Influence of magnesium(II) ions on cathodic reactions in aprotic solvents: the reduction of benzoate esters

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The use of an Mg anode in an undivided cell alters the products from many electrosynthetic reactions. In an attempt to understand this phenomenon, the influence of Mg^{II} ions on the mechanism for the reduction of benzoate esters in DMF has been investigated. It is confirmed that the presence of Mg^{II} ions in solution leads to a change in the major reaction pathway from cleavage of the ester linkage (to give benzoate ion) to dimerisation (to a diketone). The dimer is then reduced further at the same potential. Cyclic voltammetry shows that in the absence of Mg^{II}, the ester radical anion is stable, while in the presence of Mg^{II}, the radical anion dimerises rapidly and the Mg^{II} also catalyses further reduction. Voltammetry within the synthesis cell, however, shows that much of the Mg^{II} formed by dissolution of the anode is tied up by anionic products and that the dimerisation of the radical anion must occur well away from the cathode surface.

In recent years, it has become common to carry out electrosyntheses at cathodes using aprotic solvents in undivided cells with a dissolving metal anode; suitable metals include Al, Mg, Sn and Zn.[1-3] The idea was first introduced in order to facilitate the isolation of carboxylates formed by the cathodic reduction of carbon dioxide;[4,5] the dissolving metal anode led to a cation which precipitated the carboxylate as an insoluble salt. Later, dissolving anodes were used in electrolytic carboxylations[6,7] and it gradually became clear that they had a much broader application in both the laboratory and the technical scale. In the laboratory, they allow the use of very simple undivided cells and procedures for many reductive electrosyntheses in dry conditions.[1-3] From the viewpoint of the fine chemicals industry, dissolving anodes offer, for the first time, a possible way to scale up electrolyses in aprotic solvents; the anode reaction then leads to no decomposition of the solvent, change in pH or formation of organic products to contaminate the desired product at the cathode. With suitable cell design it is also possible to achieve a low cell voltage and hence energy consumption. It does, however, also require the stoichiometric (or greater) consumption of the anode metal. Even so, the use of a dissolving metal anode on a pilot scale has been demonstrated by SNPE in France[8,9] and has also been considered by Monsanto[10] and Dow[11] in the USA.

Since the mid-eighties, the number of reports of electrosyntheses using dissolving metal anodes has accelerated rapidly and a review of this work clearly shows that the dissolving metal anode influences the products formed at the cathode.[1] In many cases, the selectivity is greatly enhanced and they permit the achievement of very high yields of desired products.[1-3] Surprisingly, there have been few attempts to study the mechanism by which the improved selectivity is achieved. It is possible to suggest quite different mechanisms. For example, the metal ions could (*i*) interact intimately with radical anion and/or carbanion intermediates causing a complete change in mechanism or (*ii*) stabilise anionic products and prevent further cathodic reduction or other chemistry. On the other hand, the dissolving anode might merely provide a non-interfering anode chemistry and promote uniform dry and neutral conditions for the cathodic reaction. Clearly, some distinction between these diverse mechanistic possibilities might aid further refinement of the synthetic procedures and we are aware of only two preliminary voltammetric studies of these systems.[12,13] Hence, in this paper we report a detailed investigation using cyclic voltammetry of one reaction, the reduction of benzoate esters (C_6H_5COOR, R = CH_3 and C_6H_5) in DMF. We have selected magnesium as the dissolving anode and investigated the influence of Mg^{II} from two sources, either added as anhydrous $Mg(CF_3SO_3)_2$ or formed by anodic dissolution. In the absence of Mg^{II}, the reduction of benzoate esters in aprotic solvents has been shown by cyclic voltammetry to give relatively stable radical anions, but on the longer timescale of a preparative electrolysis, a broad spectrum of products was observed including those from cleavage of the molecules.[14,15] In an electrolysis in an undivided cell with an Mg anode, good yields of the diketone (resulting from a dimerisation of the radical anion) were reported.[12]

One further feature of electrosyntheses with dissolving metal anodes should be emphasised; the ratio of metal ion to reactant concentrations changes continuously during any batch procedure. At the commencement of an electrolyses with an Mg anode, the concentration of reactant for the organic transformation is high while the Mg^{II} concentration is zero. As the electrolysis is carried out, the reactant concentration drops while the free Mg^{II} will either increase continuously or reach a steady state (depending on its roles in the system). Hence, voltammetry experiments with an excess of Mg^{II} can only correspond to conditions rather late in the electrosynthetic procedure and maybe represent only a limiting situation of indirect relevance to the synthetic conditions.

Experimental

Chemicals

Dimethylformamide (DMF) (Fisons, 99%), employed as the solvent throughout this work, was first dried (K_2CO_3) and then distilled at reduced pressure under a nitrogen atmosphere. The middle 50% of the distillate was retained and stored over neutral alumina (Fluorochem, Super Grade) in a sealed glass vessel under dry N_2.

The supporting electrolyte, tetrabutylammonium tetrafluoroborate, was prepared by treating an aqueous solution of tetrabutylammonium hydrogen sulfate (169.77 g, 0.5 mol, Lancaster, 97%) with an equal volume of an aqueous solution of sodium tetrafluoroborate (57.1 g, 0.52 mol, Aldrich, 98%). The mixture was stirred for 5 min and the resulting insoluble salt was collected, washed with water and dried in a vacuum oven. The crude salt was then dissolved in ethyl acetate and separated from any remaining aqueous layer. The salt was recrystallized three times from ethyl acetate–light petroleum mixtures to yield 133.7 g (81%) of white crystals (mp 162–162.5 °C). The salt was stored in a vacuum desiccator, but just prior to use, the mass required for an experiment was melted under vacuum to drive off any residual solvent or adventitious water.

The following reagents were used as received: methyl benzoate (BDH, 99%), ethyl benzoate (Fluka, > 99%), phenyl benzoate (Aldrich, 99%), benzil (BDH, 98%), benzoin (Lancaster, 99%), *meso*-hydrobenzoin (Aldrich, 99%), phenetole (Aldrich, 99%), ethyl iodide (BDH, 99%), magnesium trifluoromethanesulfonate (Aldrich, 99%) and ferrocene (BDH, 99%).

Electrochemical cells

All cyclic voltammetry and chronoamperometry was carried out in a three-electrode two-compartment glass cell under a nitrogen atmosphere. The working electrode was a vitreous carbon rod (diameter 3.2 mm, Goodfellow) sealed into glass tubing to give a disc electrode, area 0.08 cm^2. Electrical contact was made by attaching copper wire to the back of the disc using silver loaded epoxy resin (RS Components). The disc surface was initially polished on a decreasing series of grades of emergy paper and then rigorously polished with alumina powder (1.0, 0.3 and 0.05 µm, Beuhler) on a moistened polishing cloth. The electrode was rinsed between the various polishing stages with water from a MilliQ system and finally with the solvent/supporting electrolyte. A platinum loop counter-electrode surrounded the working electrode. A silver wire pseudo-reference electrode (employed throughout this study) was housed within the Luggin capillary compartment. Ferrocene was added at the end of each experiment to give an internal reference. For all electrochemical experiments, a known quantity of the material under study was made up in DMF containing 0.1 mol dm^{-3} Bu_4NBF_4. Prior to, and between measurements, the solution was deoxygenated with N_2 (BOC O_2 free N_2).

The cell used for constant potential coulometry was a three compartment 'pipe-shaped' glass vessel[16] with a fine sintered glass disc separating anode and cathode chambers of equal volume (20 cm^3). The working electrode was a vitreous carbon disc (area 4.5 cm^2) sealed into glass entering the cell from one end of the 'pipe' and the counter electrode was a platinum gauze entering from the other side of the 'pipe', These two electrodes were mounted parallel to each other on either side of the sinter. A silver wire pseudo-reference electrode was housed within a Luggin capillary compartment; the tip of the Luggin capillary could be moved with respect to the surface of the working electrode. The catholyte was a defined volume of solution containing solvent/electrolyte, a known weight of reactant, magnesium salt (where stated) and a known quantity of an electroinactive compound as an internal standard to aid quantitative analysis. The anolyte was solvent/electrolyte only. The solution in the working electrode compartment was mechanically stirred and purged with N_2, prior to and during the electrolysis. Small catholyte samples were removed at regular intervals during and at the end of each synthesis, hydrolysed with 0.1 mol dm^{-3} HCl (when Mg^{II} ions were present during the synthesis) and/or treated with ethyl iodide (to convert benzoate ions to ethyl esters) and analysed by gas chromatography (GC) to monitor substrate consumption and product formation.

This divided cell was also used for the anodic formation of solutions of Mg^{II}. The anode was a rod of magnesium (diameter 7.9 mm, Goodfellow, 99.9%) and both anolyte and catholyte contained solvent/electrolyte only. Immediately before the electrolysis, the Mg rod was acid washed in 1 mol dm^{-3} hydrochloric acid to remove surface oxide layers and activate the surface. Then the Mg rod was weighed and inserted into the deoxygenated anolyte to a depth of 24 mm and a constant current of 10 mA applied immediately between the two electrodes. This was maintained until the charge passed reached 0.8 mF, *i.e.* the theoretical quantity of electricity required to electrogenerate a 20 mmol dm^{-3} solution of Mg^{II} ions in 20 cm^3 DMF–0.1 mol dm^{-3} Bu_4NBF_4. The actual amount of electrogenerated Mg^{II} ions in solution was estimated from the weight lost by the rod during an electrolysis.

All other constant current electrolyses were carried out in an undivided beaker cell (volume 40 cm^3) within a thermostatted jacket. It was equipped with a magnetic stirrer bar and a five-necked glass lid. The cell body also incorporated an interchangeable and movable (by means of a Young's joint) Luggin capillary compartment to facilitate either monitoring of the working electrode potential during electrolyses or *in situ* cyclic voltammetry on a vitreous carbon electrode (diameter 3 mm). A bifurcated nitrogen inlet allowed degassing of the solution at the base of the cell or maintenance of a nitrogen blanket over the solution. The cathode was a cylindrical stainless steel gauze (diameter 2 cm, height 4 cm, area *ca.* 50 cm^2) and a magnesium rod, pretreated as above, served as the anode. A constant current density ranging from 2–5 mA cm^{-2} was maintained between the two electrodes until the charge passed reached 1–2.5 F based on the organic substrate in solution. The course of the reaction was monitored by GC. To obtain *in situ* cyclic voltammograms, the electrolysis was interrupted and the stainless steel gauze acted as the counter-electrode in these experiments. Solution agitation was also stopped.

Instrumentation

Voltammetric experiments employed a Hi-Tek potentiostat, model DT2101, and function generator, type PPR1. Responses were recorded on a Gould series 60000 X-Y recorder and short time-scale data were recorded *via* a Gould OS4100 digital storage oscilloscope. During controlled-potential electrolyses the charge was measured by a digital integrator built in the Department workshop. Constant current was provided by a Delta Electronics SM6020 regulated DC power supply and working electrode potentials were monitored using a Phillips PM 2519 digital voltmeter.

Gas chromatography (GC) was performed with a temperature programmable Perkin-Elmer 8100 gas chromatograph equipped with an Rtx-1 capillary column (Thames Chromatography): column specifications 15 m × 0.32 mm id × 0.5 µm film. Products were identified by comparison of retention times with those for authentic materials and/or by GC–MS analyses performed on a VG analytical 70-250-SE spectrometer coupled to a gas chromatograph (BP1 Capillary column). Commercially available materials were also used to obtain response factors so as to allow quantitative estimates of yields.

Results

Reduction of the benzoate esters in the absence of Mg^{II}

Cyclic voltammograms were recorded at a vitreous carbon disc electrode (area 0.08 cm^2) for a solution of methyl benzoate (5.0 mmol dm^{-3}) in DMF–Bu_4NBF_4 (0.1 mol dm^{-3}). Fig. 1 shows a set of voltammograms recorded at potential scan rates between 20 and 500 mV s^{-1}. The curves show a well formed reduction peak at $E_p = -2.74$ V *vs.* the Cp_2Fe/Cp_2Fe^+ couple and the peak current density is proportional to the square root of the scan rate. There is also a coupled oxidation peak at $E_p = -2.68$ V. At 500 mV s^{-1}, the voltammogram has the form expected for a reversible 1e$^-$ reduction reaction, but at the lowest scan rates the anodic peak is noticeably smaller than the cathodic peak and the responses are consistent with the radical anion decomposing in a first-order chemical reaction with a half-life

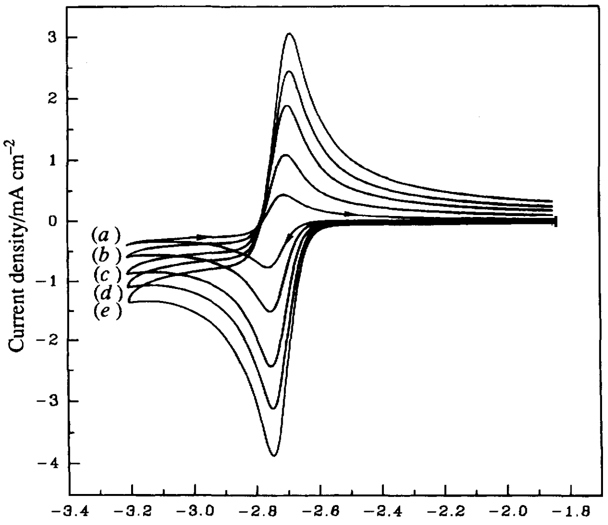


Fig. 1 Cyclic voltammograms for methyl benzoate at a vitreous carbon disc electrode. Solutions were 5 mmol dm^{-3} methyl benzoate in DMF–Bu$_4$NBF$_4$ (0.1 mol dm^{-3}). The potential scan rates (*a*) 20, (*b*) 80, (*c*) 200, (*d*) 320 and (*e*) 500 mV s^{-1}.

of *ca.* 70 s.[17] On extending the potential scan to more negative potentials, a second reduction peak, $E_p = -3.41$ V, is seen just prior to the potential limit. This second reduction process is completely irreversible, but the final product(s) of this reduction give two oxidation peaks at $E_p = -1.42$ and $+0.33$ V. The nature of these reactions have not been investigated further.

A controlled potential electrolysis was carried out in a divided cell at a large glassy carbon disc cathode (area 4.5 cm^2) for a solution of methyl benzoate (10 mmol dm^{-3}) in DMF–Bu$_4$NBF$_4$ (0.1 mol dm^{-3}). At a potential of -2.90 V, the catholyte quickly became highly coloured (orange then brown), but on opening the cell to the laboratory atmosphere, it rapidly decayed to pale yellow. When the current had dropped to a low value, the charge passed indicated that $n = 1$. At the end of the electrolysis, a cyclic voltammogram showed only a small reversible process for the reduction of remaining methyl benzoate (< 10% of the initial concentration) and no new oxidation peaks. After the electrolysis, the catholyte was treated with ethyl iodide to trap any benzoate formed and gas chromatography showed that the yield of ethyl benzoate was > 65%. No benzil was identified. Therefore, it would appear that the major reaction at the potential of the first cathodic peak of the voltammogram is given in the following reaction and the

$$C_6H_5COOMe + e^- \rightleftharpoons [C_6H_5COOMe]^{\bullet -} \longrightarrow C_6H_5COO^- + Me^\bullet \quad (1)$$

radical derived products are presumably lost as gases. The radical anions have sufficient stability that their decomposition occurs well away from the cathode surface. This voltammetry and the interpretation is very similar to that reported previously by Wagenknecht *et al.*[15]

A set of voltammograms for phenyl benzoate (5 mmol dm^{-3}) in DMF–Bu$_4$NBF$_4$ (0.1 mol dm^{-3}) are shown in Fig. 2. The voltammetry is similar to that described above. The first reduction process occurring at $E_p = -2.56$ V and the radical anion is slightly less stable, analysis of the ratio I_p^A/I_p^C as a function of scan rate giving a half-life of *ca.* 4 s. There is a second irreversible reduction process at -3.17 V, but even when the potential scan is limited to the first reduction peak, there are several anodic peaks on the reverse scan, presumably for the oxidation of species formed in the coupled chemistry of the radical anion. In general, the voltammograms recorded in this study are similar to those reported by Seeber *et al.*[14] although their curves would indicate that the radical anion is less stable than found in this study. This may indicate different levels of water in the solvent.

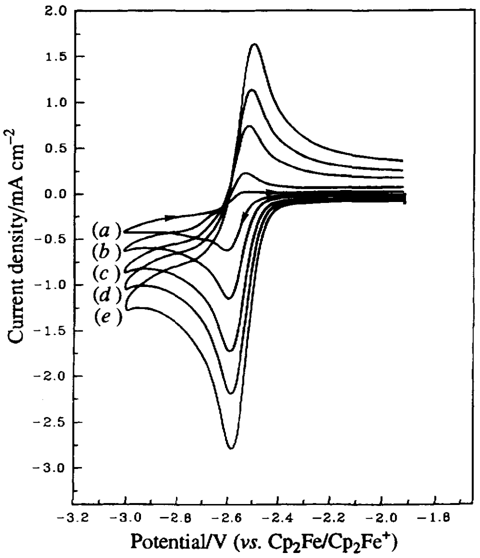


Fig. 2 Cyclic voltammograms for phenyl benzoate at a vitreous carbon disc electrode. Solutions were 5 mmol dm^{-3} phenyl benzoate in DMF–Bu$_4$NBF$_4$ (0.1 mol dm^{-3}). The potential scan rates (*a*) 20, (*b*) 80, (*c*) 200, (*d*) 320 and (*e*) 500 mV s^{-1}.

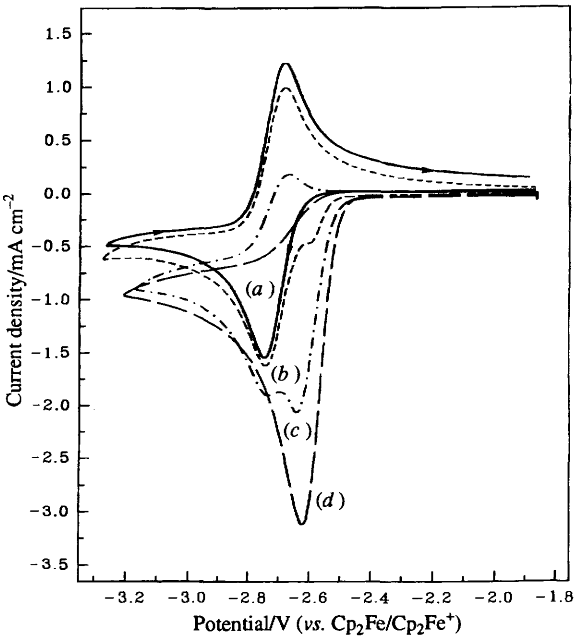


Fig. 3 Cyclic voltammograms for 5 mmol dm^{-3} methyl benzoate in DMF–Bu$_4$NBF$_4$ (0.1 mol dm^{-3}) with the addition of (*a*) 0, (*b*) 1, (*c*) 5 and (*d*) 10 mmol dm^{-3} anhydrous Mg(CF$_3$SO$_3$)$_2$. Potential scan rate 80 mV s^{-1}. Vitreous carbon disc electrode (area 0.08 cm^2).

Reduction of the benzoate esters in the presence of Mg^{II}

Fig. 3 illustrates the changes to the voltammogram recorded at 80 mV s^{-1} for methyl benzoate (5.0 mmol dm^{-3}) in DMF–Bu$_4$NBF$_4$ (0.1 mol dm^{-3}) when anhydrous Mg(CF$_3$SO$_3$)$_2$ is added stepwise to the solution. It can be seen that the addition

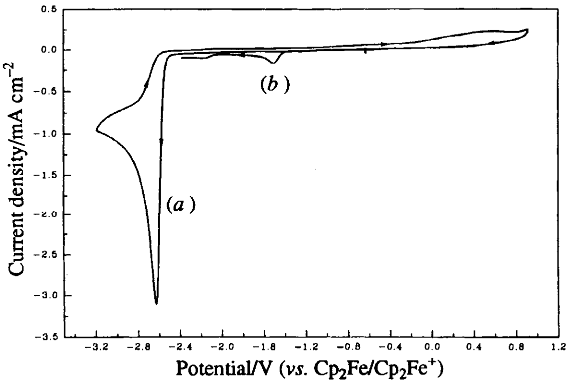


Fig. 4 Cyclic voltammograms for 5 mmol dm^{-3} methyl benzoate + 10 mmol dm^{-3} anhydrous $Mg(CF_3SO_3)_2$ in DMF–Bu_4NBF_4 (0.1 mol dm^{-3}) over a more extended potential range: (*a*) first scan and (*b*) second scan. Potential scan rate 80 mV s^{-1}. Vitreous carbon disc electrode (area 0.08 cm^2).

of Mg^{II} causes the reduction of methyl benzoate to occur more readily at less negative potentials. With 1 mmol dm^{-3} Mg^{II}, a pre-peak on the cathodic peak for the ester reduction can be seen. When the solution contains equimolar amounts of the ester and Mg^{II}, the response for the reduction of the ester to the radical anion is clearly split into two peaks at −2.66 and −2.74 V *vs.* the Cp_2Fe/Cp_2Fe^+ couple; the reduction has also become significantly less reversible. When the concentration of Mg^{II} is doubled, a single reduction peak, $E_p = -2.64$ V, is again observed, but it is completely irreversible; moreover, the cathodic peak current density is close to twice that found in the absence of Mg^{II}. It is apparent that the presence of an excess of Mg^{II} in solution leads to the rapid decomposition of the radical anion and that the product of this chemical reaction is electroactive at the same potential. The peak doubling in conjunction with the positive shift of the peak potential with Mg^{II} in solution are characteristic of an ece process.

Fig. 4 illustrates a voltammogram recorded with a positive potential limit of +0.92 V *vs.* the Cp_2Fe/Cp_2Fe^+ couple. It can be seen that on the reverse sweep positive to −0.20 V there are several rather drawn out anodic waves. Moreover, on the second forward scan, there are two new cathodic peaks at E_p = −1.51 and −2.17 V which were not present on the first scan. Hence, these reducible species must be formed in a sequence involving reduction of the ester and oxidation of the products of the decomposition of the radical anion in the presence of Mg^{II}. The compound(s) responsible for these reduction peaks are discussed below. On continual potential cycling, these peaks grow slightly, but remain small and are both completely irreversible. Surprisingly, these peaks on the voltammogram sharpen up considerably when ferrocene is present in the solution. Fig. 5 shows the first two cycles of a voltammogram for a solution containing methyl benzoate (5.0 mmol dm^{-3}), anhydrous $Mg(CF_3SO_3)_2$ (10 mmol dm^{-3}) and ferrocene (5 mmol dm^{-3}) in DMF–Bu_4NBF_4 (0.1 mol dm^{-3}). On the first reverse scan, there is a sharp anodic peak at −0.14 V just before the ferrocene oxidation and on the second forward scan, the peaks at E_p = −1.51 and −2.17 V are clearly larger than in the experiment shown in Fig. 4. It would seem that the ferrocene is acting as a redox catalyst for the oxidation step.

Throughout this programme, it was considered important to confirm that the effects observed were in fact due to the presence of Mg^{II}, rather than water added with the $Mg(CF_3SO_3)_2$. For this reason, the voltammetry was repeated using Mg^{II} prepared by the anodic dissolution of Mg metal into DMF–Bu_4NBF_4 (0.1 mol dm^{-3}) in a divided cell. The concentration of Mg^{II} in this solution was calculated assuming that the anodic dissolution is 100% current efficient although the weight loss of the anode was *ca.* 30% in excess of that expected. The changes to the voltammetry of methyl benzoate when this Mg^{II} solution was added were identical to those reported above where the source of Mg^{II} is the salt, $Mg(CF_3SO_3)_2$. In a further series of experiments, the changes to the voltammograms were shown to be reversible when the concentration of Mg^{II} was first increased and then decreased again by dilution with a solution of ester in DMF–Bu_4NBF_4 (0.1 mol dm^{-3}). It was also confirmed that a solution of $Mg(CF_3SO_3)_2$ in DMF–Bu_4NBF_4 (0.1 mol dm^{-3}) exhibits no electrochemistry within the potential range of interest. Indeed, a cyclic voltammogram recorded with the vitreous carbon disc electrode between +0.6 and −3.8 V showed no peaks. Moreover, attempts to deposit Mg metal by taking the potential more negative than −3.8 V *vs.* the Cp_2Fe/Cp_2Fe^+ couple did not appear to be successful; no deposit could be seen on the carbon surface and no anodic stripping peak was observed.

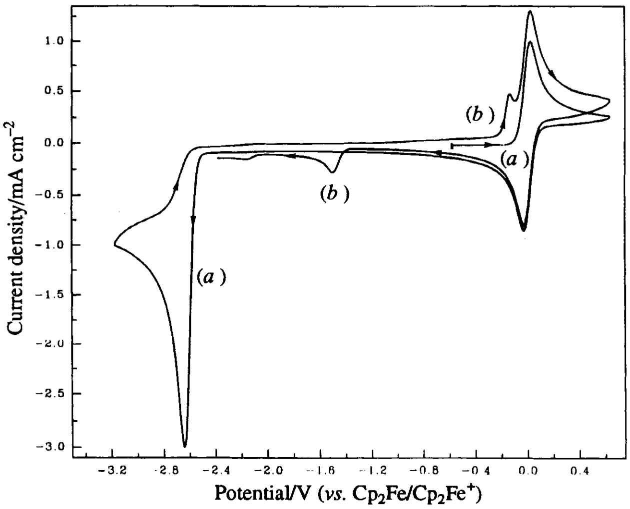


Fig. 5 Cyclic voltammograms for 5 mmol dm^{-3} methyl benzoate + 10 mmol dm^{-3} anhydrous $Mg(CF_3SO_3)_2$ in DMF–Bu_4NBF_4 (0.1 mol dm^{-3}) over the same potential range as Fig. 3, but after the addition of 5 mmol dm^{-3} ferrocene: (*a*) first scan and (*b*) second scan. Potential scan rate 80 mV s^{-1}. Vitreous carbon disc electrode (area 0.08 cm^2).

A controlled potential electrolysis was carried out in the divided cell at a large glassy carbon disc cathode (area 4.5 cm^2) for a solution of methyl benzoate (10 mmol dm^{-3}) in DMF–Bu_4NBF_4 (0.1 mol dm^{-3}) with 10 mmol dm^{-3} $Mg(CF_3SO_3)_2$ (higher concentrations led to passivation of the cathode). Initially, the cyclic voltammogram is identical to that of curve (*c*) of Fig. 3; the presence of the Mg^{II} has diminished the reversibility of the reduction of methyl benzoate and has a strong effect on the chemistry of the radical anion. At a potential of −2.90 V, no strongly coloured intermediates were formed early in the electrolysis and the electrolysis continued until $n \gg 1$. In fact, the electrolysis was terminated when $n = 1.5$. At this time, a cyclic voltammogram showed a reversible reduction for the methyl benzoate so apparently there is no Mg^{II} remaining to catalyse the reaction of the radical anion, the Mg^{II} must now be tied up by anionic products. The height of the cathodic peak is consistent with 37% of the initial methyl benzoate remaining in the catholyte and hence a value of n = 2.25 based on the ester consumed. Addition of ethyl iodide to the catholyte and GC analysis showed the complete absence of benzoate as a product. Experiments described below show that the yields of the dimeric products, benzil and benzoin are high.

The effects of adding $Mg(CF_3SO_3)_2$ to a solution of phenyl benzoate were similar to those for methyl benzoate. The

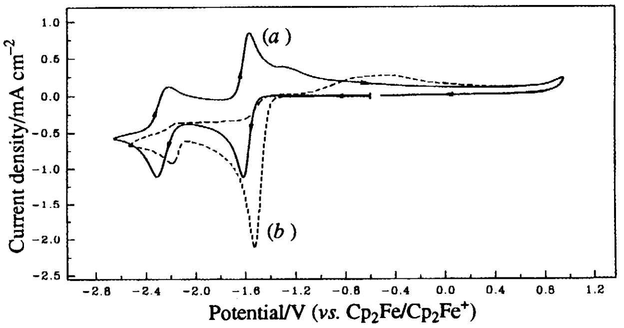


Fig. 6 Cyclic voltammograms for 5 mmol dm^{-3} benzil (*a*) before and (*b*) after the addition of 10 mmol dm^{-3} anhydrous $Mg(CF_3SO_3)_2$ in DMF–Bu_4NBF_4 (0.1 mol dm^{-3}). Potential scan rate 80 mV s^{-1}. Vitreous carbon disc electrode (area 0.08 cm^2).

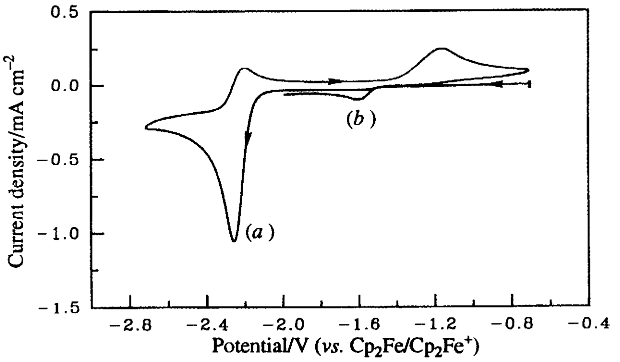


Fig. 7 Cyclic voltammograms for 5 mmol dm^{-3} benzoin in DMF–Bu_4NBF_4 (0.1 mol dm^{-3}): (*a*) first scan and (*b*) second scan. Potential scan rate 80 mV s^{-1}. Vitreous carbon disc electrode (area 0.08 cm^2).

addition of a two-fold molar excess of Mg^{II} was again sufficient to cause the height of the first reduction peak for phenyl benzoate to double and the peak potential shifts from -2.56 to -2.48 V *vs.* the Cp_2Fe/Cp_2Fe^+ couple. Again, the reverse scan shows several drawn out and small oxidation waves over the potential range -0.90 to $+0.10$ V and the second scan towards more negative potentials shows the same, small cathodic peaks at $E_p = -1.51$ and -2.17 V *vs.* the Cp_2Fe/Cp_2Fe^+ couple as observed in the voltammetry of methyl benzoate. Therefore, it must be concluded that during the first cycle a sequence of reduction and oxidation leads to the same compound(s) as formed from methyl benzoate.

Cyclic voltammetry of benzil and benzoin and the effects of addition of Mg^{II}

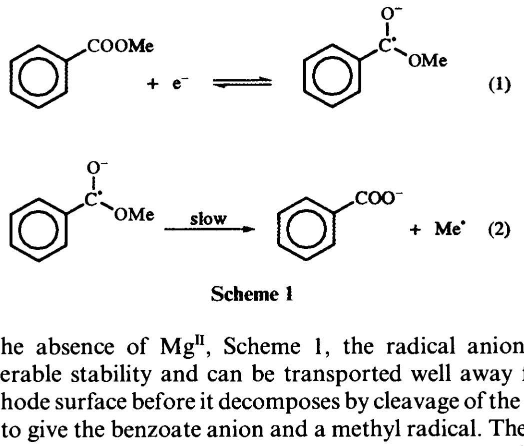
Curve (*a*) of Fig. 6 is a cyclic voltammogram for 5 mmol dm^{-3} benzil in DMF–Bu_4NBF_4 (0.1 mol dm^{-3}) at the vitreous carbon disc, recorded at 80 mV s^{-1}. The reduction occurs in two, 1e$^-$ steps at -1.61 and -2.30 V *vs.* the Cp_2Fe/Cp_2Fe^+ couple; the first appears to be completely reversible while the second, although of approximately equal height shows evidence for slow electron transfer as well as some slow coupled chemistry. The addition of $Mg(CF_3SO_3)_2$ again leads to marked changes and curve (*b*) illustrates the response when the ratio of [Mg^{II}]:[benzil] is 2:1. The first reduction step now occurs at -1.51 V. It is also completely irreversible and involves the total transfer of 2e$^-$; it seems that Mg^{II} interacts rapidly with the radical anion of benzil and the overall reduction becomes an ece process. There is also a second, but now much smaller reduction peak at more negative potentials and an anodic wave which begins at -0.98 V for the oxidation of the product from the reduction of benzil in the presence of Mg^{II}. It can be seen that the potentials of the two reduction peaks at -1.51 and -2.17 V *vs.* the Cp_2Fe/Cp_2Fe^+ couple in curve (*b*) coincide with those reported during the second cycle of a voltammogram for methyl benzoate in the presence of Mg^{II}. This is strong evidence for the formation of benzil during the voltammetry of the ester. Note that in common with similar anodic processes in the voltammetry of the esters, all the anodic waves observed in the presence of Mg^{II} are poorly formed and drawn out indicating some inhibition in their kinetics; also the observation of several waves may reflect that the product from the reductions of both methyl benzoate and benzil exist as a mixture of several species.

The voltammetry of benzoin is complex. It does not oxidise (*e.g.* to benzil) at any potential within the potential range available in DMF whether or not Mg^{II} is present. It does, however reduce, see Fig. 7. In the absence of Mg^{II}, the first reduction process occurs at -2.27 V and it is only slightly reversible. A reduction product is oxidisable at -1.20 V and on the second cycle there is a small cathodic peak whose potential corresponds to that for the reduction of benzil. It appears that a product from the reduction of benzoin is oxidised more readily than benzoin to benzil. On addition of Mg^{II}, the reduction peak for benzoin shifts slightly positive, but does not increase in height. No significant oxidation peaks are observed on the reverse sweep. The height of the cathodic peaks would indicate the transfer of only 1e$^-$ in both the presence and absence of Mg^{II}. It is possible that the benzoin itself acts as a proton donor, then the 2e$^-$ reduction of one benzoin molecule may be followed by protonation by a second molecule of benzoin. If the resulting alkoxide is electroinactive, the peak will appear as an overall 1e$^-$ reduction of benzoin.

The interpretation of the chemistry of these compounds is complicated by uncertainties about the form of the reduced species; *e.g.* the two electron reduction of each carbonyl group in the benzil molecule could lead to $>$CHOH, $>$CHO$^-$, $>$CHO$^-$Mg^{2+} or $>$C$^-$–O$^-$Mg^{2+} type species depending on the availability of Mg^{II} and proton donors (*e.g.* trace water, an OH group in the substrate). Certainly, the oxidation and reduction of a substrate containing a $>$CHOH group will not be the same as *e.g.* the species, $>$CHO$^-$Mg^{2+}, which is perhaps a more likely product from the reduction of the corresponding substrate containing a $>$C=O group when Mg^{II} is present. Hence, benzoin is a poor model for 'reduced benzil' in these solutions.

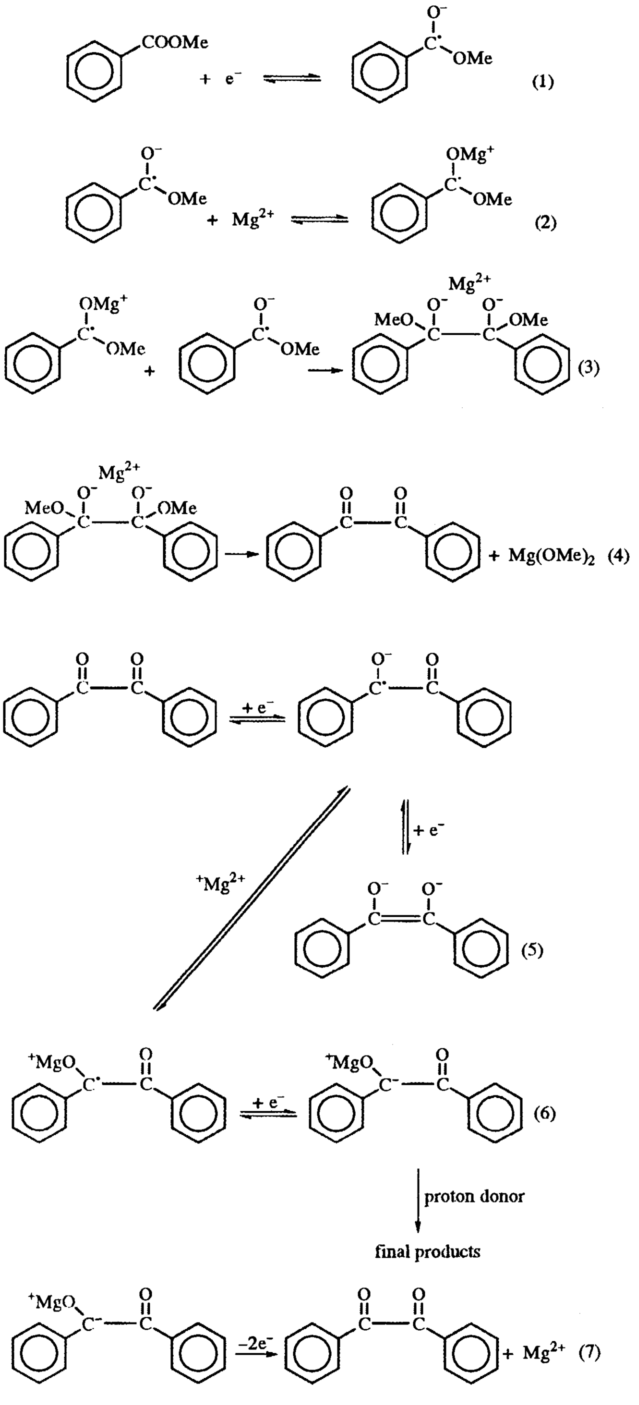
Mechanism for the reduction of benzoate esters in the presence of magnesium ions

The mechanisms proposed for the reduction of methyl benzoate in the aprotic medium are set out in Schemes 1 and 2.



Scheme 1

In the absence of Mg^{II}, Scheme 1, the radical anion has considerable stability and can be transported well away from the cathode surface before it decomposes by cleavage of the ester group to give the benzoate anion and a methyl radical. The fate of the methyl radical is unknown although coulometry shows



Scheme 2

that it does not reduce (most likely because it is formed in bulk solution where the concentration of reducing species is low) and since no products were observed by GC, it is probable that they are gases, CH_4 and/or C_2H_6.

In the presence of an excess of Mg^{II}, Scheme 2, the initial reduction of the ester is immediately followed by a chemical interaction between the radical anion and the Mg^{II} cation; the Mg^{II} may behave as a Lewis acid towards the negatively charged intermediate or the interaction may be regarded as the ion pairing or the formation of Mg–O bond. It is proposed that this interaction catalyses the formation of a dimer; in the scheme, the C–C bond formation is written as a reaction between the Mg^{II} complexed radical anion and a second radical anion, reaction (3), because it is thought that the opposite charges on the intermediates will assist the reaction. The same type of product could also arise by dimerisation of the Mg^{II} complexed radical anion. The formation of benzil then occurs by loss of the magnesium methoxide, reaction (4), a process probably driven by the higher stability of this alkoxide compared with the Mg^{II}–diol intermediate. Since Mg^{II} is present in solution, the reduction of benzil is an ece reaction and its reduction involves $2e^-$ per benzil molecule. Overall, therefore, the reduction of two methyl benzoate molecules involves $4e^-$. As a result, the voltammogram for methyl benzoate shows peak doubling on addition of an excess of Mg^{II} and methyl benzoate reduction then appears to be an ece reaction.

As discussed in the previous section, the exact structure of the product from the reduction of benzil in the presence of excess Mg^{II} is unclear. Indeed, as noted in the discussion of Fig. 4, the reverse scan of the voltammogram for the solution of methyl benzoate + excess Mg^{II} shows several small and drawn out oxidation waves and it may therefore be that the final product exists as a mixture of species whose composition depends on the availability of trace water or other proton donors. Certainly, several alternative structures could be written for the final product of reaction (6), but it is certain that Mg^{II} is involved and hence that benzoin is a poor model for this intermediate. The second cycle of the voltammogram for this solution shows the reduction peaks at -1.51 and -2.17 V and these coincide with the peaks for the reduction of benzil in the presence of Mg^{II}. Therefore, it is clear that benzil is formed by a reaction such as reaction (7) during the back scan. These reduction peaks are, however, small and it is difficult to assess whether this is due to the large potential separation of the peaks on the voltammogram combined with the complexity of the processes for the oxidation of 'reduced benzil' and their slow kinetics or whether Scheme 2 perhaps represents only one of several reaction pathways.

The importance of the reactions of Scheme 2 is, however, more readily defined by potential step experiments on a solution containing methyl benzoate and excess Mg^{II} ions. The potential step sequence selected was -1.90 V→-2.90 V (10 s)→$+0.50$ V (<1 s)→-1.90 V (<1 s). The first step is from a potential where no electrode reaction occurs to one where the reduction of methyl benzoate is mass transport controlled and, indeed, the current/time transient has the form predicted by the Cottrell equation with $n = 2$. The third potential is selected to be as positive as possible without oxidation of the solvent/electrolyte so that the oxidation of the 'reduced benzil' intermediates back to benzil is as complete as possible. The final potential was chosen so that the reduction of benzil is diffusion controlled, but methyl benzoate is not reduced. It was also wished to use established theory[16,18] to analyse quantitatively the transients during the second and third pulses; this would require the establishment of a concentration profile for the 'reduced benzil' intermediate at the end of the first pulse where its concentration is independent of distance from the electrode surface. This is clearly not possible as, in practice, the concentration of the product of the electrode reaction will drop sharply through the diffusion layer. It may be shown,[19] however, that a situation which approximates to the desired profile may be created by employing a first pulse which is very long compared with any experiment designed to examine this concentration profile. Effectively, only the profile relatively close to the surface is then important and over this distance the change in concentration is small. Fig. 8 shows a typical current/time response during the second and third pulses of an experiment with a solution containing 5 mol dm^{-3} methyl benzoate and 10 mmol dm^{-3} Mg^{II}. It can be seen that both transients show the expected fall in current with time. Moreover, during the oxidation pulse (NB at a very positive potential) the currents have the values predicted by the Cottrell

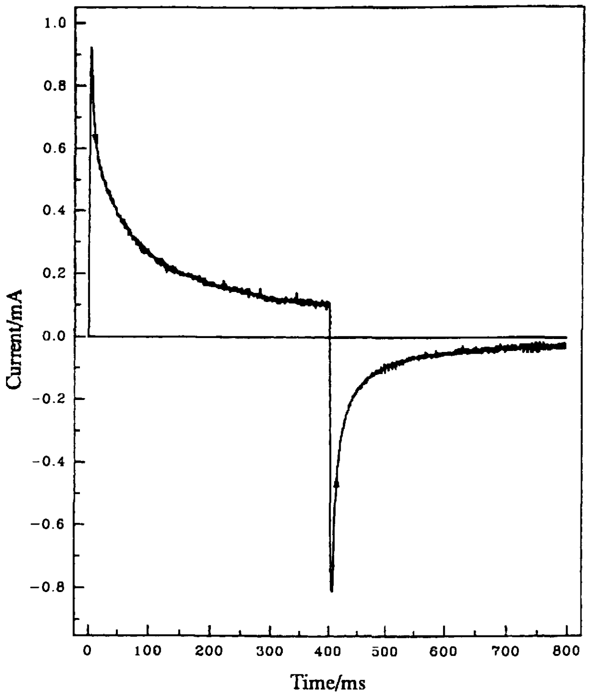


Fig. 8 Current/time transients during the second and third pulses of the potential step sequence -1.90 V$\rightarrow$2.90 V (10 s)$\rightarrow$+0.50 V (0.4 s)$\rightarrow-1.90$ V (0.4 s) *vs.* the Cp_2Fe/Cp_2Fe^+ couple. The solution was 5 mmol dm^{-3} methyl benzoate + 10 mmol dm^{-3} anhydrous $Mg(CF_3SO_3)_2$ in $DMF-Bu_4NBF_4$ (0.1 mol dm^{-3}). Vitreous carbon disc electrode (area 0.08 cm^2).

Table 1 Currents at the end of the second and third pulses as a function of pulse length. The pulse sequence was -1.90 V$\rightarrow$2.90 V (10 s)$\rightarrow$+0.50 V (τ s)$\rightarrow-1.90$ V (τ s) *vs.* the Cp_2Fe/Cp_2Fe^+ couple and the solution was 5 mmol dm^{-3} methyl benzoate + 10 mmol dm^{-3} anhydrous $Mg(CF_3SO_3)_2$ in $DMF-Bu_4NBF_4$ (0.1 mol dm^{-3}). Vitreous carbon disc electrode (area 0.08 cm^2).

Pulse length, τ/s	Current after τ/μA Pulse B	Current after τ/μA Pulse C	$-I_{red}/I_{ox}$
0.04	480	-85	0.18
0.10	265	-60	0.23
0.20	170	-40	0.23
0.40	110	-25	0.23
1.00	60	-15	0.25

equation assuming that the concentration of reactant, the 'reduced benzil' intermediate, is 2.5 mmol dm^{-3} (*i.e.* half the initial methyl benzoate concentration) and, as is reported in Table 1, the current on the reduction pulse corresponds to the value ($I_b/I_f \approx 0.25$) expected for the complete reduction of a stable species produced during the oxidation process.[18] Hence, the transients are consistent with the mechanism of Scheme 2 as the only reaction pathway. Certainly, they would confirm that the initial reduction of methyl benzoate in the presence of Mg^{II} leads to dimers in quantitative yields.

Electrochemical reduction of methyl benzoate in an undivided cell with a magnesium anode

An electrolysis was carried out with a constant current of 2 mA cm^{-2} in an undivided cell with a magnesium anode and a steel gauze cathode. The solution contained 25 mmol dm^{-3} methyl benzoate in $DMF-Bu_4NBF_4$ (0.1 mol dm^{-3}). At intervals during the passage of 2 F, the electrolysis was interrupted and a cyclic voltammogram was recorded *in situ* in the cell using a small vitreous carbon disc electrode. At the end of the electrolysis, the major product identified by GC analysis was benzil (yield > 50%) and this suggests that the 'reduced benzil' formed in the electrolysis is air oxidised before GC analysis. Certainly, dimers are formed in high yield.

Before the start of this electrolysis, the cyclic voltammogram recorded between -2.0 and -3.0 V showed a reversible process at -2.74 V for the reduction of methyl benzoate. As the electrolysis proceeded, the shape of the voltammogram remained unchanged although the size of the peaks diminished as the ester was consumed. There is no tendency to form two peaks or to observe an ece reaction as was reported above when Mg^{II} is added to the solution. It must therefore be concluded that there is no build up of free Mg^{II} in solution (although the anode showed the expected weight loss and independent experiments confirmed that Mg^{II} is the product of anodic dissolution in similar conditions). Clearly, all the Mg^{II} formed at the anode is tied up by anionic products from the cathode reaction and their subsequent chemistry. Moreover, it must be concluded that the change in product, due to the use of an Mg anode and an undivided cell, cannot be due to changes in the chemistry within the diffusion layer at the cathode surface. The dimeric products must be formed in the bulk solution by reaction between the radical anion from the cathode and Mg^{II} from the anode. There is, however, no reason to believe that the mechanism of the chemistry is different from that proposed in Scheme 2 above except that the benzil will only be reduced when it returns to the cathode surface.

Conclusions

Without doubt, the presence of Mg^{II} ions in solution has a large effect on the mechanism and products of the reduction of benzoate esters in aprotic solvents. In the absence of Mg^{II}, the radical anion is relatively stable and the product is formed by cleavage of the ester to give benzoate as the major product. With a ratio of Mg^{II}:substrate > 1 in solution, the reduction of the ester becomes an ece reaction; the radical anion reacts rapidly to form benzil which reduces further. Both short timescale pulse experiments and controlled potential electrolyses show that the major products are dimeric. When the electrolysis is carried out in an undivided cell with an Mg^{II} anode there is never an excess of Mg^{II}. The Mg^{II} is tied up by anionic products and a cyclic voltammogram in the electrolyte does not show the effect caused by Mg^{II}. On the other hand, the major products are confirmed to be dimeric and it is proposed that the Mg^{II} formed at the anode influences the products from the cathode reaction through reactions in the bulk electrolyte.

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