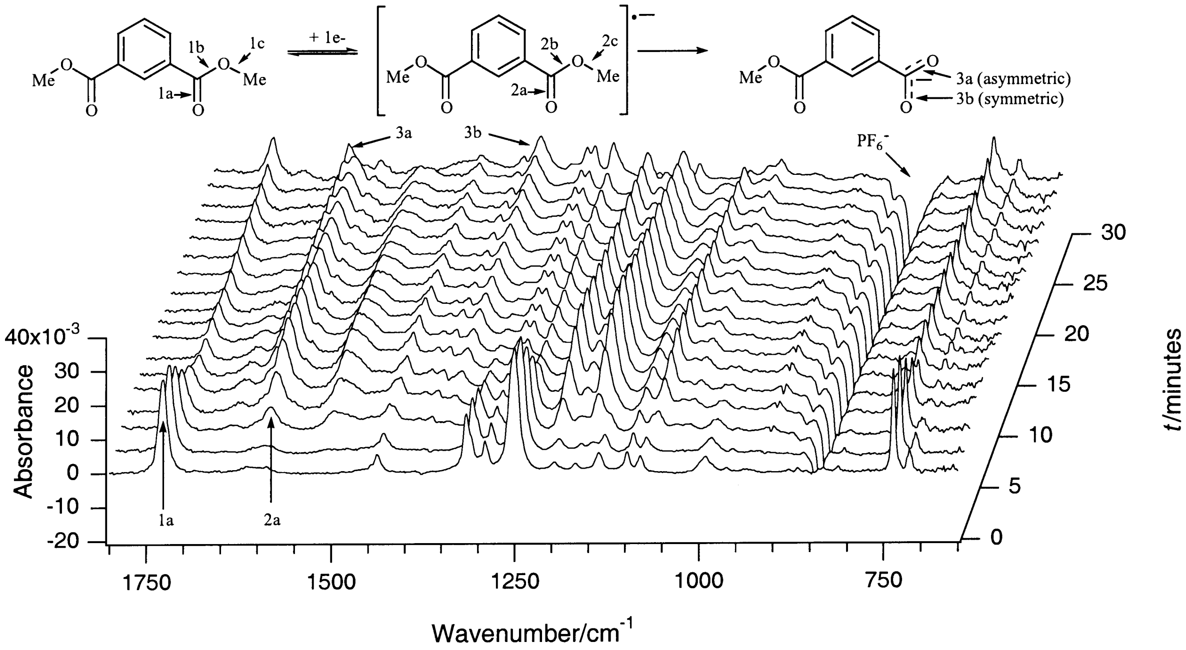


Fig. 6 Background (CH_3CN with 0.1 M Bu_4NPF_6) subtracted *in situ* FTIR spectra obtained during the one-electron bulk electrochemical reduction (applied $E = -2.5$ V *vs.* Fc/Fc^+) of 20 mM dimethyl benzene-1,3-dicarboxylate at room temperature.

of the *para*-substituted diesters, indicating that the spectroscopic features of individual carboxylate radical anions should preferably be ascertained by correlating a range of compounds and analytical techniques (electrochemistry, EPR, UV–VIS, *etc*).

The final spectrum was obtained after allowing dry air to enter the solution, thereby allowing complete conversion of the radical anion into the ester/carboxylate anion (**3**). This allowed the unambiguous assignment of the asymmetric carboxylate anion stretch at 1620 cm^{-1} (3a) (20 cm^{-1} higher than band 2a observed in the anion radical spectrum) and symmetric carboxylate anion stretch at 1355 cm^{-1} (3b).

3.4 EPR spectroscopy

For the purpose of proving that the intermediate bands detected in the ATR-FTIR spectra were due to paramagnetic dicarboxylate anion radicals, solutions of the radical anions were generated under identical conditions and concentration (to the ATR-FTIR experiments) then transferred under nitrogen to a silica flat cell for EPR spectroscopic analysis. Previous reports on the EPR spectra of the dicarboxylate anion radicals were obtained at concentrations ≤1 mM in order to minimise the effects of line broadening caused by electron exchange reactions.[15–17,19,26,27] The EPR spectra obtained after exhaustive one-electron reduction of 20 mM of the starting materials were of a suitable intensity expected for such high concentrations. The spectra of dipropyl benzene-1,4-dicarboxylate and dipropyl pyridine-2,5-dicarboxylate consisted of a single line (ΔH_{pp} = 1 and 2 G, respectively) whilst the anion radical of dimethyl benzene-1,3-dicarboxylate showed additional hyperfine structure (see ESI †). The EPR spectra of the anion radicals of the two benzene-based esters diminished by approximately 40% over a period of one hour while the spectrum of the pyridine-based diester radical anion diminished by approximately 10% over the same time period. Accurate kinetic analysis of the stability of the anion radicals in the two-compartment ATR-FTIR cell is difficult since it is inevitable that some of the anion radicals will migrate through the frit separating the working and auxiliary electrode compartments, or interact with charged species generated in the counter electrode compartment.[16] Overall, the EPR and ATR-FTIR spectroscopic data are consistent with the anion radicals being stable on a minutes to hours time-scale in deoxygenated and moisture-free environments.

4 Conclusions

In situ electrochemical-FTIR spectroscopy using an ATR diamond composite probe was successfully applied to a study of the reduction of solution phase aromatic diesters in a two-compartment electrolysis cell. The diesters (**1**) were first reduced to the anion radicals (**2**), which subsequently decomposed to form the carboxylate anions (**3**). In most instances the spectra obtained represented mixtures of all three species due to the partial decomposition of the radical as it was being produced. Analysis of the spectra from several compounds helped to identify bands that can now be considered as characteristic of carboxylate anion radicals. For dipropyl pyridine-2,5-dicarboxylate the anion radical (**2**) was sufficiently stable in air-free solutions to enable its further reduction to the dianion (**4**), which rapidly decomposed to form the dicarboxylate dianion (**5**).

It was observed that the C=O bond stretch that occurs in the neutral esters (**1**) was missing from the spectra of the anion radicals (**2**). The O–C–R stretch present in the neutral esters at 1120–1130 cm^{-1} shifted to 1075–1085 cm^{-1} in the anion radicals (**2**), whilst the C–C(=O)–O stretch at ~1280–1250 cm^{-1} present in the spectra of the neutral esters shifted by only a small amount (~0–10 cm^{-1} lower) in the spectra of the anion radicals (**2**). The shift in the O–C–R stretch to lower wavenumber (weaker bond strength) correlates with the decomposition of the anion radicals *via* cleavage of the alkyl–oxygen bond. The anion radicals (**2**) showed a strong absorbance between 1600 and 1575 cm^{-1}, which occurred at a slightly lower wavenumber than the asymmetric carboxylate stretch in the corresponding carboxylate anions (**3**) (1620–1600 cm^{-1}), suggesting that the carbonyl bond length/strength in the anion radicals was intermediate between a C=O and C–O bond (similar to the carboxylate anions).

Acknowledgements

The author thanks the ARC for the award of a QEII Research Fellowship and Mr Paul Sui for constructing the glass electrochemical-FTIR cell.

References

1 A. J. Bard and L. R. Faulkner, in *Electrochemical Methods: Fundamentals and Applications*, 2nd edn., Wiley, New York, 2001, p. 700.

2 J. K. Foley, C. Korzeniewski, J. L. Daschbach and S. Pons, *Electroanal. Chem.*, 1986, **14**, 309.

3 K. Ashley and S. Pons, *Chem. Rev.*, 1988, **88**, 673.

4 S. B. Khoo, J. F. Foley, C. Korzeniewski, S. Pons and C. Marcott, *J. Electroanal. Chem.*, 1987, **233**, 223.

5 (*a*) S. P. Best, R. J. H. Clark, R. C. S. McQueen and R. P. Cooney, *Rev. Sci. Instrum.*, 1987, **58**, 2071; (*b*) S. P. Best, S. A. Ciniawsky and D. G. Humphrey, *J. Chem. Soc., Dalton Trans.*, 1996, 2945.

6 W. R. Heineman, J. N. Burnett and R. W. Murray, *Anal. Chem.*, 1968, **40**, 1974.

7 P. A. Flowers and G. Mamantov, *Anal Chem.*, 1989, **61**, 190.

8 N. J. Harrick, *Internal Reflectance Spectroscopy*, Wiley, New York, 1967.

9 W. M. Doyle, *Appl. Spectrosc.*, 1990, **44**, 50.

10 R. E. Sheridan and A. J. Rein, *R&D Magazine*, 1991, **33**, 100.

11 M. Milosevic, D. Sting and A. Rein, *Spectroscopy (Amsterdam)*, 1995, **10**, 44.

12 W. M. Doyle and B. Nadel, *Spectroscopy (Amsterdam)*, 1996, **11**, 35.

13 R. D. Webster, *Magn. Reson. Chem.*, 2000, **38**, 897.

14 ASI Applied Systems, Inc., Millersville, MD, USA (http://www.asirxn.com).

15 R. D. Webster, A. M. Bond and R. G. Compton, *J. Phys. Chem.*, 1996, **100**, 10288.

16 R. D. Webster, A. M. Bond and T. Schmidt, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1365.

17 R. D. Webster and A. M. Bond, *J. Org. Chem.*, 1997, **62**, 1779.

18 R. D. Webster and A. M. Bond, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1075.

19 R. D. Webster, *J. Chem. Soc., Perkin Trans. 2*, 1999, 263.

20 R. D. Webster, A. M. Bond and D. C. Coomber, *J. Electroanal. Chem.*, 1998, **442**, 217.

21 T. Awata, M. M. Baizer, T. Nonaka and T. Fuchigami, *Chem. Lett.*, 1985, 371.

22 J. H. Wagenknecht, R. D. Goodin, P. J. Kinlen and F. E. Woodard, *J. Electrochem. Soc.*, 1984, **131**, 1559.

23 R. M. Silverstein and F. X. Webster, in *Spectrometric Identification of Organic Compounds*, 6th edn., Wiley, New York, 1998, ch. 3.

24 M. Walter and L. Ramaley, *Anal. Chem.*, 1973, **45**, 165.

25 P. T. Kissinger and W. R. Heineman, eds., in *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker, New York, 1984, p. 119.

26 M. Hirayama, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 2234.

27 J. Voss, W. Schmüser and K. Schlapkohl, *J. Chem. Res. (S)*, 1977, 144.