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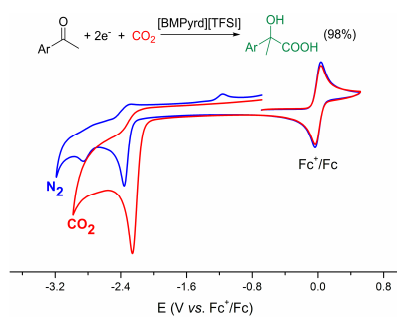
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## Table of Contents Graphic:



High-yield electrocarboxylation of acetophenone can be achieved in dry [BMPyrd][TFSI].

# Electrocarboxylation of acetophenone in ionic liquids: the influence of proton availability on product distribution

Shu-Feng Zhao,<sup>†‡</sup> Mike Horne,<sup>\*‡</sup> Alan M. Bond<sup>†</sup> and Jie Zhang<sup>\*†</sup>

## Abstract

The electroreduction of acetophenone has been investigated in two ionic liquids (1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BMMIM][BF<sub>4</sub>]; [H<sub>2</sub>O] = 9.2 mM) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPyrd][TFSI]; [H<sub>2</sub>O] = 1.0 mM) under both N<sub>2</sub> and CO<sub>2</sub> atmospheres using transient cyclic voltammetry, near steady-state voltammetry, bulk electrolysis technique and numerical simulations. The proton availability in both solvents is low. In dry ionic liquids under a N<sub>2</sub> atmosphere, the sole reduction product detected is a dimer. The rate constants for dimer formation determined by analysis of experiment and simulation are  $5.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $4.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , in [BMMIM][BF<sub>4</sub>] and [BMPyrd][TFSI], respectively. In dry [BMMIM][BF<sub>4</sub>] under a CO<sub>2</sub> atmosphere, the products of the electroreduction of acetophenone are mixtures of 2-hydroxy-2-phenylpropionic acid, 1-phenylethanol and dimers. By contrast, the major reduction product in dry [BMPyrd][TFSI] is 2-hydroxy-2-phenylpropionic acid, suggesting this ionic liquid is a suitable medium for electrocarboxylation. In water saturated [BMPyrd][TFSI] ([H<sub>2</sub>O] = 0.63 M), dimers are the major products under both N<sub>2</sub> and CO<sub>2</sub> atmospheres. The dimerization rate constant determined for this reaction under an N<sub>2</sub> atmosphere was  $1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ; more than three orders of magnitude higher than found in dry [BMPyrd][TFSI]. Presumably strong interactions between the acetophenone radical anions and water through an extensive hydrogen bonding network lead to larger degree of charge delocalization and thus favour dimer formation.

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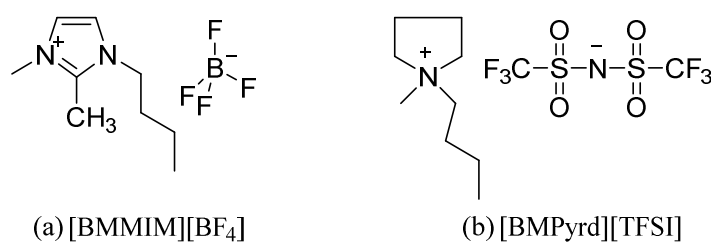
## Introduction

Formation of 2-hydroxy-2-arypropanoic acids via electrocarboxylation of aromatic ketones have been recognized as an environmental friendly route to the production of these widely used anti-inflammatory agents.<sup>1, 2</sup> In recent years, several research groups including ours, have demonstrated the possibility of producing 2-hydroxy-2-arypropanoic acid with high yield via the electrocarboxylation of aromatic ketones in molecular solvents, such as dimethylformamide (DMF<sup>3</sup>), *N*-methyl-2-pyrrolidone (NMP<sup>4, 5</sup>) and acetonitrile (MeCN<sup>6</sup>). Common by-products in the electrocarboxylation of aromatic ketones are pinacols and alcohols arising from dimerization and hydrogenation reactions, respectively.<sup>7</sup> It has been suggested by Scialdone et al.<sup>5, 8</sup> that reaction conditions and the nature of the aromatic ketones dramatically affect the selectivity of the electrocarboxylation process. Isse et al.<sup>9</sup> have shown the yields of carboxylate, dimers and alcohol are strongly media dependent due to the variation in the CO<sub>2</sub> solubility and proton availability in these media. As expected, those with higher CO<sub>2</sub> solubilities and lower proton availabilities favour carboxylate formation.

Room-temperature ionic liquids (RTILs) have received considerable attention in recent years due to their attractive physical and chemical properties, such as negligible volatility, high thermal and chemical stability, low toxicity and non-flammability.<sup>10-16</sup> In addition, their good conductivity, wide electrochemical potential windows and the ability to dissolve large amounts of CO<sub>2</sub> and organic compounds make RTILs potentially very useful media for electrocarboxylation reactions.<sup>17, 18</sup> So far, reactants including alkenes<sup>19</sup>, alcohols<sup>20-22</sup>, halides<sup>23, 24</sup> and ketones<sup>25</sup> have been investigated in this content with promising outcomes.

Of all the ionic liquids examined to date, the imidazolium based ionic liquids have received more attention due to their low melting points, ease of synthesis and good electrochemical stability. Our group<sup>26</sup> has reported the electroreduction of acetophenone in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) under N<sub>2</sub> and CO<sub>2</sub> atmospheres. Under a N<sub>2</sub> atmosphere, acetophenone undergoes a one-electron reduction process followed by rapid dimerization. This finding is consistent with the electrochemistry of acetophenone in several imidazolium and ammonium based ionic liquids under a N<sub>2</sub> atmosphere reported by Lagrost et al.<sup>27</sup> However, under a CO<sub>2</sub> atmosphere, the electroreduction of acetophenone is an overall two-electron, chemically irreversible process which leads to the formation of 1-phenylethanol, instead of 2-hydroxy-2-phenylpropionic acid, the product expected from an

electrocarboxylation reaction. The proton-coupled electron transfer pathway which forms 1-phenylethanol requires the presence of a sufficiently strong proton donor, which is not available in neat [BMIM][BF<sub>4</sub>]. It is postulated that the presence of CO<sub>2</sub> enhances the C-2 hydrogen donating ability of [BMIM]<sup>+</sup> resulting from the strong complex formation between the deprotonated form of [BMIM]<sup>+</sup>, *N*-heterocyclic carbene, and CO<sub>2</sub>. To provide further evidence to support this postulate and to identify other ionic liquids that are suitable for electrocarboxylation, a systematic investigation has now been undertaken to examine the influence of proton availability in ionic liquids on electrocarboxylation.



**Scheme 1** Structures of (a) [BMMIM][BF<sub>4</sub>] and (b) [BMPyrd][TFSI]

In this paper, we report the results of detailed studies of the electrochemical reduction of acetophenone in two ionic liquids: 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BMMIM][BF<sub>4</sub>]) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([BMPyrd][TFSI]) (Scheme 1), under N<sub>2</sub> and CO<sub>2</sub> atmospheres. The ionic liquid [BMMIM][BF<sub>4</sub>] was chosen since it is structurally similar to [BMIM][BF<sub>4</sub>] except that a methyl group is substituted for the reactive C-2 hydrogen. Sowmiah et al.<sup>28</sup> have shown substitution at the C-2 position of the imidazolium cation prevents side reactions which involve the reactive C-2 hydrogen since [BMMIM][BF<sub>4</sub>] is a weaker acid than [BMIM][BF<sub>4</sub>] (pK<sub>a</sub><sup>29</sup> of [BMIM][BF<sub>4</sub>] is about 21-23). Consequently, [BMMIM][BF<sub>4</sub>] may provide a more suitable medium for electrocarboxylation than [BMIM][BF<sub>4</sub>]. Moreover, investigation of electrocarboxylation in a medium where the C-2 hydrogen is absent, could also provide indirect evidence about the role of this hydrogen atom in the formation of 1-phenylethanol during the electroreduction of acetophenone in [BMIM][BF<sub>4</sub>] under a CO<sub>2</sub> atmosphere. The ionic liquid [BMPyrd][TFSI] also was chosen because of its low proton availability. It has been used as an electrolyte in the development of lithium batteries where reactive protons need to be avoided.<sup>30</sup> To assess the influence of adventitious water, which is a common impurity in ionic liquids that provides a source of protons, electroreduction of acetophenone was also investigated in water saturated [BMPyrd][TFSI] under N<sub>2</sub> and CO<sub>2</sub> atmospheres.

## Experimental

### Chemicals

Acetophenone (ReagentPlus®, 99%) and ferrocene ( $\geq 98\%$ ) were purchased from Sigma Aldrich and used as received. Acetonitrile (MeCN) of analytical grade purity was also purchased from Sigma Aldrich and dried over 4Å molecular sieves to remove residual water prior to use. [BMMIM][BF<sub>4</sub>] and [BMPyrd][TFSI] were purchased from IOLITEC (Germany) and when required, these ionic liquids were dried over basic alumina for at least 24 h,<sup>31</sup> then placed under vacuum at 80 °C for 24 h prior to use. The water content after these procedures was  $165 \pm 5$  ppm (or 9.2 mM) for [BMMIM][BF<sub>4</sub>] and  $15 \pm 5$  ppm (or 1.0 mM) for [BMPyrd][TFSI], as determined by Karl Fischer titration (Metrohm 831 Karl Fischer coulometer). Tetra(*n*-butyl)ammonium hexafluorophosphate ([Bu<sub>4</sub>N][PF<sub>6</sub>], GFS Chemicals, Inc, 98%) was recrystallised twice with ethanol prior to use. Other reagents (purities > 98%) were purchased from Sigma Aldrich and were used as received.

Water saturated [BMPyrd][TFSI] was prepared according to the procedure described elsewhere<sup>18</sup>. The ionic liquid was added to a large quantity of water in a glass tube then the mixture was sonicated for several minutes to ensure the ionic liquid was water saturated. After standing for 24 h, the two phases were separated by centrifuging at 9000 rpm (Eppendorf, MiniSpin® plus). The immiscible water layer was decanted off and the water concentration of the saturated ionic liquid was found to be 0.63 M using the Karl Fisher method.

### Voltammetric measurements

Voltammetric measurements were performed using a CHI700 electrochemical analyser (CH Instruments, Texas, USA) with a standard three-electrode electrochemical cell. For transient cyclic voltammetric experiments, a glassy carbon working electrode was used (GC, 1.0 mm diameter), whereas for steady-state voltammetric measurements, carbon-fiber microdisk electrodes were used (nominally 7.0 μm diameter). Platinum wires were used as both the quasi-reference and counter electrodes. The quasi-reference potential scale was converted the Fc<sup>+</sup>/Fc (Fc = ferrocene) reference potential scale and all potentials are quoted against Fc<sup>+</sup>/Fc. Working electrodes were polished using a 0.3 μm or 0.05 μm aqueous alumina slurry on a polishing cloth (BAS), sonicated in deionised water, rinsed with water and acetone, and then dried under a flow of nitrogen before use.

All voltammetric experiments were undertaken at room temperature ( $22 \pm 2$  °C). Experiments with carefully dried ionic liquids were undertaken under a  $N_2$  atmosphere in a dry box to minimize the effect of atmospheric water and oxygen. Experiments with water saturated ionic liquids were carried out on the bench-top with a slightly positive  $N_2$  pressure inside the electrochemical cell to minimize the entry of  $O_2$  and  $H_2O$  vapour. The exact radii ( $r$ ) of the carbon-fiber microdisk electrodes (nominally 7.0  $\mu m$  and 33  $\mu m$  diameters) used for quantitative studies were determined to be 3.6  $\mu m$  and 17  $\mu m$ , respectively, based on the steady-state diffusion controlled limiting current ( $I_L$ ) for the oxidation of Fc in MeCN containing 0.1 M  $[Bu_4N][PF_6]$ , using Equation (1)<sup>32</sup> and the known diffusion coefficient ( $D$ ) for Fc in this solution of  $2.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ <sup>33</sup>.

$$I_L = 4nFrDC \quad (1)$$

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

Simulations of the voltammograms were undertaken using DigiElch<sup>®</sup> software (Elchsoft, Kleinromstedt, Germany). A two-dimensional mass transport model was used to take into account the contribution from radial diffusion at slow scan rates. The Butler-Volmer model was used to describe the potential-dependent kinetics of the heterogeneous electron transfer.

### Bulk electrolysis

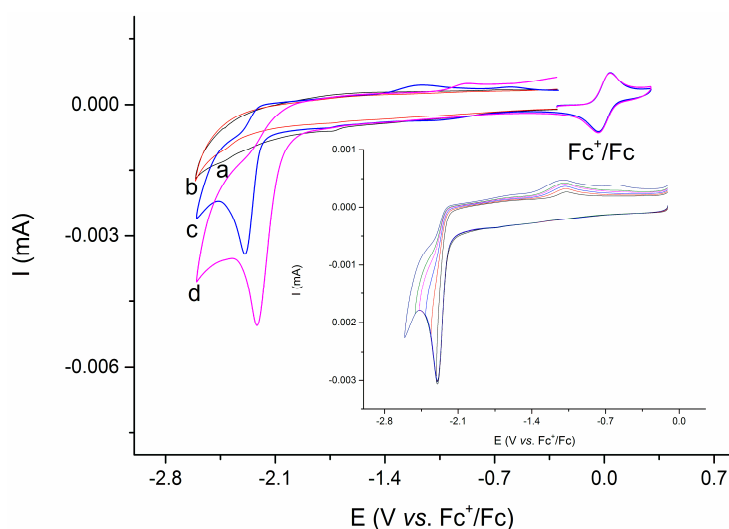
Potentiostatic bulk electrolysis were undertaken at  $22 \pm 2$  °C, unless otherwise stated, under either  $N_2$  or  $CO_2$  atmospheres in an undivided cell equipped with a glassy carbon tube cathode, a magnesium (Mg) sacrificial anode and a silver wire quasi-reference electrode mounted into a tube sealed with a permeable glass frit. The solution used was 5 mL of either  $[BMMIM][BF_4]$  or  $[BMPyrd][TFSI]$  containing 25 mM of acetophenone and a constant stream of  $CO_2$  or  $N_2$  flowed through the cell during the electrolysis. After electrolysis, the reaction mixture was hydrolysed with HCl (pH  $\sim 3$ ) and extracted three times with diethyl ether, dried over anhydrous  $MgSO_4$  and evaporated, and then analysed by the GC-MS method (HP 6890A gas chromatograph equipped with a 5973 N mass selective detector, Agilent, USA).

## Results and discussion

### 1. Electrochemistry of acetophenone in dry $[BMMIM][BF_4]$

As described above, the electrochemical reduction of acetophenone in [BMIM][BF<sub>4</sub>] under a CO<sub>2</sub> atmosphere forms 1-phenylethanol in a proton coupled reaction involving the C-2 hydrogen on the imidazolium cation. In [BMMIM][BF<sub>4</sub>] the C-2 hydrogen is absent. Therefore, electroreduction of acetophenone was first undertaken in dry [BMMIM][BF<sub>4</sub>] to investigate the role played by the C-2 hydrogen on the imidazolium cation during electrochemical reduction of acetophenone in [BMIM][BF<sub>4</sub>] under a CO<sub>2</sub> atmosphere and to assess its suitability for using as reaction medium for electrocarboxylation.

### 1.1. Voltammetric studies

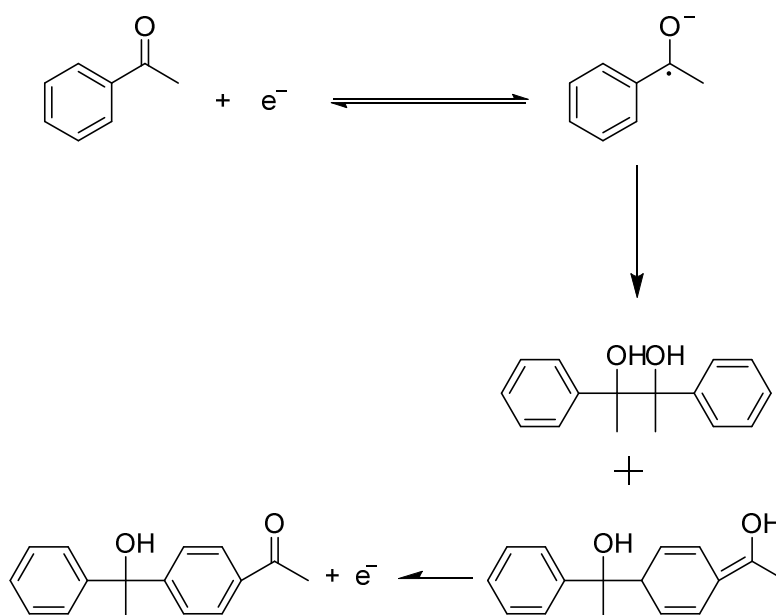


**Fig. 1** Cyclic voltammograms recorded at a 1.0 mm diameter GC electrode (scan rate = 0.1 V s<sup>-1</sup>) in neat dry [BMMIM][BF<sub>4</sub>] under (a) N<sub>2</sub> or (b) CO<sub>2</sub> atmospheres (1 atm) and dry [BMMIM][BF<sub>4</sub>] containing 10 mM acetophenone under (c) N<sub>2</sub> or (d) CO<sub>2</sub> atmospheres (1 atm). Cyclic voltammograms for the Fc<sup>+</sup>/Fc process (around 0 V) with 5 mM Fc present in the same acetophenone solutions are included for comparison. The inset shows voltammograms recorded in 10 mM acetophenone solutions in an N<sub>2</sub> atmosphere with different negative limits of potential using a scan rate of 0.1 V s<sup>-1</sup>.

Electroreduction of 10 mM acetophenone under both N<sub>2</sub> and CO<sub>2</sub> atmospheres was investigated by cyclic voltammetry (Fig. 1). Under a N<sub>2</sub> atmosphere (c), an irreversible reduction process at -2.32 V was observed, which is consistent with previous work in the acetophenone reduction in [BMIM][BF<sub>4</sub>]<sup>26</sup>, suggesting that the electroreduction of acetophenone was followed by a rapid homogeneous chemical reaction leading to the formation of a species that is electrochemically inactive in the potential region close to the reduction process. Based on these observations and results from the literature<sup>26, 27, 34</sup>, the homogeneous chemical process is assigned to the dimerization of acetophenone radical anion.

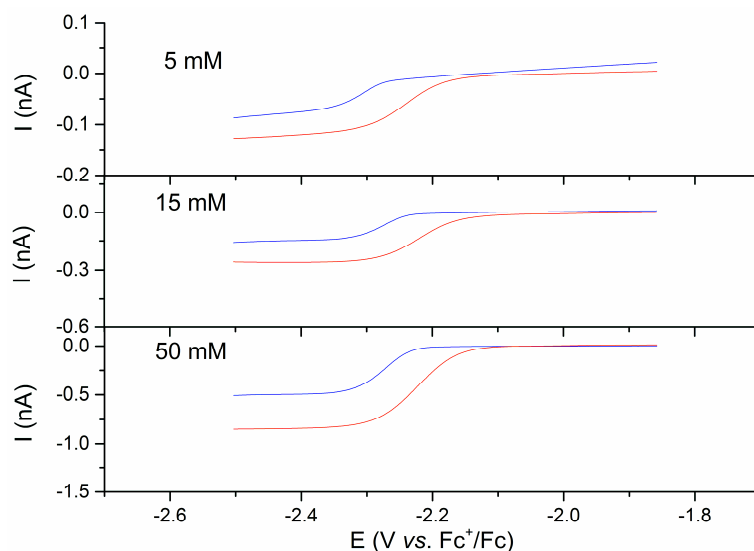


After the scan is reversed, a small oxidation process is observed at -1.20 V. This process, also reported by Amatore et al. in the electroreduction of acetophenone in DMF<sup>34</sup> and Zhao et al. in the electroreduction of acetophenone in [BMIM][BF<sub>4</sub>]<sup>26</sup>, was attributed to the oxidation of a head-to-tail type of dimer (1-[4-(1-hydroxy-ethylidene)-cyclohexa-2,5-dienyl]-1-phenyl-ethanol). A minor oxidation process was observed at -0.64 V. This process was not observed either in the absence of acetophenone or when the switching potential was more positive (inset figure of Fig. 1), which suggest that it is resulted from further electroreduction of the acetophenone. Based on these experimental observations and the results from the literature<sup>26, 34</sup>, the following reaction schemes is proposed.



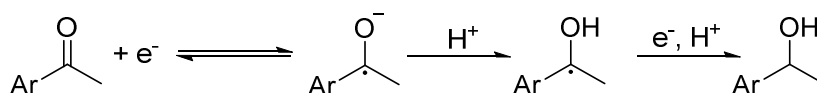
**Scheme 2** Reaction scheme proposed for reduction of acetophenone in [BMMIM][BF<sub>4</sub>] under a N<sub>2</sub> atmosphere

Under a CO<sub>2</sub> atmosphere in [BMMIM][BF<sub>4</sub>], the acetophenone reduction peak current increased significantly and the peak potential shifted positively from -2.32 V to -2.27 V. It has been reported that the presence of CO<sub>2</sub> can decrease the viscosity of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide,<sup>35, 36</sup> so it is tempting to propose that the same effect increases the diffusion coefficient of the electroactive species in this case. However, the fact that the oxidation and reduction peak currents simultaneously measured for the Fc<sup>+</sup>/Fc process are virtually identical under N<sub>2</sub> or CO<sub>2</sub> atmospheres rules out this possibility. Consequently, the increased peak current and positive shift of peak potential for acetophenone reduction in the presence of CO<sub>2</sub> can be attributed to the presence of new chemistry, and one that may also involve an additional electron transfer step.

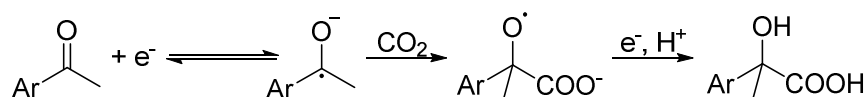


**Fig. 2** Near steady-state voltammograms for the reduction of acetophenone (5 mM, 15mM and 50 mM) in [BMMIM][BF<sub>4</sub>] recorded at a carbon-fiber microdisk electrode (7.2  $\mu\text{m}$  diameter) at a scan rate of 1  $\text{mV s}^{-1}$  under N<sub>2</sub> (—) and CO<sub>2</sub> (—) atmospheres.

To verify whether the new chemistry occurred during acetophenone reduction involves an additional electron transfer process, near-steady-state voltammograms for acetophenone reduction were recorded at a carbon-fiber microdisk electrode (7.2  $\mu\text{m}$  diameter) under N<sub>2</sub> and CO<sub>2</sub> atmospheres. The results obtained with three different acetophenone concentrations (5.0, 15.0 and 50.0 mM) are shown in Fig. 2. In all cases, the steady-state diffusion controlled limiting currents obtained under a CO<sub>2</sub> atmosphere are almost twice as large as those obtained under a N<sub>2</sub> atmosphere. Consequently, it is proposed that acetophenone undergoes a two-electron reduction reaction under a CO<sub>2</sub> atmosphere in [BMMIM][BF<sub>4</sub>]. According to the literature results,<sup>5, 26</sup> this two-electron process could form an alcohol, or an acid, or a combination of both according to the reactions described in Schemes 3 and 4.



**Scheme 3** A proton coupled electron transfer reaction for acetophenone reduction



**Scheme 4** Reaction scheme for electrocarboxylation of acetophenone

## 1.2. Bulk electrolysis

In order to identify the details of the reaction pathway for acetophenone reduction in dry [BMMIM][BF<sub>4</sub>] under both N<sub>2</sub> and CO<sub>2</sub> atmospheres, preparative scale bulk electrolysis experiments were undertaken using a large glassy carbon cylindrical tube cathode and a Mg sacrificial anode in an undivided cell<sup>26</sup>. After bulk electrolysis of 25 mM acetophenone in [BMMIM][BF<sub>4</sub>], the products were extracted with diethyl ether and identified by GC-MS. Since [BMMIM][BF<sub>4</sub>] is quite viscous, the electrolysis was undertaken at 50 °C to increase the mass transport rate. The product distributions are summarized in Table 1.

**Table 1.** Products<sup>a</sup> obtained from preparative scale reductive electrolysis of 25 mM acetophenone in dry [BMMIM][BF<sub>4</sub>] at 50 °C

Atmosphere (P = 1 atm)	Electricity consumption (F mol <sup>-1</sup> )	Applied potential (V vs. Fc <sup>+</sup> /Fc)	Product yield (%) <sup>b</sup>		
			dimer	acid	alcohol
N <sub>2</sub>	1.0	-2.32	100	0	0
CO <sub>2</sub>	2.0	-2.27	25	15	60

<sup>a</sup>Dimer = 1-[4-(1-hydroxy-ethylidene)-cyclohexa-2,5-dienyl]-1-phenyl-ethanol, 2,3-diphenyl-butane-2,3-diol and other unidentified dimers, acid = 2-hydroxy-2-phenylpropionic acid, alcohol = 1-phenylethanol.

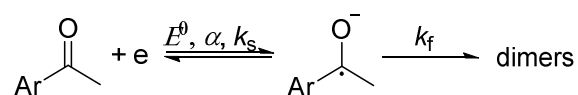
<sup>b</sup>Gas chromatography yields based on the reactant consumed.

Under a N<sub>2</sub> atmosphere, the only products detected were dimers. The fact that acetophenone undergoes a one-electron reduction leading to the formation of dimers (100%) (Scheme 2), is consistent with the result obtained in other ionic liquids.<sup>26, 27</sup> By contrast, under a CO<sub>2</sub> atmosphere the products consist of 1-phenylethanol (60%), 2-hydroxy-2-phenylpropionic acid (15%), and dimers (25%). Trace amounts of unidentified compounds were also detected. 1-Phenylethanol is the predominant product even though the water impurity is not a sufficiently strong acid and [BMMIM][BF<sub>4</sub>] does not contain C-2 hydrogen that becomes reactive under a CO<sub>2</sub> atmosphere due to the formation of a stable CO<sub>2</sub>-carbene complex.<sup>26</sup> Since the bond energy of C-C (348 kJ mol<sup>-1</sup>) is smaller than C-H (423 kJ mol<sup>-1</sup>)<sup>37</sup>, CH<sub>3</sub><sup>+</sup> could be abstracted from [BMMIM][BF<sub>4</sub>] in the same way as H<sup>+</sup> is abstracted from [BMIM][BF<sub>4</sub>] when CO<sub>2</sub> is present. If this is the case, CH<sub>3</sub><sup>+</sup> can further react with water (9.2 mM in [BMMIM][BF<sub>4</sub>]) to produce H<sup>+</sup> required for the formation of 1-phenylethanol. The results in Table 1 also suggest that although two-electron transfer pathways are dominant during the electroreduction of acetophenone, the contribution from the one electron pathway is also significant. This is consistent with the near steady-state voltammetric data (Fig. 2) which show that current is nearly double under a CO<sub>2</sub> atmosphere instead of N<sub>2</sub>.

### 1.3. Kinetics of the dimerization reaction following acetophenone reduction in dry [BMMIM][BF<sub>4</sub>] under a N<sub>2</sub> atmosphere

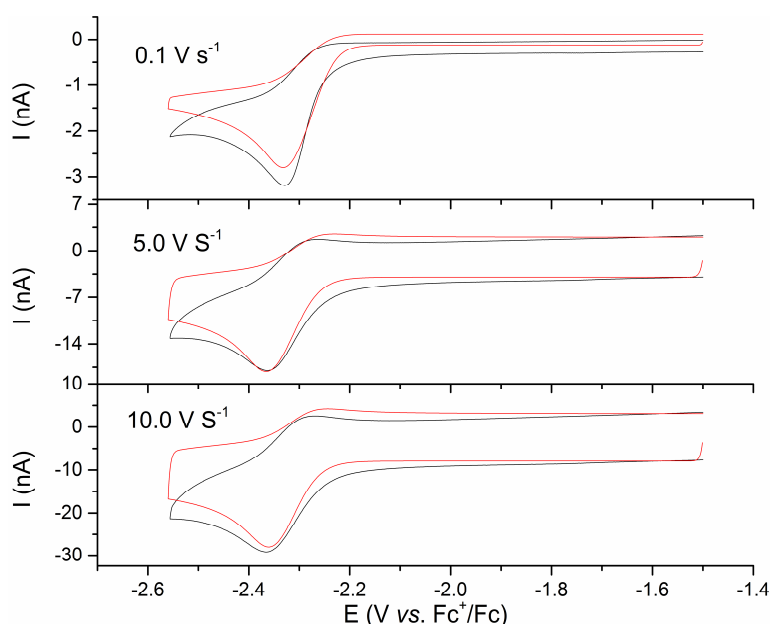
Voltammetric data at a macrodisk GC electrode show that the homogeneous dimerization reaction kinetics coupled to electron transfer is fast (Fig. 1). To quantify these kinetics using transient voltammetry, a sufficiently fast scan rate is required so that the kinetics becomes relatively slow with respect to the time scale of the measurement. However, uncompensated resistance ( $IR_u$  drop) effects often become substantial at fast scan rates. Microelectrode voltammetry is conventionally used to overcome this problem<sup>38, 39</sup>. With a 33  $\mu\text{m}$  diameter carbon-fiber microdisk electrode and a scan rate of 0.1  $\text{V s}^{-1}$ , acetophenone reduction is completely irreversible. Partially reversible voltammograms, as required for quantifying the kinetics of the dimerization reaction, were obtained at the higher scan rates of 5.0  $\text{V s}^{-1}$  and 10.0  $\text{V s}^{-1}$ .

To quantify the dimerization kinetics in [BMMIM][BF<sub>4</sub>], simulations of the mechanism described in Scheme 5 were undertaken.



**Scheme 5** Reaction scheme proposed for reduction of acetophenone in [BMMIM][BF<sub>4</sub>] under a N<sub>2</sub> atmosphere.

where,  $E^0$ ,  $\alpha$  and  $k_s$  represent the formal reversible potential, the charge transfer coefficient and the electron transfer rate constant respectively, and  $k_f$  stands for the overall rate constant of the dimerization reactions. Simulated voltammograms obtained using parameters specified in the caption of Fig. 3 agree well with the experimental data. The major discrepancy between experimental and simulated voltammograms is attributed to the fact that the double layer capacitance ( $C_d$ ) is independent of potential as assumed in the simulations. The diffusion coefficient of  $7.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  used for acetophenone was calculated from the steady-state diffusion controlled limiting current (Fig. 2) using Equation (1). The diffusion coefficients of species derived from reduction of acetophenone were assumed to be the same as for acetophenone.



**Fig. 3** Cyclic voltammogram (—) for the reduction of 10 mM acetophenone in [BMMIM][BF<sub>4</sub>] under a N<sub>2</sub> atmosphere recorded at a carbon-fiber microdisk electrode (34 μm diameter) at different scan rates. The simulated voltammograms (---) were based on the mechanism described in Scheme 5 using the parameters:  $E^0 = -2.32$  V,  $k_s = 0.035$  cm s<sup>-1</sup>,  $\alpha = 0.50$ ,  $R_u = 2.5 \times 10^6$  Ω,  $C_d = 7.8 \times 10^{-6}$  F,  $D = 7.2 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup> for all species,  $k_f = 5.0 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup>.

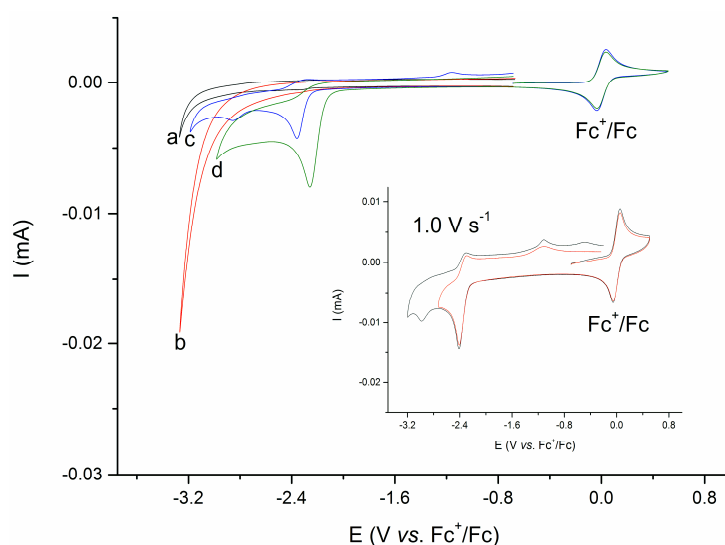
The second order rate constant for the dimerization reactions is estimated to be  $5 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> based on comparisons of experiment with theory. This value is lower than that of  $1 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> reported in [BMIM][BF<sub>4</sub>]<sup>26</sup> and  $3 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> -  $4 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> reported in imidazolium based ionic liquids.<sup>27</sup> On the basis of their studies in imidazolium ionic liquids and molecular solvents, Lagrost *et al.*<sup>27</sup> suggested that the rate of the dimerization reaction is enhanced significantly in ionic liquids because the acetophenone radical anion forms a strong ion pair with the cation of the ionic liquid. Subsequent electron delocalization weakens the repulsion between acetophenone radical anions, thus favouring the formation of dimers. The relatively low dimerization rate constant observed in [BMMIM][BF<sub>4</sub>] therefore suggests the acetophenone anion and [BMMIM]<sup>+</sup> interact only weakly. Moreover, this ionic liquid is viscous ( $\eta = 650$  cp<sup>40</sup>), so mass transport for the bimolecular reaction will also be slow.

Under a CO<sub>2</sub> atmosphere, the electroreduction of acetophenone remained completely chemically irreversible, even at a scan rate of 10000 V s<sup>-1</sup> (maximum value available with the potentiostat used). Thus, the kinetics of the follow-up chemical reactions is now too fast to be measured.

## 2. Electrochemistry of acetophenone in [BMPyrd][TFSI]

## 2.1. Voltammetric studies

Another ionic liquid which should be suitable for the electrocarboxylation of acetophenone is 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMPyrd][TFSI]. It has no readily available protons and a wide electrochemical window of -3.0 V to +2.5 V (vs. Ag/Ag<sup>+</sup>)<sup>41</sup>. Consequently, decomposition of [BMPyrd][TFSI] during electroreduction of acetophenone should be negligible. Thus, carefully dried [BMPyrd][TFSI] (< 20 ppm, water, ca. 1.0 mM) also was chosen for investigation of the electrocarboxylation of acetophenone. Cyclic voltammograms were obtained at a 1.0 mm diameter GC working electrode with a scan rate of 0.1 V s<sup>-1</sup> for 10 mM acetophenone in dry [BMPyrd][TFSI] under both N<sub>2</sub> and CO<sub>2</sub> atmospheres (Fig. 4).

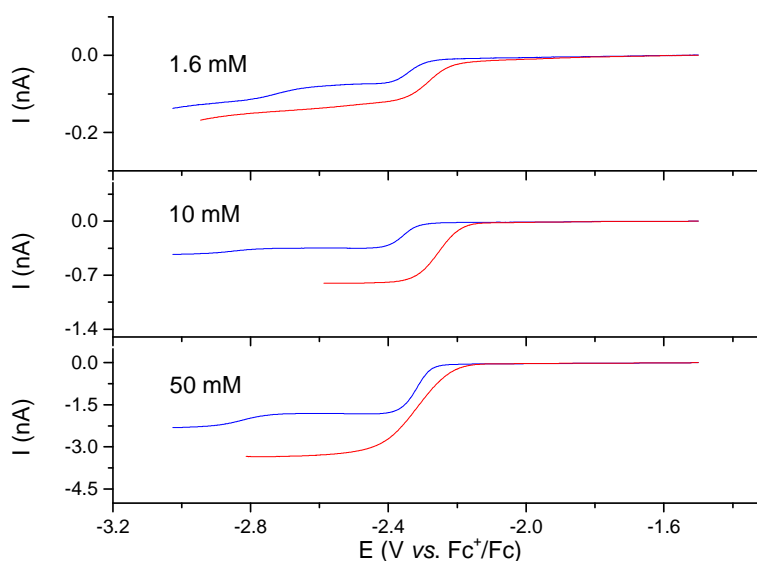


**Fig. 4** Cyclic voltammograms recorded at a 1.0 mm diameter GC electrode (scan rate = 0.1 V s<sup>-1</sup>) in dry [BMPyrd][TFSI] under (a) N<sub>2</sub> or (b) CO<sub>2</sub> atmospheres (1 atm), and for dry [BMPyrd][TFSI] containing 10 mM acetophenone under (c) N<sub>2</sub> and (d) CO<sub>2</sub> atmospheres (1 atm). The Fc/Fc<sup>+</sup> process (around 0 V) is included for comparison. The inset figure shows cyclic voltammograms as in (c) but at a scan rate of 1.0 V s<sup>-1</sup>.

Under a N<sub>2</sub> atmosphere, two well-resolved reduction processes are observed with reduction peak potentials of -2.36 V and -2.85 V, respectively (Fig. 3, c). This is consistent with results reported in molecular solvents (DMF<sup>34, 42</sup>, MeCN<sup>6</sup> and NMP<sup>7</sup>). The reduction processes are assigned to the initial formation of the acetophenone radical anion and then the dianion. The first reduction process is partially reversible at a scan rate of 1.0 V s<sup>-1</sup> suggesting that the follow up chemical reaction is not too rapid. An oxidation process of a head-to-tail type of dimer was also observed at -1.13 V on the positive potential direction scan. A second small oxidation process was also observed at -0.51 V on the positive potential direction scan

when the scan rate was  $0.1 \text{ V s}^{-1}$  and the potential was reversed after traversing the second reduction process. Consequently, this process is assigned to the oxidation of a product formed as a result of the second reduction process.

In dry [BMPyrd][TFSI] saturated with  $\text{CO}_2$ , the peak current for the first reduction process increased significantly, while the peak potential shifted from  $-2.36 \text{ V}$  to a more positive value  $-2.26 \text{ V}$  and the second reduction process disappeared completely. These observations are similar to those made in [BMMIM][ $\text{BF}_4$ ], which again suggests that an overall two electron transfer step may occur via the proton coupled electron transfer pathway described in Scheme 3 or the electrocarboxylation pathway described in Scheme 4.



**Fig. 5** Near steady-state voltammograms for the reduction of acetophenone (1.6 mM, 10 mM and 50 mM) in dry [BMPyrd][TFSI] recorded at a carbon-fiber microdisk electrode ( $7.0 \mu\text{m}$  diameter) at a scan rate =  $1 \text{ mV s}^{-1}$  under  $\text{N}_2$  (—) and  $\text{CO}_2$  (—) atmospheres.

The near steady-state voltammograms for acetophenone reduction were also conducted in dry [BMPyrd][TFSI] at a carbon-fiber microdisk electrode ( $7.0 \mu\text{m}$  diameter) under both  $\text{N}_2$  and  $\text{CO}_2$  atmospheres. The results obtained with three different acetophenone concentrations (1.6, 10.0 and 50.0 mM) are shown in Fig. 5.

Under a  $\text{N}_2$  atmosphere, the steady-state diffusion controlled limiting current for the second reduction process ( $I_{L2}$ ) was significantly smaller than that of the first reduction process ( $I_{L1}$ ). The ratio of the steady-state diffusion controlled limiting currents ( $I_{L1}/I_{L2}$ ) increases as the acetophenone concentration increases (Table 2). This unequal steady-state diffusion controlled limiting current for two one-electron reduction processes and a similar concentration dependence of  $I_{L1}/I_{L2}$  was also observed in the electroreduction of benzophenone in the same ionic liquid<sup>43</sup>. This behaviour was attributed to the formation of a

complex (or dimer) between acetophenone and the electrogenerated acetophenone dianion that is electrochemically inactive in the potential region of acetophenone dianion formation.

**Table 2.** The ratios of the near steady-state diffusion controlled limiting currents ( $I_{L1}/I_{L2}$ ) for the first and second acetophenone reduction processes under a  $N_2$  atmosphere in dry [BMPyrd][TFSI] as a function of the concentration of acetophenone.<sup>a</sup>

$C_{\text{Acetophenone}}/\text{mM}$	$I_{L1}/I_{L2}$
1.6	1.68
10	3.81
50	3.84

<sup>a</sup> Experimental conditions are as specified in the caption to Fig. 3.

Under a  $CO_2$  atmosphere, only one reduction process was observed with the steady-state diffusion controlled limiting currents almost twice of that for one-electron reduction of acetophenone to the acetophenone radical anion under a  $N_2$  atmosphere, implying that an overall two-electron transfer reaction occur via the electrocarboxylation route (Scheme 4) since dry [BMPyrd][TFSI] has no readily available protons.

## 2.2. Bulk electrolysis

Preparative scale bulk electrolysis experiments were also undertaken in dry [BMPyrd][TFSI] using a GC tube cathode and a Mg anode in an undivided cell. After electrolysis under  $N_2$  and  $CO_2$  atmospheres, the products of the electrolysis were separated and identified via GC-MS. Reaction products and yields are summarized in Table 3.

**Table 3.** Products<sup>a</sup> obtained from preparative scale reductive electrolysis of 25 mM acetophenone in dry [BMPyrd][TFSI] at 22 °C

Atmosphere (P = 1 atm)	Electricity consumption ( $F \text{ mol}^{-1}$ )	Applied potential (V vs. $Fc^+/Fc$ )	Product yield (%) <sup>b</sup>		
			dimer	acid	alcohol
$N_2$	1.0	-2.1	100	0	0
$CO_2$	2.0	-2.3	2	98	0

<sup>a</sup>Dimer = 1-[4-(1-hydroxy-ethylidene)-cyclohexa-2,5-dienyl]-1-phenyl-ethanol and 2,3-diphenyl-butane-2,3-diol and other unidentified dimers, acid = 2-hydroxy-2-phenylpropionic acid, alcohol = 1-phenylethanol.

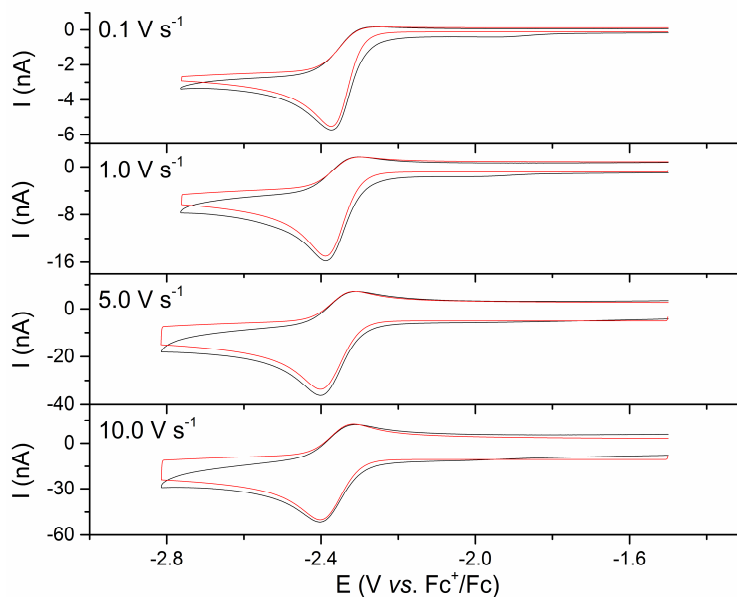
<sup>b</sup>Gas chromatography yields based on the reactant consumed.



Under a N<sub>2</sub> atmosphere, one-electron electroreduction of acetophenone in dry [BMPyrd][TFSI] followed by a dimerization reaction (Scheme 2) is the major reaction pathway. When the preparative scale bulk electrolysis experiments were undertaken under a CO<sub>2</sub> atmosphere, a 98% yield of 2-hydroxy-2-phenylpropionic acid was obtained in dry [BMPyrd][TFSI], confirming that electrocarboxylation reaction is the major reaction pathway.

### 2.3. Kinetics of the dimerization reaction for acetophenone reduction in dry [BMPyrd][TFSI] under a N<sub>2</sub> atmosphere

To quantify the kinetics of acetophenone reduction in dry [BMPyrd][TFSI] under a N<sub>2</sub> atmosphere, a 34 μm diameter carbon-fiber microdisk electrode was also used at scan rates that provided to obtain voltammograms with partial chemical reversibility (Fig. 6). Simulations used to obtain the theoretical data were based on reaction Scheme 5. The diffusion coefficient of  $2.62 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  for acetophenone used in the simulations was calculated from the steady-state diffusion controlled limiting current for acetophenone reduction and use of Equation (1). The diffusion coefficients of species derived from reduction of acetophenone were assumed to be the same as for acetophenone. Simulated voltammograms obtained using parameters specified in the caption of Fig. 6 agree well with experimental data. The second order rate constant for the dimerization reactions of  $4.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  obtained in [BMPyrd][TFSI] is significantly lower than found in [BMMIM][BF<sub>4</sub>], suggesting even weaker interaction of acetophenone radical anions and pyrrolidinium cations based on the mechanism proposed by Lagrost *et al.*<sup>27</sup>. Therefore, in addition to its advantage of low proton availability, slower dimerization kinetics make [BMPyrd][TFSI] a suitable medium for electrocarboxylation of aromatic ketones.



**Fig. 6** Cyclic voltammogram (—) for the reduction of 10 mM acetophenone in [BMPyrd][TFSI] under a  $N_2$  atmosphere recorded at a carbon-fiber microdisk electrode (34  $\mu\text{m}$  diameter) at different scan rates. The simulated voltammograms (---) are based on the mechanism described in Scheme 5 using the parameters:  $E^0 = -2.36$  V,  $k_s = 0.035$   $\text{cm s}^{-1}$ ,  $\alpha = 0.50$ ,  $R_u = 2.5 \times 10^5$   $\Omega$ ,  $C_d = 8.63 \times 10^{-10}$  F,  $D = 2.62 \times 10^{-7}$   $\text{cm}^2 \text{s}^{-1}$  for all species,  $k_f = 4.0 \times 10^3$   $\text{M}^{-1} \text{s}^{-1}$ .

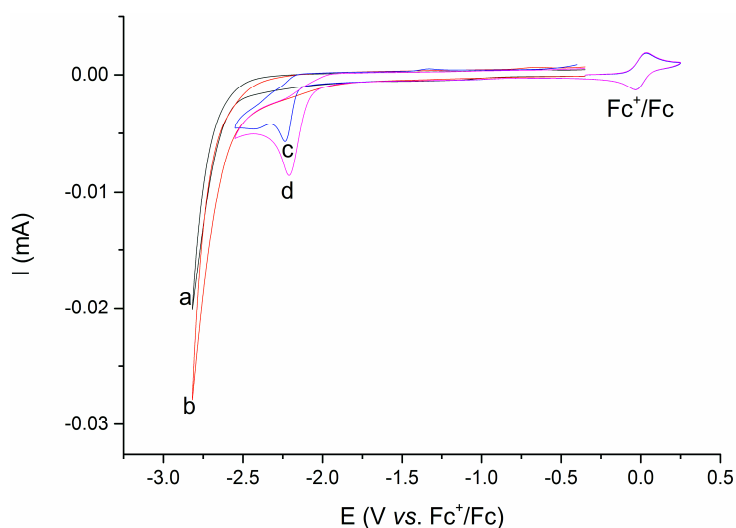
Under a  $\text{CO}_2$  atmosphere, the electroreduction of acetophenone remained chemically irreversible even at the maximum scan rate of to 10000  $\text{V s}^{-1}$  available, so the kinetics of the follow-up carboxylation reaction is too fast to be measured under our experimental conditions.

### 3. Electrochemistry of acetophenone in water saturated [BMPyrd][TFSI]

#### 3.1. Voltammetric studies

One of the most significant impurities in ionic liquids is water. Even “hydrophobic” ionic liquids absorb significant amounts of water over a short period of time<sup>44</sup>. Generally, even commercially available high-purity hydrophobic ionic liquids contain up to 100 ppm of water. Although ionic liquids have been widely applied in synthetic reactions, separations, extractions and electrochemical processes, the effects of the acid/base chemistry of  $\text{H}_2\text{O}$  on electrochemical processes in ionic liquids have not been adequately investigated. However, it is well recognized that water impurities in molecular solvents dramatically alter the kinetics and reaction pathways of many reactions involving inorganic, organic, and biological

molecules.<sup>45, 46</sup> Our voltammetric studies suggest that the benzophenone dianion is highly sensitive to H<sub>2</sub>O in ionic liquids<sup>47</sup>.



**Fig. 7** Cyclic voltammograms recorded at a 1.0 mm diameter GC electrode (scan rate = 0.1 V s<sup>-1</sup>) in water saturated [BMPyrd][TFSI] under (a) N<sub>2</sub> or (b) CO<sub>2</sub> atmospheres (1 atm), and for water saturated [BMPyrd][TFSI] containing 10 mM acetophenone under (c) N<sub>2</sub> and (d) CO<sub>2</sub> atmospheres (1 atm). The  $\text{Fc}^+/\text{Fc}$  process (around 0 V) with 3.6 mM Fc is included for comparison.

To investigate the effect of added water on the electrochemical reduction of acetophenone in water saturated [BMPyrd][TFSI], cyclic voltammograms of 10 mM acetophenone were recorded at a 1.0 mm diameter GC electrode under both N<sub>2</sub> and CO<sub>2</sub> atmospheres (Fig. 7). Under a N<sub>2</sub> atmosphere, two processes were observed with reduction peak potentials of -2.10 V and -2.44 V. The fact that reduction occur at a more positive potential than that in dry [BMPyrd][TFSI], implies that protonation and/or hydrogen-bonding reactions involving acetophenone anions occur in the presence of water. Upon saturation with CO<sub>2</sub>, only one reduction process was observed in the water saturated ionic liquid. In comparison with the first reduction process recorded under a N<sub>2</sub> atmosphere, the peak current has increased significantly and the peak potential also has shifted slightly from -2.10 V to -2.07 V. These observations suggest that two-electron processes may dominate on the voltammetric timescale, preassembly due to proton available from H<sub>2</sub>CO<sub>3</sub>. It should be noted that the peak currents of acetophenone under N<sub>2</sub> and CO<sub>2</sub> atmospheres are larger than found in dry [BMPyrd][TFSI]. This phenomenon is attributed to a decrease in viscosity in the presence of H<sub>2</sub>O, since a similar increase in current was also observed for the  $\text{Fc}/\text{Fc}^+$  process.

### 3.2. Bulk electrolysis

Preparative scale bulk electrolysis experiments were also undertaken under N<sub>2</sub> and CO<sub>2</sub> atmospheres for acetophenone reduction in water saturated [BMPyrd][TFSI]. The products of the electrolysis were separated and identified by GC-MS. The products and their yields are summarized in Table 4.

**Table 4.** Products<sup>a</sup> obtained from preparative scale reductive electrolysis of 25 mM acetophenone in water saturated [BMPyrd][TFSI] at 22 °C

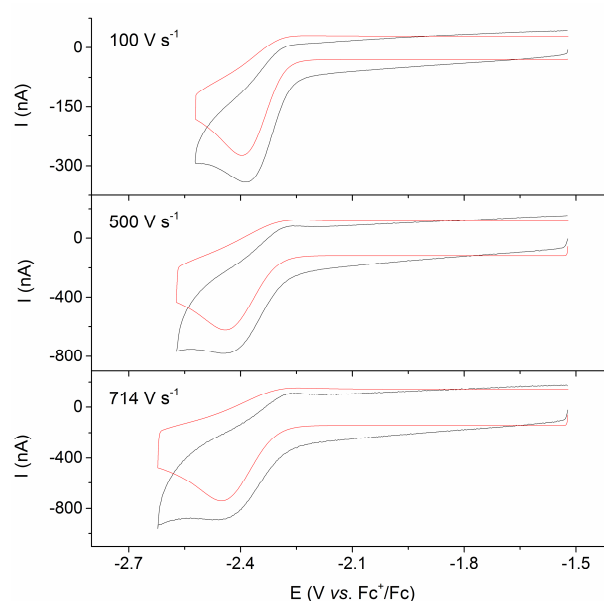
Atmosphere (P = 1 atm)	Electricity consumption (F mol <sup>-1</sup> )	Applied potential (V vs. Fc <sup>+</sup> /Fc)	Product yield (%) <sup>b</sup>		
			dimer	acid	alcohol
N <sub>2</sub>	1.0	-2.10	100	0	0
CO <sub>2</sub>	2.0	-2.07	100	0	0

<sup>a</sup>Dimer = 1-[4-(1-hydroxy-ethylidene)-cyclohexa-2,5-dienyl]-1-phenyl-ethanol and 2,3-diphenyl-butane-2,3-diol and other unidentified dimers, acid = 2-hydroxy-2-phenylpropionic acid, alcohol = 1-phenylethanol.

<sup>b</sup>Gas chromatography yields based on the reactant consumed.

Under a N<sub>2</sub> atmosphere, dimers are the sole products, confirming that one-electron electroreduction of acetophenone followed by the dimerization reaction is the major reaction pathway. Under a CO<sub>2</sub> atmosphere, dimers are again the sole products. This is in contrast with the voltammetric data which suggests that a two-electron reduction process is involved. This apparent discrepancy may be due to the fact that hydration of CO<sub>2</sub> to form H<sub>2</sub>CO<sub>3</sub> as required for the two-electron reaction pathway is both thermodynamically and kinetically unfavourable<sup>48</sup>. In the case of the voltammetric study, a sufficient amount of time was available to saturate [BMPyrd][TFSI] with CO<sub>2</sub> and to achieve CO<sub>2</sub> equilibration. Therefore, the amount of H<sub>2</sub>CO<sub>3</sub> available may be sufficient to significantly influence the reaction pathway for voltammetric reduction 10 mM acetophenone due to the higher mobility of either H<sub>2</sub>CO<sub>3</sub> or H<sup>+</sup> dissociated from H<sub>2</sub>CO<sub>3</sub>. However, in bulk electrolysis experiments, significantly higher concentration of acetophenone (25 mM) was used. More importantly, the amount of H<sub>2</sub>CO<sub>3</sub> once depleted, is negligible on the timescale of the dimerization. Consequently, dimers are the major products.

### 3.3. Kinetics of the dimerization reaction during acetophenone reduction in water saturated [BMPyrd][TFSI] under a N<sub>2</sub> atmosphere



**Fig. 8** Cyclic voltammogram (—) for the reduction of 17 mM acetophenone in wet [BMPyrd][TFSI] under a  $N_2$  atmosphere recorded at a carbon-fiber microdisk electrode (34  $\mu\text{m}$  diameter) at different scan rates. The simulated voltammograms (---) are based on the mechanism described in Scheme 5 using the parameters:  $E^0 = -2.36$  V,  $k_s = 0.035$   $\text{cm s}^{-1}$ ,  $\alpha = 0.50$ ,  $R = 7.0 \times 10^3$   $\Omega$ ,  $C_d = 2.43 \times 10^{-10}$  F,  $D = 4.19 \times 10^{-7}$   $\text{cm}^2 \text{s}^{-1}$  for all species,  $k_f = 1.0 \times 10^7$   $\text{M}^{-1} \text{s}^{-1}$ .

To further quantify the kinetics of acetophenone reduction in water saturated [BMPyrd][TFSI] under a  $N_2$  atmosphere, a 34  $\mu\text{m}$  diameter carbon-fiber microdisk electrode was employed at fast scan rates up to 714  $\text{V s}^{-1}$  to achieve voltammetric data with partial chemical reversibility (Fig. 8). Simulations using parameters specified in the caption of Fig. 8 were then used to obtain the theoretical cyclic voltammograms based on the reaction mechanism given in Scheme 5. The diffusion coefficient of  $4.19 \times 10^{-7}$   $\text{cm}^2 \text{s}^{-1}$  for acetophenone used in the simulations was calculated from the steady-state diffusion controlled limiting current for acetophenone reduction and use of Equation (1). The diffusion coefficients of species derived from reduction of acetophenone were assumed to be the same as for acetophenone. The second order rate constant for the dimerization reactions is estimated to be  $1.0 \times 10^7$   $\text{M}^{-1} \text{s}^{-1}$  based on the experiment versus theory comparisons. This value is significantly higher than that of  $4.0 \times 10^3$   $\text{M}^{-1} \text{s}^{-1}$  obtained in dry [BMPyrd][TFSI], implying stronger interaction between acetophenone radical anions and water. It has been suggested that aromatic ketones<sup>43, 45, 49, 50</sup> and quinones<sup>51</sup>, and their reduced forms form extensive hydrogen bonding networks with water in organic solvents and ionic liquids.

Presumably, this type of hydrogen bonding networks could form between acetophenone anions and water, resulting in a higher degree of charge delocalization and hence favour dimer formation.

## Conclusions

Electrochemical studies of acetophenone were undertaken under both N<sub>2</sub> and CO<sub>2</sub> atmospheres in dry [BMMIM][BF<sub>4</sub>], and dry and water saturated [BMPyrd][TFSI] to investigate the influence of proton availability from the ionic liquid itself and from adventitious water on electrocarboxylation.

In dry [BMMIM][BF<sub>4</sub>] and [BMPyrd][TFSI], results obtained under a N<sub>2</sub> atmosphere support a mechanism involving overall reduction of acetophenone followed by dimerization reactions with an rate constant of  $5.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $4.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. These values are considerably smaller than obtained in imidazolium based ionic liquids<sup>26, 27</sup> presumably due to weaker interaction between the acetophenone radical anion and the cations of these ionic liquids. Under a CO<sub>2</sub> atmosphere, the results indicate that acetophenone reduction involves a combination of dimerization, a proton coupled two-electron transfer reaction and electrocarboxylation pathways in dry [BMMIM][BF<sub>4</sub>], revealing that even when the reactive C-2 hydrogen in [BMIM][BF<sub>4</sub>] is substituted by a methyl group, demethylation of imidazolium cation under a CO<sub>2</sub> atmosphere could occur to form a stable *N*-heterocyclic carbene complex with CO<sub>2</sub>. By contrast, dry [BMPyrd][TFSI] is a much more suitable medium for electrocarboxylation and provides a yield of carboxylic acid as high as 98%. The reusability of this ionic liquid for electrocarboxylation of acetophenone is an important consideration in green chemistry. In this context it may be noted that the workup required to undertake GC-MS measurements after electrolysis demonstrates that the products and unreacted acetophenone can be completely separated from [BMPyrd][TFSI] using a simple solvent extraction method. Consequently, it can be proposed that reusability of this ionic liquid could be achieved using the same method.

In water saturated [BMPyrd][TFSI], product distribution analysis by GC-MS after bulk electrolysis suggests that dimers are the only products produced under both N<sub>2</sub> and CO<sub>2</sub> atmospheres. Under a N<sub>2</sub> atmosphere, an overall dimerization rate constant of  $1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  was obtained by comparison of experimental and simulated voltammetric data. This value is more than three orders of magnitude higher than that obtained in dry [BMPyrd][TFSI], indicating the key role of water on the kinetics of dimerization. Stronger hydrogen-bonding

interaction between acetophenone radical anions and water may lead to enhanced charge delocalization thus favour dimer formation.

The results obtained from these studies also demonstrate that precautions should be taken to dry ionic liquids carefully to achieve electrocarboxylation since water may promote the undesirable reactions by providing protons in the case of [BMMIM][BF<sub>4</sub>] or enhancing the kinetics of dimerization in the case of water-saturated [BMPyrd][TFSI].

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