Green Chemistry

Cite this: *Green Chem.*, 2011, **13**, 3461

www.rsc.org/greenchem

PAPER

A unique proton coupled electron transfer pathway for electrochemical reduction of acetophenone in the ionic liquid [BMIM][BF_4] under a carbon dioxide atmosphere

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Received 30th July 2011, Accepted 16th September 2011
DOI: 10.1039/c1gc15929a

The mechanism of electrochemical reduction of acetophenone in 1-butyl-3-methylimidazolium tetrafluroborate ([BMIM][BF_4]) under nitrogen (N_2) and carbon dioxide (CO_2) atmospheres have been investigated using transient voltammetry, steady-state voltammetry, bulk electrolysis and numerical simulation. Under a N_2 atmosphere, acetophenone undergoes a one-electron reduction to the radical anion followed by rapid dimerization reactions with an apparent rate constant of 1.0×10^6 M^{-1} s^{-1}. In contrast, under a CO_2 atmosphere, the electrochemical reduction of acetophenone is an overall two-electron transfer chemically irreversible process with the final electrolysis product being 1-phenylethanol, instead of the anticipated 2-hydroxy-2-phenylpropionic acid resulting from an electrocarboxylation reaction. A proton coupled electron transfer pathway leading to the formation of 1-phenylethanol requires the presence of a sufficiently strong proton donor which is not available in neat [BMIM][BF_4]. However, the presence of CO_2 enhances the C-2 hydrogen donating ability of $[BMIM]^+$ due to strong complex formation between the deprotonated form of $[BMIM]^+$, *N*-heterocyclic carbene, and CO_2, resulting in a thermodynamically favorable proton coupled electron transfer pathway.

Introduction

Electrochemical studies of ketones have received considerable attention in recent years due to their applications in the pharmaceutical industry as precursors for the formation of high value chemicals using an environmentally friendly electrocarboxylation reaction with carbon dioxide.[1–3]

Acetophenone, which represents one of the most widely studied ketones,[4–6] has the ability of accepting one or two electrons. In conventional solvents, such as dimethylformamide (DMF), acetonitrile (MeCN), *N*-methyl-2-pyrrolidone (NMP), methanol water mixtures *etc.*, and under a N_2 atmosphere, acetophenone undergoes a one-electron reduction reaction followed by a homogeneous dimerization reaction leading to the formation of electro-inactive 2,3-diphenyl-butane-2,3-diol.[7] Upon addition of a sufficiently strong acid, this one-electron reduction process can be converted into an overall two-electron reduction process through a proton coupled electron transfer reaction pathway, with 1-phenylethanol as the main product.[8] Under a CO_2 atmosphere, the intermediate complex of the one-electron reduced form of acetophenone radical anion and CO_2 can accept an additional electron to form 2-hydroxy-2-phenylpropionic acid.[9] However, due to the competitive co-existence of the dimerization route, the reduction reaction also generates dimers. The ratio between 2-hydroxy-2-phenylpropionic acid and dimers depends on the experimental conditions. In particular, the solvent significantly affects both the kinetics and thermodynamics of dimerization and electrocarboxylation reactions.

Several groups, including us, have reported the preparative scale electrocarboxylation reaction of acetophenone in conventional organic solvents using an undivided electrolysis cell equipped with an appropriate cathode and a sacrificial anode.[9–12] 2-Hydroxy-2-phenylpropionic acid was obtained in good yield. However, with the growing demand for environmentally friendly processes, efforts need to be devoted to eliminate the use of volatile and toxic solvents, such as DMF, NMP and MeCN. In recent years, room-temperature ionic liquids (RTILs) have been advocated in green chemical applications in organic synthesis because they may exhibit desirable properties such as negligible volatility, thermal and chemical stability, low toxicity and non-flammability. In addition, their high conductivity, wide electrochemical potential windows and the ability to dissolve large amounts of CO_2 and organic substrates[13–17] make RTILs very

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useful media for electrocarboxylation reactions.[18–23] Lagrost and co-workers have reported the electrochemistry of acetophenone in several imidazonium and ammonium based ionic liquids containing bis(trifluromethylsulfonyl)imide anion under a N_2 atmosphere.[24] They found that electroreduction of acetophenone in these ionic liquids follows an EC (heterogeneous electron transfer followed by a chemical reaction) mechanism with the C step being a rapid dimerization reaction. However, detailed mechanistic studies of electrochemistry of acetophenone in ionic liquids in the presence of CO_2 have not been reported.

In this paper, we report detailed electrochemical studies of acetophenone in the ionic liquid [BMIM][BF_4] under both N_2 and CO_2 atmospheres using transient cyclic voltammetry, steady-state voltammetry, bulk electrolysis and numerical simulation.

Experimental

Chemicals

[BMIM][BF_4] was purchased from IOLITEC (Germany). The ionic liquid was dried under vacuum at 80 °C for 24 h prior to use. The water content in [BMIM][BF_4] after such a pretreatment step is 60 ± 10 ppm as measured by Karl Fischer titration. Acetophenone (ReagentPlus®, 99%), 4-methoxy acetophenone (99%), MeI (ReagentPlus®, 99.5%), diethyl ether (Analytical reagent, >99%) and ferrocene (≥98%) were purchased from Sigma Aldrich and used as received. [Bu_4N][PF_6] (GFS Chemicals, Inc, 98%) was recrystallised twice with ethanol prior to use.

Voltammetric measurements

Voltammetric measurements were undertaken with a CHI760 electrochemical analyzer (CH Instruments, Texas, USA) using a standard three-electrode cell. For transient cyclic voltammetric experiments, glassy carbon (GC (1.8 and 3 mm diameters)) or other metallic macrodisc electrodes (Ag (2 mm diameter), Cu (2 mm diameter), Ni (2 mm diameter), Ti (2 mm diameter) and Pt (2 mm diameter)) or a carbon fiber microdisc electrode (33 μm diameter) was used as the working electrode. Ag wire was used as the quasi-reference electrode and Pt wire was used as the counter electrode. This quasi reference potential scale was then converted to the Fc/Fc^+ (Fc = ferrocene) reference potential scale. Working electrodes were polished using 0.3 μm or 0.05 μm alumina slurry on a polishing cloth (BAS), sonicated in deionised water, rinsed with water and acetone and then dried with nitrogen before use. For the steady-state voltammetric measurements, a carbon fiber microdisc electrode (7 μm diameter) was used together with the aforementioned counter and reference electrodes. All voltammetric experiments were undertaken at room temperature of 25 ± 2 °C in a dry box. The exact radii (r) of the carbon fiber microdisc electrodes used for quantitative studies were determined to be 3.6 and 18 μm respectively, based on the steady-state diffusion limiting current (I_L) for the oxidation of Fc in MeCN/0.1 M [Bu_4N][PF_6], using the following equation[25] and a known diffusion coefficient (D) value of 2.4×10^{-5} $cm^2\ s^{-1}$.[26]

$$I_L = 4nFrDC \tag{1}$$

where n is the number of electrons transferred ($n = 1$ in this case); F is Faraday's constant and C is the concentration of Fc.

Simulations of the voltammograms were undertaken with the DigiElch® software package. A two-dimensional mass transport model was used to take into account the contribution from radial diffusion at slow scan rates. Butler–Volmer kinetics was used to describe the potential-dependent kinetics of the heterogeneous electron transfer.

Bulk electrolysis

Potentiostatic bulk electrolysis was undertaken at 25 °C under both N_2 and CO_2 atmospheres in an undivided cell equipped with a glassy carbon beaker cathode, a magnesium sacrificial anode and a silver wire quasi-reference electrode immersed into [BMIM][BF_4] and separated by a glass frit. A slow stream of CO_2 (to provide a constant supply of the reactant) or N_2 (to prevent O_2 from entering the electrolysis cell) was applied during the electrolysis. 5 mL of [BMIM][BF_4] containing 50 mM acetophenone was used for electrolysis. The duration of electrolysis, defined as the time required to reach theoretical value of electricity consumption for a completed electrolysis, is typically about 10 h due to the low mass transport rate associated with highly viscous [BMIM][BF_4]. After electrolysis under a N_2 atmosphere, the products were extracted three times with diethyl ether. After the electrolysis under a CO_2 atmosphere, the reaction mixture was esterified in [BMIM][BF_4] by adding anhydrous K_2CO_3 (1 mmol) and MeI (3 mmol) with stirring the mixture at 50–60 °C for 5 h. After this step, the reaction mixture was extracted three times with diethyl ether. Finally, the organic layer was dried with anhydrous $MgSO_4$, filtered, concentrated and then analyzed by GC–MS (HP 6890A gas chromatograph equipped with a 5973 N mass selective detector, Agilent, USA).

Results and discussion

Transient cyclic voltammograms of acetophenone reduction at a macrodisc electrode

Electroreduction of acetophenone occurs in the very negative potential region where direct electroreduction of CO_2 may also occur. Therefore, cyclic voltammetric experiments were first conducted to identify suitable electrodes for the investigation of acetophenone reduction in [BMIM][BF_4] under a CO_2 atmosphere without suffering any interference from the direct electroreduction of CO_2. Cyclic voltammograms of 10 mM acetophenone (under a N_2 atmosphere) and saturated CO_2 were obtained at several commonly used electrodes, including Ag (2 mm diameter), Cu (2 mm diameter), Ni (2 mm diameter), Ti (2 mm diameter), Pt (2 mm diameter) and GC (3 mm diameter), at a scan rate of 0.05 V s^{-1} (Fig. 1). In all cases, no companion oxidation process was observed to accompany the electroreduction of acetophenone within the potential region of investigation when the potential direction was reversed and scanned in the positive potential direction. This suggests that the reduction of acetophenone is chemically irreversible on the time scale of the measurement due to the presence of a homogeneous reaction involving the electrogenerated acetophenone radical anion. The homogeneous reaction coupled to electron transfer is most likely the dimerization reaction according to the previous studies in both conventional solvents[7,8] and ionic liquids.[24,27] The electroreduction of acetophenone remained fully irreversible

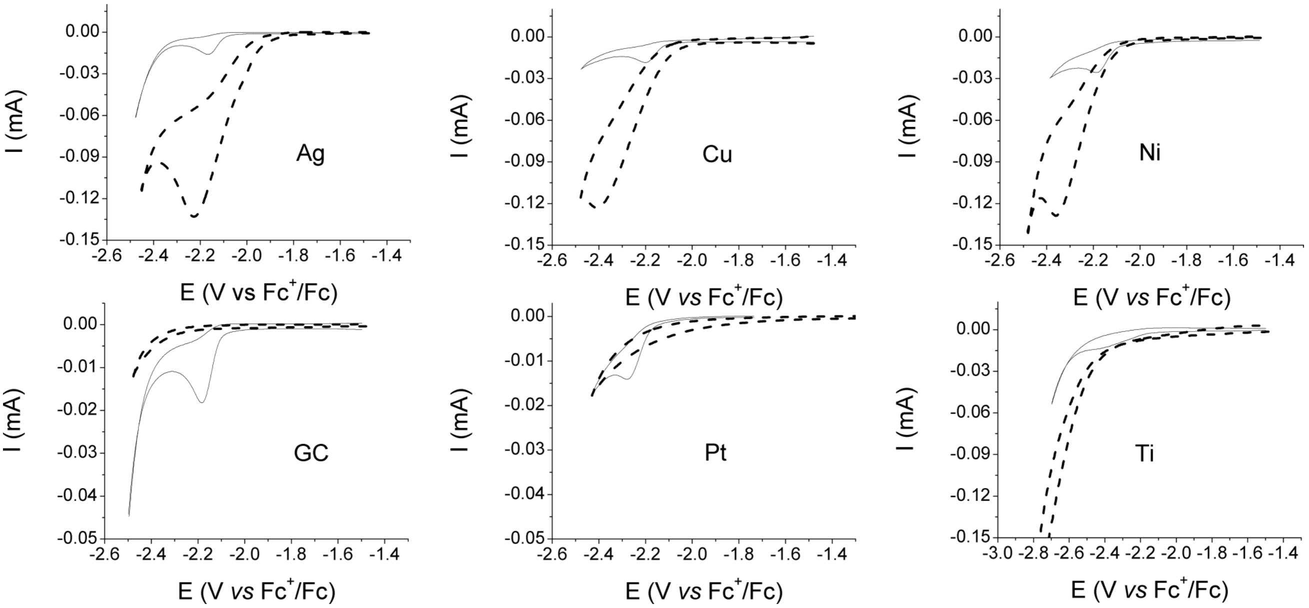


Fig. 1 Cyclic voltammograms recorded at a scan rate of 0.05 V s^{-1} using designated working electrodes (Ag, Cu, Ni, Ti and Pt (2 mm diameter), and GC (3 mm diameter)) in [BMIM][BF$_4$] containing 10 mM acetophenone under a N$_2$ atmosphere (—) and saturated CO$_2$ at 1 atm (---).

Table 1 Peak potentials (V *vs.* Fc$^+$/Fc) obtained for the reduction of CO$_2$ and acetophenone in [BMIM][BF$_4$] at designated electrodes under voltammetric conditions[a]

Electrodes	Ag	Cu	Ni	Pt	Ti	GC
E_{P,CO_2}	−2.23	−2.34	−2.36	—	—	—
$E_{P,acetophenone}$	−2.17	−2.20	−2.19	−2.27	−2.49	−2.18

[a] Experimental conditions are summarized in Fig. 1.

even when a scan rate of 10 V s^{-1} was used. The peak potential for acetophenone reduction at the Ti electrode (−2.49 V) is much more negative than those recorded at Cu (−2.20 V), Ni (−2.19 V), glass carbon (GC) (−2.18 V) and Ag (−2.17 V). The electroreduction of acetophenone at the Pt electrode (−2.27 V), although not as negative as at Ti, is much closer to the solvent negative potential limit, which is more positive at the Pt electrode.

Direct electroreduction of CO$_2$ also occurs at all electrodes in the potential range of acetophenone reduction except for the GC electrode. GC is known to be a more inert electrode, compared to metallic electrodes for direct CO$_2$ reduction.[28] Peak potentials for the irreversible reduction of both acetophenone and CO$_2$ are summarized in Table 1.

Based on the observations outlined above, GC was selected as the electrode material of choice for detailed investigations of the electroreduction of acetophenone under both N$_2$ and CO$_2$ atmospheres. Under a N$_2$ atmosphere, the acetophenone reduction peak current is proportional to the square root of the scan rate in the range of 0.05 V s^{-1} to 1.0 V s^{-1}. This suggests that both the heterogeneous electron transfer and coupled homogeneous reaction are rapid on the time scale of these measurements.[25] A small oxidation process at −1.09 V was also observed in the reverse cycle of potential after the irreversible reduction of acetophenone (Fig. 2). This indicates the formation of a new compound during the electroreduction of acetophenone. The fact that the oxidation peak current increases almost proportionally with the increase in acetophenone concentration (Fig. 3), suggests that this new compound is not resulting from the reaction between water (less than 3.0 mM in the [BMIM][BF$_4$] used in our studies) or other impurities in [BMIM][BF$_4$] and the electroreduction products of acetophenone. A similar observation reported by Amatore and co-workers[8] in their studies of electroreduction of acetophenone in DMF in the presence of cyclodextrin was attributed to the formation of a head-to-tail type of dimer (1-[4-(1-hydroxy-ethylidene)-cyclohexa-2,5-dienyl]-1-phenyl-ethanol). To investigate whether this is also the case in our study, voltammetric experiments with 4-methoxy acetophenone were also undertaken. The formation of a

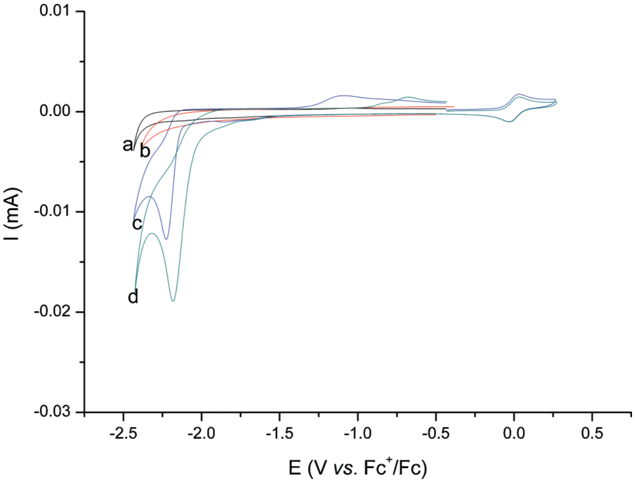
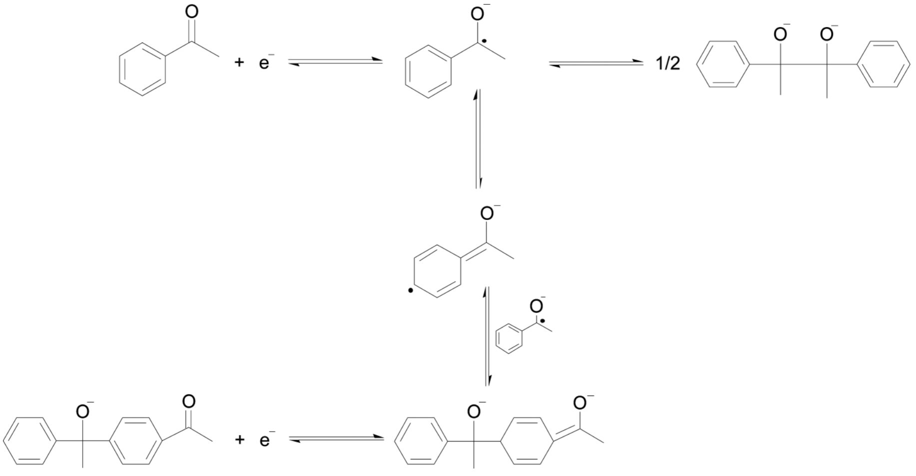


Fig. 2 Cyclic voltammograms recorded at a 1.8 mm diameter GC electrode (scan rate = 0.1 V s^{-1}) in neat [BMIM][BF$_4$] under (a) N$_2$ or (b) CO$_2$ (1 atm) atmospheres, and for [BMIM][BF$_4$] containing 10 mM acetophenone under (c) N$_2$ and (d) CO$_2$ (1 atm) atmospheres. Cyclic voltammograms obtained for the Fc/Fc$^+$ process (around 0 V) with 2.7 mM Fc are included for comparison.



Scheme 1 Reaction scheme proposed for reduction of acetophenone in [BMIM][BF$_4$] under a N$_2$ atmosphere.

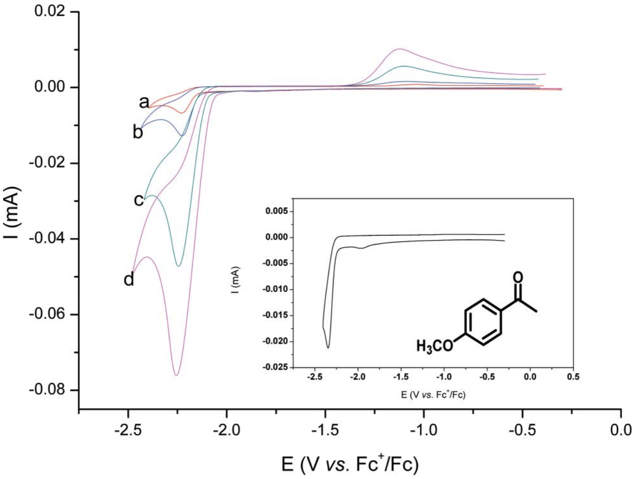


Fig. 3 Cyclic voltammograms (scan rate = 0.1 V s^{-1}) recorded under a N$_2$ atmosphere with a 1.8 mm diameter GC electrode in [BMIM][BF$_4$] containing designated concentrations of acetophenone (a: 5 mM, b: 10 mM, c: 50 mM and d: 100 mM). The inset figure shows a cyclic voltammogram (scan rate = 0.1 V s^{-1}) of 10 mM 4-methoxy acetophenone recorded under a N$_2$ atmosphere with a 3.0 mm diameter GC electrode in [BMIM][BF$_4$].

head-to-tail type of dimer is prevented during this electroreduction process due to the presence of a methoxy group at the *para* position on the aromatic ring. The fact that no oxidation process was observed (see inset of Fig. 3) suggests that the small oxidation peak at –1.09 V (Fig. 3) could be assigned to the oxidation of the head-to-tail type of dimer. Based on these experimental observations and the results from the literature,[8,24] the following reaction scheme is proposed. The important roles played by the ionic liquid during the formation of dimers[24] are omitted in Scheme 1 for simplicity.

Upon saturation of [BMIM][BF$_4$] with CO$_2$, the acetophenone reduction peak current magnitude increased significantly and the peak potential shifted to a more positive value. Compton and co-workers found that the viscosity of 1-ethyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide decreased by nearly 20% when saturated with CO$_2$.[29] To ascertain if the observation of increased current in the presence of CO$_2$ is due to the decrease in viscosity of [BMIM][BF$_4$], Fc was added to the solution and cyclic voltammograms of the reversible Fc$^+$/Fc process were also recorded under both N$_2$ and CO$_2$ atmospheres (Fig. 2). The fact that the oxidation peak current for the Fc$^+$/Fc process remains essentially unaltered suggests that the viscosity of [BMIM][BF$_4$] does not vary appreciably in the presence of CO$_2$. Consequently, the increase of acetophenone reduction peak current and positive shift of peak potential in the presence of CO$_2$ are attributed to the occurrence of new chemistry, likely involving an additional electron transfer step. In the presence of CO$_2$, a minor new oxidation process with a peak potential of –0.68 V was found in the reverse potential scan direction after the potential was switched following the irreversible reduction of acetophenone.

Steady-state voltammograms of acetophenone reduction at a carbon fiber microdisc electrode

To gain further mechanistic insights, near steady-state voltammetric measurements of acetophenone reduction under both N$_2$ and CO$_2$ atmospheres were undertaken in [BMIM][BF$_4$] with a 7 μm diameter carbon fiber microdisc electrode. The results obtained with three different acetophenone concentrations (1.0, 10.0 and 50.0 mM) are shown in Fig. 4. The steady-state diffusion limiting currents are proportional to the concentration of acetophenone under both CO$_2$ and N$_2$ atmospheres. Importantly, the steady-state diffusion limiting currents obtained under a CO$_2$ atmosphere are twice those obtained under N$_2$. Since acetophenone is believed to undergo a one-electron reduction reaction under a N$_2$ atmosphere (Scheme 1), an overall two-electron transfer reaction must occur under a CO$_2$ atmosphere. The doubling of the steady-state current in the presence of CO$_2$ implies that the follow-up chemistry is not rate limiting and is faster than the dimerization reaction (Scheme 1). Under our experimental conditions, acetophenone is likely to undergo a two-electron reduction pathway *via* a proton coupled electron transfer reaction described in Scheme 2 which is known to occur in the presence of a sufficiently strong acid[8] or *via* the electrocarboxylation reaction described in Scheme 3 which has

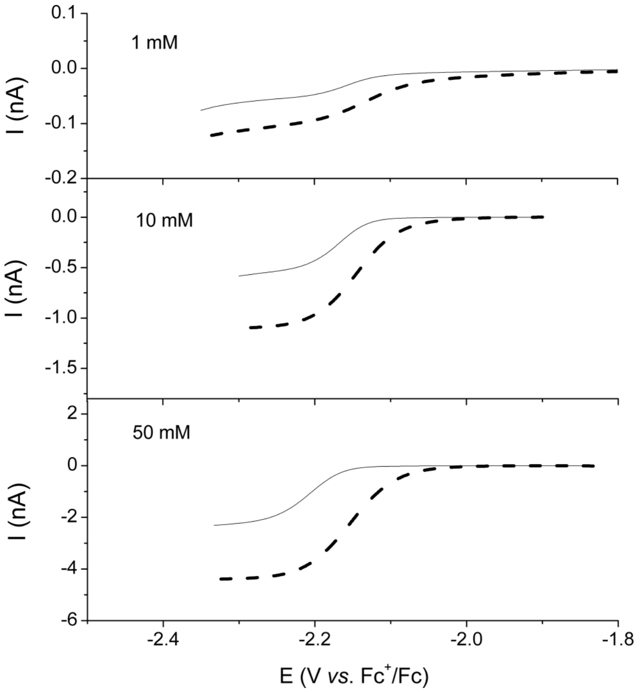
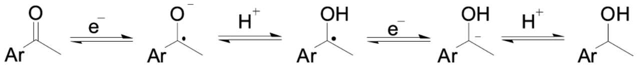
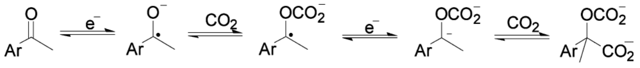


Fig. 4 Near steady-state voltammograms for the reduction of acetophenone (1 mM, 10 mM and 50 mM) in [BMIM][BF_4] recorded at a carbon fiber microdisc electrode (7.2 μm diameter) at a scan rate of 10 mV s^{-1} under N_2 (—) or CO_2 (---) atmospheres.



Scheme 2 Reaction scheme for reduction of acetophenone in acidic media.



Scheme 3 Reaction scheme for reduction of acetophenone in conventional solvent media under a CO_2 atmosphere.

been found to apply in conventional molecular solvents, such as MeCN, DMF and NMP, in the presence of CO_2.[9,10,30]

Preparative scale bulk electrolysis

To verify that Scheme 1 is applicable to the acetophenone reduction under a N_2 atmosphere and to identify which of the reaction pathways applies under a CO_2 atmosphere, preparative scale bulk electrolysis experiments were undertaken using a large glassy carbon beaker cathode and a Mg sacrificial anode in an undivided cell.

After electrolysis under a N_2 atmosphere, the products of the electrolysis were separated from [BMIM][BF_4] by extraction with diethyl ether. Products obtained after electrolysis and identified by GC–MS along with their yields are summarized in Table 2. No 1-phenylethanol could be detected by GC–MS analysis. These results confirm that the formation of dimers (100%) after electroreduction of acetophenone (Scheme 1) is the major reaction pathway. However, the GC–MS results do not provide information on the proportion of each dimer since they are essentially indistinguishable by GC–MS under our experimental conditions.

Under a CO_2 atmosphere, one possible product is 2-hydroxy-2-phenylpropionic acid resulting from the electrocarboxylation reaction. To identify this product by GC–MS, it is necessary to convert the acid to an ester through an esterification reaction with MeI. After esterification, products were separated from [BMIM][BF_4] by extraction with diethyl ether. Products obtained after electrolysis were identified by GC–MS and their yields determined; all results are summarized in Table 2. The data obtained reveal that the formation of 1-phenylethanol after electroreduction of acetophenone (Scheme 2) is the major reaction pathway, an outcome which is totally different to that found in molecular solvents (DMF, MeCN and NMP).[9,12] In these conventional organic solvents, carboxylation and dimerization reactions are the major chemical reactions that follow radical anion formation. This pathway is also highly unexpected in the [BMIM][BF_4] medium, since a proton coupled electron transfer reaction pathway (Scheme 2) requires the presence of a moderately strong acid.[8] The acidity of [BMIM][BF_4] is very weak (pK_a about 21–23.[31]). Furthermore, previous studies by Fredlake *et al.*[32] suggest that the addition of CO_2 to ionic liquids does not modify the strength of hydrogen bonds between ionic liquids and the solvatochromic dye, Reichardt's dye 33. Consequently, the enhanced proton donating ability of [BMIM][BF_4] in the presence of CO_2 is assumed to be induced by another thermodynamically favorable processes.

In order to establish a possible mechanism which supports a proton coupled electron transfer pathway, it is crucial to identify the source of the proton. In the ionic liquid [BMIM][BF_4], a proton may be derived from a trace impurity (*e.g.* H_2O) or the C-2 hydrogen in [BMIM]$^+$.[31] Since the water content in the [BMIM][BF_4] used in these studies is relatively low (less than 3.0 mM), the C-2 hydrogen of [BMIM]$^+$ is the most likely source of the proton. In principle, [BMIM]$^+$ can donate its C-2 hydrogen to a strong base, such as the electrogenerated acetophenone

Table 2 Products[a] obtained from preparative scale reductive electrolysis of 50 mM acetophenone in [BMIM][BF_4]

Atmosphere (P = 1 atm)	Anode/Cathode	Charge/F mol^{-1}	Applied potential (V *vs.* Fc$^+$/Fc)	Product yield (%)[b] dimer	acid	alcohol	Conv. (%)[c]
N_2	Mg/GC	1.0	–2.28	100	0	0	66
CO_2	Mg/GC	2.0	–2.23	trace	1[d]	97	65

[a] Dimer = 1-[4-(1-hydroxy-ethylidene)-cyclohexa-2,5-dienyl]-1-phenyl-ethanol and 2,3-diphenyl-butane-2,3-diol; acid = 2-hydroxy-2-phenylpropionic; alcohol = 1-phenylethanol. [b] Gas chromatography yields based on the consumed substrate. [c] Acetophenone reduced/total acetophenone. [d] Identified after conversion to an ester through an esterification reaction with CH_3I.

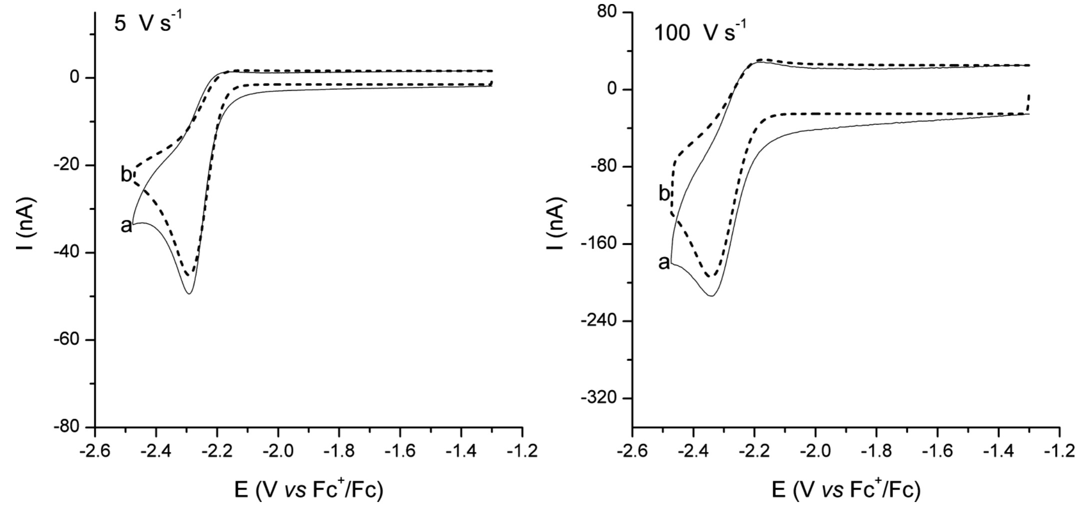
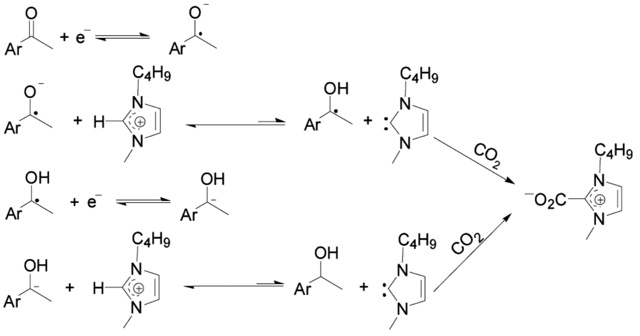


Fig. 5 (a) Cyclic voltammogram for the reduction of 10 mM acetophenone in [BMIM][BF$_4$] recorded at a carbon fiber microdisc electrode (36 µm diameter) at scan rates of 5 V s^{-1} or 100 V s^{-1} and (b) voltammograms simulated based on the mechanism described in Scheme 5 and the parameters: $E^0 = -2.265$ V, $k_s = 0.035$ cm s^{-1}, $\alpha = 0.5$, $R = 30\,000\ \Omega$, $C_d = 2.3 \times 10^{-10}$ F, $D = 5 \times 10^{-7}$ cm^2 s^{-1} for all species, $k_f = 1.0 \times 10^6$ M^{-1} s^{-1}.

radical anion, and form a *N*-heterocyclic carbene.[33] However, the acidity of [BMIM]$^+$ is too weak to favour this scenario and the dimerization reaction of the acetophenone radical anion is very rapid. Therefore, the proton coupled electron transfer reaction pathway (Scheme 2) leading to the formation of 1-phenylethanol does not occur in neat [BMIM][BF$_4$] under a N$_2$ atmosphere. However, the situation prevailing in the presence of CO$_2$ is different. It has been reported that CO$_2$ can form a highly stable complex with *N*-heterocyclic carbene.[34–36] The follow up process in the presence of CO$_2$ is highly thermodynamically and kinetically favorable. Plausibly, [BMIM]$^+$ could donate its C-2 hydrogen much more readily to the electrogenerated acetophenone radical anion and the benzhydrol monoanion. Consequently, it is proposed that a proton coupled electron transfer reaction can occur favorably through the reaction pathway given in Scheme 4.



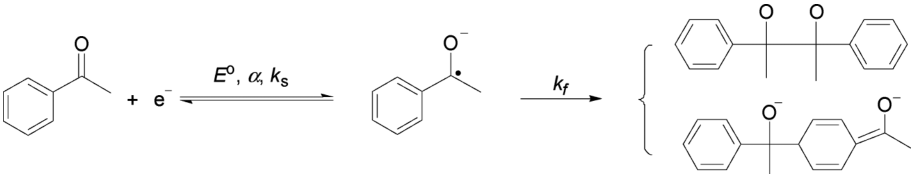
Scheme 4 Reaction scheme proposed for reduction of acetophenone in [BMIM][BF$_4$] under a CO$_2$ atmosphere.

Kinetics of coupled homogeneous chemical reactions occurring during the electroreduction of acetophenone

Voltammetric data obtained at a 1.8 mm diameter macrodisc GC electrode suggest that the coupled homogeneous reaction kinetics are very fast (Fig. 2). In order to quantify fast kinetics using transient voltammetry, a sufficiently fast scan rate is required so that the kinetics becomes relatively slow with respect to the time scale of the measurement. In order to overcome the intolerable uncompensated resistance effects occurring at very fast scan rates when using a macroelectrode, microelectrodes are conventionally used.[37–41] Consequently, a 36 µm diameter carbon fiber microdisc electrode was used to obtain very fast scan rate voltammetric data for acetophenone reduction under both N$_2$ and CO$_2$ atmospheres.

Under a N$_2$ atmosphere, the electroreduction of acetophenone is completely chemically irreversible at a scan rate of 5 V s^{-1}. The partial chemical reversibility required for quantifying the kinetics was achieved when the scan rate was increased to 100 V s^{-1} (Fig. 5). To quantify the kinetics of dimerization reactions using numerical simulation, a simplified reaction mechanism was proposed in Scheme 5 taking into account the combined contribution from two dimerization reactions.

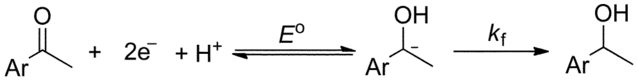
In this scheme, E^0, α and k_s represent the formal reversible potential, electron transfer coefficient and formal heterogeneous electron transfer rate constant, respectively. k_f stands for the apparent rate constant of dimerization reactions. For quantitative



Scheme 5 Simplified reaction scheme proposed for reduction of acetophenone in [BMIM][BF$_4$] under a N$_2$ atmosphere.

numerical simulations, it is important to accurately know the diffusion coefficients of all species involved in the reaction. The diffusion coefficient of 5.0×10^{-7} cm^2 s^{-1} for acetophenone is calculated from the steady-state diffusion limiting current of acetophenone reduction (Fig. 4) using eqn (1). The diffusion coefficients of other species involved in the reactions are assumed to be the same as for acetophenone. Simulated voltammograms obtained using a heterogeneous electron transfer rate constant of 0.035 cm s^{-1}, taken from the previous studies by Lagrost *et al.*,[24] a D value of 5.0×10^{-7} cm^2 s^{-1} and other parameters specified in the caption of Fig. 5 agree well with the experimental results. The major discrepancy between experimental results and simulated data is attributed to the fact that double layer capacitance (C_d) is not constant as assumed in the simulations. The second order rate constant for the dimerization reactions is estimated to be 1.0×10^6 M^{-1} s^{-1} based on the experiment *versus* theory comparisons. This value falls within the range of 0.8×10^5 M^{-1} s^{-1} to at least 4.0×10^6 M^{-1} s^{-1} reported previously for the same system in other imidazolium based ionic liquid media.[24,27]

Under a CO_2 atmosphere, the electroreduction of acetophenone remained completely chemically irreversible even at a scan rate of to 5 000 V s^{-1} (the upper limiting achievable with our potentiostat). Thus, the kinetics of the follow-up chemical reaction are now too fast to be measured under our experimental conditions. However, this observation explains why dimer formation is negligible under a CO_2 atmosphere. A lower limit of the rate constant associated with the chemical reaction is estimated to be 3.0×10^5 s^{-1}. This value is obtained using a numerical simulation based on a simplified reaction mechanism described in Scheme 6. In Scheme 6, it is assumed that the first process is reversible and the second protonation of the benzhydrol monoanion is the rate limiting step. Since the protons provided by the ionic liquid in the presence of CO_2 are in large excess, the activity of the proton donor remains constant during the reaction and therefore is included in the k_f term.



Scheme 6 Simplified reaction scheme proposed for reduction of acetophenone in [BMIM][BF_4] under a CO_2 atmosphere.

Conclusions

Electroreduction of acetophenone in [BMIM][BF_4] under both N_2 and CO_2 atmospheres has been investigated using transient voltammetric, steady-state voltammetric, bulk electrolysis techniques, and numerical simulation. The results support a mechanism involving electroreduction followed by dimerization reactions under a N_2 atmosphere, with an apparent dimerization rate constant of 1.0×10^6 M^{-1} s^{-1} being estimated from comparison of experimental data measured by fast scan rate cyclic voltammetry and theoretical data obtained from numerical simulation. Unexpectedly, under a CO_2 atmosphere, the reaction is consistent with proton transfer coupled with an electron transfer reaction leading to the formation of 1-phenylethanol. This surprising outcome is explained by the enhanced C-2 hydrogen donating ability of [BMIM]$^+$ resulting from the strong complex formation between the deprotonated form of [BMIM]$^+$, *N*-heterocyclic carbene, and CO_2. In this case, the follow up chemical reactions are too fast to be measured by cyclic voltammetry under our experimental conditions. A lower limit of the rate constant associated with the rate limiting chemical reaction step in this process is estimated to be 3.0×10^5 s^{-1} by numerical simulation based on a simplified reaction scheme.

Research of this kind should lead to new insights into the reactivity of aromatic ketones in ionic liquids in the presence of CO_2 and other molecules in a green chemistry context. Further investigations using other aromatic ketones and room temperature ionic liquids are in progress.

Acknowledgements

This work was financially supported by the Project for the National Natural Science Foundation of China (20973065), “Chen Guang” project supported by Shanghai Municipal Education Commission and Shanghai Education Development Foundation, China (10CG26), Basic Research in Natural Science Issued by Shanghai Municipal Committee of Science, China (08dj1400100), the Fundamental Research Funds for the Central Universities, China, Shanghai Leading Academic Discipline Project, China (B409) and the Australian Research Council.

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