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Electrochemical reduction of aromatic ketones in 1-butyl-3-methylimidazolium-based ionic liquids in the presence of carbon dioxide: the influence of the ketone substituent and the ionic liquid anion on bulk electrolysis product distribution

Shu-Feng Zhao,[†‡] Mike Horne,[*‡] Alan M. Bond[†] and Jie Zhang[*†]

[†] School of Chemistry and Australian Research Council Centre of Excellence for Electromaterials Science, Monash University, Clayton, Victoria, 3800, Australia. E-mail: jie.zhang@monash.edu; Tel: +61 3 99056289; Fax: +61 3 99054597.

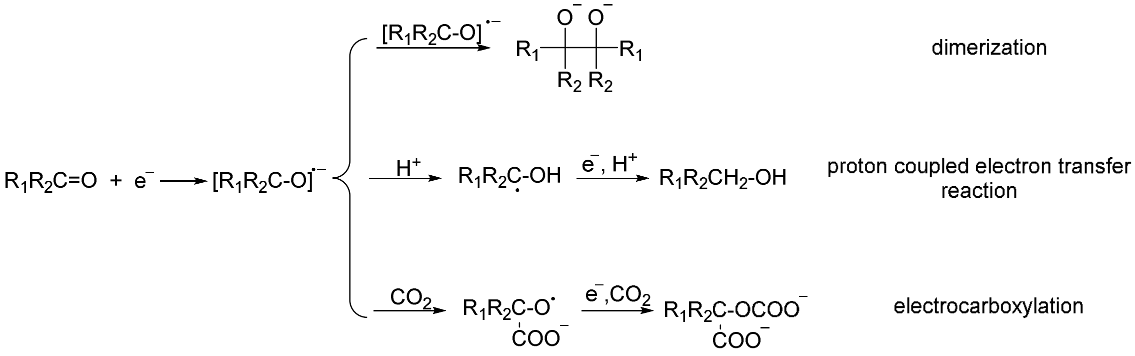
[‡] CSIRO Process Science and Engineering, Box 312, Clayton South, Victoria, 3168, Australia. Email: Mike.Horne@csiro.au; Tel: +61 3 9545 8866; Fax: +61 3 9562 8919.

Abstract

Electrochemical reduction of aromatic ketones, including acetophenone, benzophenone and 4-phenylbenzophenone, has been undertaken in 1-butyl-3-methylimidazolium-based ionic liquids containing tetrafluoroborate ($[BF_4]^-$), trifluoromethanesulfonate ($[TfO]^-$) and tris(pentafluoroethyl)trifluorophosphate ($[FAP]^-$) anions in the presence of carbon dioxide in order to investigate the ketone substituent effect and the influence of the acidic proton on the imidazolium cation (C2-H) on bulk electrolysis product distribution. For acetophenone, the minor products were dimers (< 10%) in all ionic liquids, which are the result of acetophenone radical anion coupling. For benzophenone and 4-phenylbenzophenone, no dimers were formed due to steric hindrance. In these cases, even though carboxylic acids were obtained, the main products generated were alcohols (> 50%) derived from proton coupled electron transfer reactions involving the electrogenerated radical anions and C2-H. In the cases of both acetophenone and benzophenone, the product distribution is essentially independent of the ionic liquid anion. By contrast, 4-phenylbenzophenone shows a product distribution that is dependent on the ionic liquid anion. Higher yields of carboxylic acids (~40%) are obtained with $[TfO]^-$ and $[FAP]^-$ anions because in these ionic liquids the C2-H is less acidic, making the formation of alcohol less favourable. In comparison with benzophenone, a higher yield of carboxylic acid (> 30% versus ~15%) was obtained with 4-phenylbenzophenone in all ionic liquids due to the weaker basicity of 4-phenylbenzophenone radical anion.

1. Introduction

Hydroxy carboxylic acids are an important class of compound that have been widely used as intermediates in the production of pharmaceutical materials[1-5] such as anti-inflammatory agents, cosmetic drugs and spasmolytics. Conventional synthesis of hydroxyl carboxylic acids proceeds via the corresponding cyanohydrins using ketones as precursors. However, the use of highly toxic cyanides makes this method less palatable for pharmaceutical applications. Consequently, alternative synthetic routes for producing hydroxy carboxylic acids have been extensively explored,[6-9] and among these alternatives, the electrocarboxylation of aromatic ketones which involves bulk electrolysis in the presence of carbon dioxide has been recognized as being effective and environmentally benign.[9-16] So far, the majority of bulk electrolysis studies under a carbon dioxide (CO_2) atmosphere have been carried out in molecular solvents such as dimethylformamide (DMF)[5, 14, 17], *N*-methyl-2-pyrrolidone (NMP)[11-13] and acetonitrile (MeCN)[5, 14]. Apart from the major hydroxy carboxylic acid products, common side products in the electroreduction of aromatic ketones under a CO_2 atmosphere are dimers and alcohols which are derived from dimerization and proton coupled electron transfer reactions, respectively (**Scheme 1**). Isse *et al.*[18] have shown that the product distribution is strongly medium dependent. Higher yields of carboxylic acids were obtained when solvents with higher CO_2 solubilities and lower proton availabilities are used.



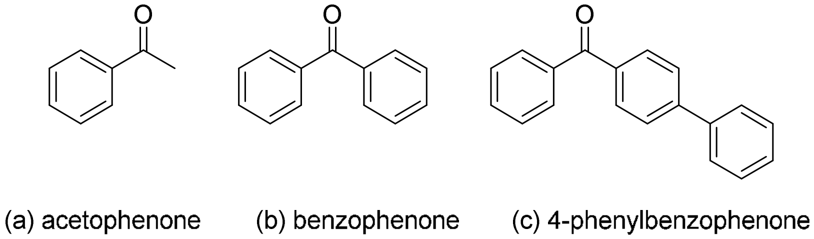
Scheme 1 Competing reaction pathways for the electroreduction of aromatic ketones under a CO_2 atmosphere.

In recent years, ionic liquids[19-21] have received considerable attention in both fundamental and applied electrochemical research because they are inherently conductive, exhibit excellent electrochemical stability, and display versatile solvent properties that differ from those found with molecular solvents containing added supporting electrolytes. From the thousands of ionic liquids reported so far, those based on the imidazolium cation[20, 22] are most commonly used for the electrocarboxylation of organic compounds such as alkenes,[23] alcohols[24-26], ketones[5, 16, 27, 28] and halides[29-31] because they are synthesised easily and can dissolve large amounts of many organic compounds and CO_2. However, when using 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) as the medium for bulk electrolysis of acetophenone under a CO_2 atmosphere, Zhao *et al.*[28] found that 1-phenylethanol was the main product with a high yield of 97%. It was proposed in that study that the presence of CO_2 enhances the C2-H donating ability in $[Bmim]^+$ due to strong complex formation between deprotonated $[Bmim]^+$, *N*-heterocyclic carbene (NHC), and CO_2, resulting in a thermodynamically favourable proton coupled electron transfer pathway. This postulated mechanism is supported by observations made during the electroreduction of acetophenone under CO_2 in dry 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([Bmmim][BF_4]) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Bmpyrd][TFSI]), both of which have low proton availabilities.[16] In dry [Bmmim][BF_4] where the reactive C2-H is substituted by a methyl group, a significant amount of 2-hydroxy-2-phenylpropionic acid (15% yield) was obtained, even though 1-phenylethanol (60% yield) was still the major product. By contrast, in dry [Bmpyrd][TFSI] where a reactive proton source is essentially absent[32], the carboxylic acid yield is 98%. Clearly, the reaction mechanism is strongly dependent on the proton availability in ionic liquids: those with a lower proton availability favour carboxylate formation. It is also noteworthy that in a recent study by Feroci *et al.*[33], a significant yield of the product generated from the reaction between NHC and benzaldehyde was detected when benzaldehyde was added to [Bmim][BF_4] after reductive electrolysis. This experimental evidence further supports the proposed mechanism based on a proton coupled electron transfer reaction involving the radical anion of the substrate and C2-H in [Bmim][BF_4] under a CO_2 atmosphere.

The results[16, 28] to date from our laboratory show that the imidazolium-based ionic liquids previously used are not suitable for electrocarboxylation of aromatic ketones due to the acid-base chemistry associated proton coupled electron transfer reaction involving reactive C2-H of imidazolium cations and the basic electrogenerated aromatic ketone radical anions. Cathodic instability[34, 35] also may be an issue. In principle, the thermodynamics and kinetics of the undesirable acid-base reaction depend on the basicity of the proton acceptor (the radical anion of the aromatic ketone) and the acidity of the proton donor, C2-H. The former can be varied by introducing electron donating or withdrawing groups substituted onto the aromatic ketone. The latter is governed by the ionic liquid anion as suggested by studies using NMR[36], voltammetry, infrared spectroscopy and thermogravimetric techniques[33]. According to ^{1}H NMR data reported by Cremer *et al.*[36] on imidazolium-based ionic liquids with a common cation, but different anions ([Cl]$^-$, [Br]$^-$, [I]$^-$, [NO_3]$^-$, [BF_4]$^-$, [PF_6]$^-$, [TfO]$^-$ (trifluoromethanesulfonate), [TFSI]$^-$, [FAP]$^-$ (tris(pentafluoroethyl)trifluorophosphate) and [Pf_2N]$^-$ (bis(pentafluoroethylsulfonyl)imide)), the C2-H chemical shift is the smallest with ionic liquids having [FAP]$^-$ as an anion. This implies that imidazolium-based ionic liquids having [FAP]$^-$ anions exhibit with the weakest acidity of the C2-H within the range of anions investigated in their study. In addition, Feroci *et al.*[33] have suggested that the rate of reaction between NHC and CO_2 is affected by the nature of the ionic liquid anion. This group's investigations with imidazolium-based ionic liquids having [BF_4]$^-$, [PF_6]$^-$, [TfO]$^-$, [TFSI]$^-$ and

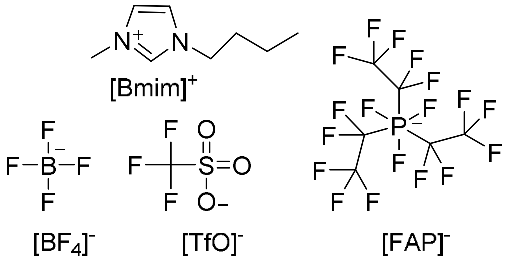
$[CF_3CO_2]^-$ as anions, showed that the rate of the reaction between NHC and CO_2 was much slower when $[TfO]^-$ was the ionic liquid anion. Presumably, weaker NHC interaction with CO_2 occurs when $[TfO]^-$ or $[FAP]^-$ anions are present. As a result, the acidity of the C2-H is lower. It therefore follows that the distribution of products from the electroreduction of aromatic ketones under a CO_2 atmosphere depends on the nature of both the substrate and ionic liquid anion.

In this study, bulk electrolysis of the aromatic ketones acetophenone, benzophenone and 4-phenylbenzophenone (**Scheme 2**) has been investigated under a CO_2 atmosphere in [Bmim][BF_4], 1-butyl-2,3-dimethylimidazolium trifluoromethanesulfonate ([Bmim][TfO]) and 1-butyl-2,3-dimethylimidazolium tris(pentafluoroethyl)trifluorophosphate ([Bmim][FAP]) (structures shown in **Scheme 3**) in order to probe the aromatic ketone substituent effect and the influence of the ionic liquid anions on the product distribution.



(a) acetophenone (b) benzophenone (c) 4-phenylbenzophenone

Scheme 2 Structures of aromatic ketones: (a) acetophenone, (b) benzophenone and (c) 4-phenylbenzophenone.



Scheme 3 Structures of ionic liquids: [Bmim][BF_4]; [Bmim][TfO]; [Bmim][FAP].

2. Experimental section

Chemicals

[Bmim][BF_4] was purchased from IOLITEC (Germany). [Bmim][TfO] and [Bmim][FAP] were purchased from Merck (99%). The ionic liquids were dried over basic alumina for at least 24 h, then placed under vacuum at 80 ^oC for 24 h prior to use. The water content after these procedures as measured by Karl-Fischer titration (Metrohm 831 Karl Fischer coulometer) was 65 ± 10 ppm (or 3.0 mM) for [Bmim][BF_4], 118 ± 10 ppm (or 7.1 mM) for [Bmim][TfO] and 43 ± 10 ppm (or 2.0 mM) for [Bmim][FAP]. Acetophenone (ReagentPlus®, 99%), benzophenone (ReagentPlus®, 99%), diethyl ether (Analytical reagent, > 99%) and ferrocene (Fc) (≥ 98%) were purchased from Sigma Aldrich, while 4-phenylbenzophenone was purchased from ABCR GmbH & CO. KG (Germany). All the aromatic ketones were used as received.

Voltammetric measurements

Voltammetric measurements were made using a CHI 700 electrochemical workstation (CH Instruments, Texas, USA) and a standard three-electrode cell. For transient cyclic voltammetric experiments, a glassy carbon macrodisc electrode (GC, d = 1.0 mm) was used as the working electrode. Platinum wire was used as both the quasi-reference and counter electrodes. Addition of 5 mM Fc to each experiment and studies on its voltammetry allowed the Pt quasi-reference potential scale to be converted into the Fc/Fc^+ reference potential scale. The working electrodes were polished with an aqueous 0.3 μm alumina slurry on a polishing cloth (Buehler), sonicated in deionized water, rinsed with deionized water and acetone, and then dried under a flow of nitrogen before use. All voltammetric experiments were undertaken at room temperature (20 ± 2 ^oC). Experiments with carefully dried ionic liquids were undertaken under a nitrogen atmosphere in a dry box to minimize the effect of atmospheric water and oxygen.

Bulk electrolysis and product analysis

Unless otherwise stated, controlled potential bulk electrolysis experiments were undertaken at 20 ± 2 ^{o}C, under a CO_2 atmosphere in a two compartment divided cell equipped with glassy carbon rods as both cathode and anode. A silver wire mounted into a capillary sealed with a sintered glass disk served as a quasi-reference electrode. [Bmpyrd][TFSI] was used as the electrolyte in the reference electrode element. The same solution 50 mM of the selected aromatic ketone in the selected ionic liquid was used in both compartments of the cell. A constant stream of CO_2 flowed through the cell to maintain a constant concentration of CO_2 throughout the electrolysis period. After electrolysis, the catholyte was acidified with aqueous HCl (pH ~ 3), extracted three times with diethyl ether. The products remaining after extraction were evaporated to dryness. After dissolving in diethyl ether, the product was analysed by HPLC (High-performance liquid chromatography system equipped with a UV detector detection wavelength of 254 nm, Agilent 1200 Infinity Series, Agilent, USA) using a C18 column (Waters). The mobile phase was a mixture of water and acetonitrile (90/10).

3. Results and Discussion

3.1 Voltammetric studies

Cyclic voltammetric experiments were initially undertaken on the aromatic ketones in all three imidazolium-based ionic liquids under both N_2 and CO_2 atmospheres. Based on previous studies on the electroreduction of acetophenone in [Bmim][BF_4][28], GC is known to be relatively inert for direct CO_2 reduction in the potential region of acetophenone reduction.

Thus, GC was chosen for detailed investigations for the electroreduction of aromatic ketones in all three imidazolium-based ionic liquids under both N_2 and CO_2 atmospheres. These analyses focussed on how the ketone susbstituent and the ionic liquid anion affected the electrochemical reduction of aromatic ketones and reactivity of the electrochemically generated radical anions under a CO_2 atmosphere.

Cyclic voltammograms obtained at a scan rate of 0.1 V s^{-1} at a 1.0 mm GC electrode in neat [Bmim][BF_4] and after addition of 10 mM benzophenone under either N_2 or CO_2 atmospheres. Data in absence (curve a in Figure 1) and presence (curve b in Figure 1) of CO_2 in neat [Bmim][BF_4] suggest that direct electroreduction of CO_2 at a GC electrode is minimal in the potential region related to reduction of the ketones. The results also confirm that the negative potential window limit at a GC electrode is sufficient for reduction of aromatic ketones under our experimental conditions. Consequently, GC was as the electrode material for a detailed investigation of the electroreduction of aromatic ketones under both N_2 and CO_2 atmospheres. In the N_2 case, two reduction processes (curve c in **Figure 1**) were observed with peak potentials of -2.02 and -2.11 V *vs* Fc/Fc^+, respectively. A small counter oxidation component was detected when the potential was reversed immediately after the first reduction process (curve d in **Figure 1**), suggesting that the initial step is partially reversible on the voltammetric timescale recorded in **Figure 1**. In contrast, no oxidation component was detected for the second reduction process, suggesting that this process is chemically irreversible under these conditions. Based on the studies in DMF[37] and [Bmim][BF_4][38], the first process is assigned to the reduction of benzophenone to the benzophenone radical anion. In the second reduction process, the radical anion is further reduced to the dianion which is rapidly protonated by the C2-H from the imidazolium cation. The magnitude of the current for the second process is significantly smaller than for the first one, even though both processes are one electron reductions (**Figure 1**). This difference is attributed to the formation of an adduct between benzophenone and its dianion[38]. This adduct is then oxidized at -0.67 V in the reverse (positive potential direction) sweep of potential.[38]

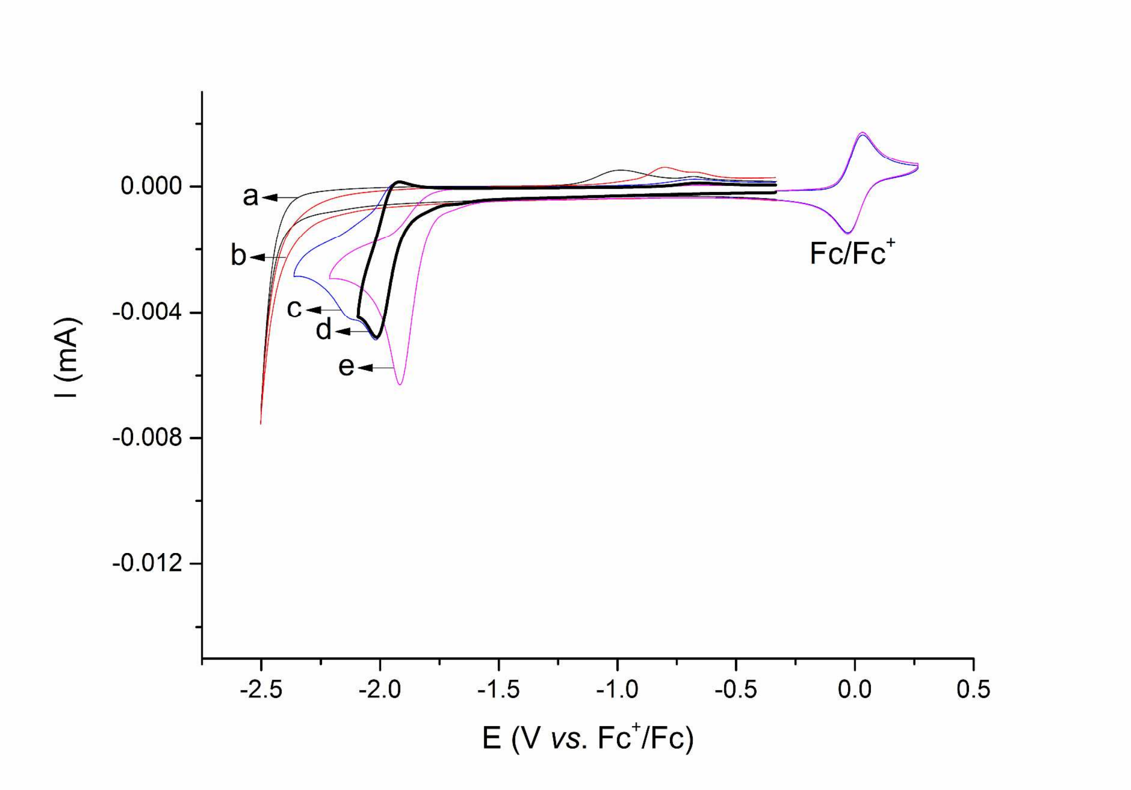


Figure 1 Cyclic voltammograms recorded at a 1.0 mm diameter GC electrode (scan rate = 0.1 V s^{-1}) in neat [Bmim][BF_4] under (a) N_2 or (b) CO_2 atmospheres (1 atm), and after addition of 10 mM benzophenone under (c and d) N_2 or (e) CO_2 atmospheres (1 atm). The Fc/Fc^+ process (at 0 V) derived from oxidation of 5.0 mM Fc is included for comparison purposes.

Upon saturation of [Bmim][BF_4] with CO_2, the two redu[i]ction processes merged into one and a larger total reduction current was evident. The peak potential shifted in the positive direction from -2.02 V to -1.92 V *vs* Fc/Fc^+. Compton *et al.*[39] found that the diffusion coefficient of Fc in CO_2-saturated (1 atm) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][TFSI]) is significantly higher compared to that found in N_2-saturated [Emim][TFSI] (1 atm). If a diffusion coefficient change of this magnitude also applies in our study, the increase in the peak current could be attributed to enhanced diffusivity. To assess this possibility under our experimental conditions, a control experiment using 5 mM Fc was conducted in [Bmim][BF_4] containing 10 mM benzophenone under both N_2 and CO_2 atmospheres (curves c and e in **Figure 1**). The results suggest that the oxidation peak current for the reversible Fc/Fc$^+$ process[40, 41, 42] in [Bmim][BF_4] remains essentially unaltered by the replacement of N_2 with CO_2. Since the peak current associated with a reversible electron transfer process is proportional to the square root of the diffusion coefficient when the effect of uncompensated resistance is negligible,[43] this result implies that the diffusion coefficient of Fc and presumably that of benzophenone remain essentially unaltered. Consequently, the enhanced reduction current and positive shift of peak potential associated with the benzophenone reduction process under a CO_2 atmosphere relative to a N_2 one, are attributed to the presence of a new multi-electron reaction pathway. Analogous observations in DMF[5, 10], MeCN[10] and NMP[11-13] were attributed to the presence of an overall two electron transfer step that is a result of either a proton coupled electron transfer pathway, or an electrocarboxylation pathway, or a combination of both.

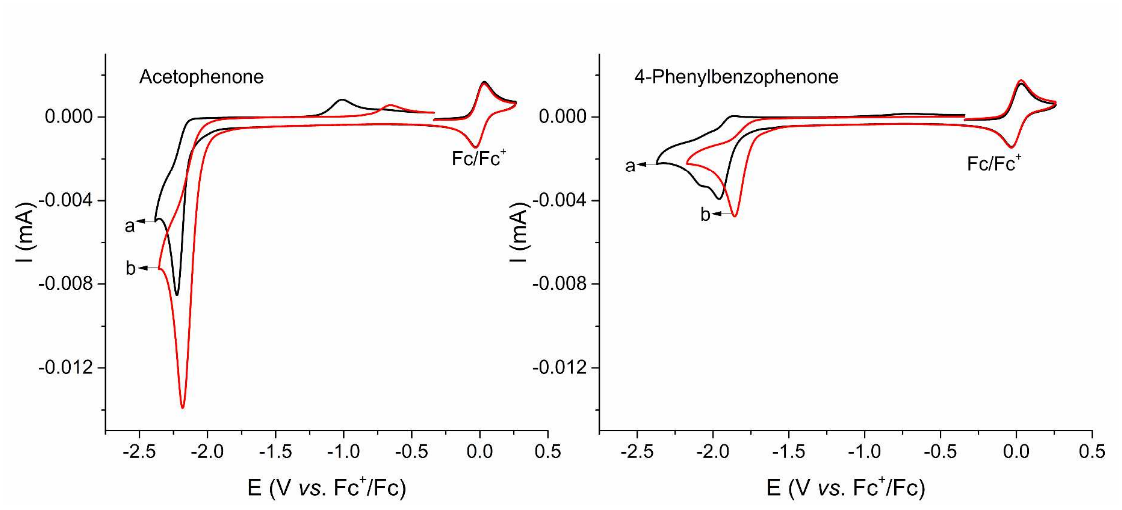


Figure 2 Cyclic voltammograms obtained at a 1.0 mm diameter GC electrode (scan rate = 0.1 V s^{-1}) in [Bmim][BF$_4$] containing 10 mM acetophenone and 4-phenylbenzophenone under (a) N_2 or (b) CO_2 atmospheres (1 atm).

Related results were obtained with acetophenone and 4-phenylbenzophenone (**Figure 2**), except that only one reduction process was observed for acetophenone reduction under a N_2 atmosphere. Based on previous reports,[28, 44, 45] this may result from rapid dimerization of the acetophenone radical anion to form products that cannot be further reduced within the potential window available in [Bmim][BF$_4$]. A small oxidation peak observed at -1.09 V under a N_2 atmosphere was assigned to the oxidation of the head-to-tail type of dimer based on results available in previous studies[28]. Again, control experiments with the Fc/Fc$^+$ reference process suggest that the increased peak current magnitude under a CO_2 atmosphere is not attributable to an enhanced mass transport rate. Consequently, the voltammetric changes in the presence of CO_2 imply the introduction of new chemistry. It is also worth noting that the magnitudes of the peak currents for the irreversible reduction of benzophenone and 4-phenylbenzophenone are smaller than that of acetophenone in all ionic liquids. This is due to differences in their diffusion coefficients and the reactivity of the electrogenerated radical anions. In comparison with acetophenone[41], a smaller diffusion coefficient for benzophenone[40] in dry [Bmpyrd][TFSI] also has been reported in our previous studies.

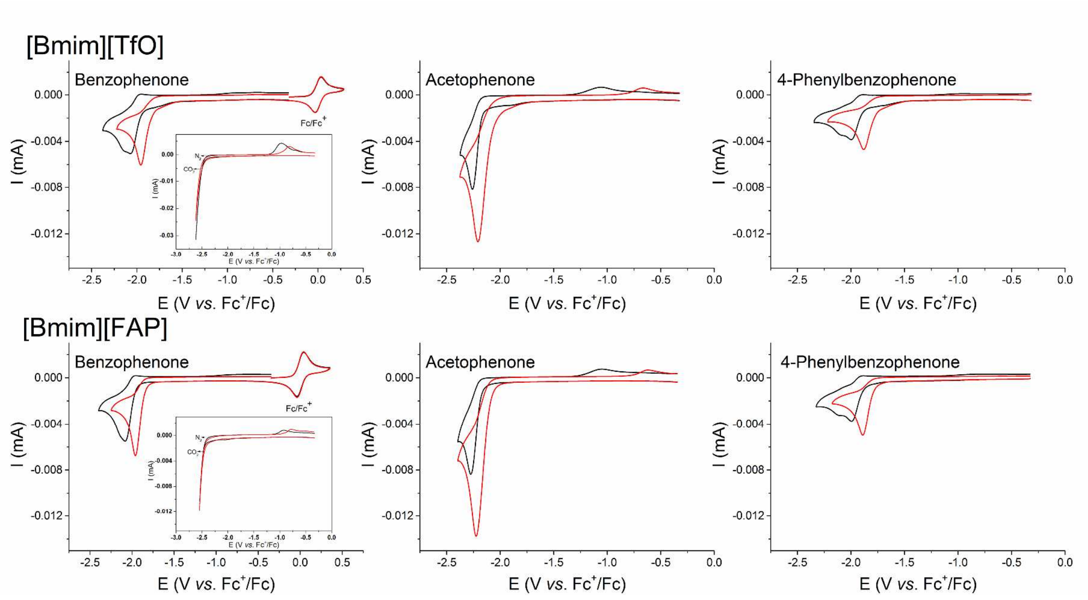


Figure 3 Cyclic voltammograms obtained at a 1.0 mm diameter GC electrode (scan rate = 0.1 V s^{-1}) in [Bmim][TfO] and [Bmim][FAP] containing 10 mM benzophenone, acetophenone and 4-phenylbenzophenone under (—) N_2 or (—) CO_2 atmospheres (1 atm). The insert figures show cyclic voltammograms recorded at a 1.0 mm diameter GC electrode (scan rate = 0.1 V s^{-1}) in neat [Bmim][TfO] and [Bmim][FAP] under N_2 or CO_2 atmospheres (1 atm).

Cyclic voltammograms obtained for the neat [Bmim][TfO] and [Bmim][FAP] ionic liquids and after addition of aromatic ketones (**Figure 3**) are similar to those in [Bmim][BF_4] under either N_2 or CO_2 atmospheres. The cathodic potential window limits are about at -2.4 *vs.* Fc/Fc$^+$ at a GC electrode in both ionic liquids under either N_2 or CO_2 atmospheres. In all cases, the increase of reduction current for reduction of the aromatic ketones under a CO_2 atmosphere is attributed to the introduction of new chemistry that involves the transfer of more electrons than applies under a N_2 atmosphere.

Peak potentials are summarized in **Table 1**. Under a N_2 atmosphere, the peak potential associated with the first reduction processes (E_{p1,N_2}) of acetophenone, benzophenone and 4-

phenylbenzophenone in three ionic liquids are -2.25 ± 0.03 V, -2.05 ± 0.03 V and -1.98 ± 0.02 V *vs* Fc/Fc$^+$, respectively. Assuming the reversible potential of the reference Fc/Fc$^+$ process is independent on the identity of the ionic liquid, these voltammetric data leads to the conclusion that the E_{p1,N_2} values are not strongly dependent on the identity of the ionic liquid, which is consistent with results reported for electroreduction of benzophenone in ionic liquids[38]. However, E_{p1,N_2}values vary substantially with the identity of the ketone substituent. The most negative peak potential was observed for acetophenone reduction while the corresponding values for benzophenone and 4-phenylbenzophenone are more positive because they contain electron withdrawing phenyl and diphenyl groups. This aromatic ketone substituent effect has also been observed in organic solvent media.[5]

Table 1 Peak potential data extracted from the cyclic voltammograms[a] of aromatic ketones recorded at 1.0 mm diameter GC electrode in imidazolium-based ionic liquids under N_2 and CO_2 atmospheres at 22 °C.

Aromatic ketone	Ionic liquid	E_{p1,N_2}[b]/V *vs* Fc/Fc$^+$	E_{p,CO_2}[c]/V *vs* Fc/Fc$^+$	ΔE[d]/mV *vs* Fc/Fc$^+$
Acetophenone	[Bmim][BF_4]	-2.23	-2.18	50
	[Bmim][TfO]	-2.26	-2.21	50
	[Bmim][FAP]	-2.28	-2.23	50
Benzophenone	[Bmim][BF_4]	-2.02	-1.92	100
	[Bmim][TfO]	-2.07	-1.95	120
	[Bmim][FAP]	-2.08	-1.96	120
4-Phenylbenzophenone	[Bmim][BF_4]	-1.96	-1.86	100
	[Bmim][TfO]	-2.00	-1.88	120
	[Bmim][FAP]	-2.00	-1.89	110

[a] Experimental conditions are as stated in the caption to **Figure 1**.
[b] Peak potential for first process in the reduction of the aromatic ketone under a N_2 atmosphere.
[c] Peak potential under a CO_2 atmosphere.
[d] Separation between the first reduction peak potential under a N_2 atmosphere and the reduction peak potential under a CO_2 atmosphere.

Under a CO_2 atmosphere, all reduction peak currents increase significantly and the peak potentials (E_{p,CO_2}) shift positively. For benzophenone and 4-phenylbenzophenone, the second reduction process disappears completely. The peak potentials (E_{p,CO_2}) for reduction under CO_2 for acetophenone, benzophenone and 4-phenylbenzophenone in three ionic liquids are -2.20 ± 0.03 V, -1.94 ± 0.02 V and -1.87 ± 0.02 V *vs* Fc/Fc^+, respectively, at a scan rate of 0.1 V s^{-1} and independent on the identity of the ionic liquid anion. Thus, peak potential differences (ΔE) obtained under N_2 and CO_2 atmospheres are also essentially ionic liquid anion independent, which in turn suggests that the kinetics of the coupled homogeneous reaction (probably pseudo first order[43]) are not highly sensitive to the identity of the ionic liquid anion.

3. 2 Bulk electrolysis of the aromatic ketones under a CO_2 atmosphere.

To identify which reaction pathway is followed during electroreduction of the aromatic ketones under a CO_2 atmosphere, preparative scale bulk electrolysis experiments were undertaken in ionic liquids using GC rods as both cathode and anode in a divided cell. After electrolysis, the cathodic products were separated and identified *via* HPLC analysis, and the results are summarized in **Table 2**.

Table 2 Products derived from reduction of 50 mM aromatic ketone in imidazolium-based ionic liquids under a CO_2 atmosphere.

Aromatic ketone	Ionic liquid	E_{app}[a]/V *vs* Fc/Fc^+	Product yield[b]/%		
			Acid	Alcohol	Dimer
Acetophenone[c]	[Bmim][BF_4]	-2.25	0.0	90.6[f]	9.4
	[Bmim][TfO]	-2.30	0.0	93.6	6.4
	[Bmim][FAP]	-2.32	0.0	90.6	9.4
Benzophenone[d]	[Bmim][BF_4]	-2.10	16.2	83.4	0.0
	[Bmim][TfO]	-2.12	14.5	85.3	0.0
	[Bmim][FAP]	-2.05	15.0	83.1	0.0
4-Phenylbenzophenone[e]	[Bmim][BF_4]	-2.05	32.8	66.5	0.0
	[Bmim][TfO]	-2.00	38.5	60.5	0.0

[Bmim][FAP]	-2.07	40.7	59.0	0.0

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[a] Applied potential used for bulk electrolysis.

[b] HPLC yields based on the consumed substrate.

[c] Acid = 2-hydroxy-2-phenylpropionic acid; alcohol = 1-phenylethanol; dimer = 1-[4-(1-hydroxy-ethylidene)-cyclohexa-2,5-dienyl]-1-phenyl-ethanol and 2,3-diphenyl-butane-2,3-diol.

[d] Acid = 2-hydroxy-2,2-diphenylacetic acid; alcohol = diphenylmethanol; dimer = 1,1,2,2,-tetraphenylethane-1,2-diol.

[e] Acid = 2-([1,1'-biphenyl]-4-yl)-2-hydroxy-2-phenylacetic acid; alcohol = [1,1'-biphenyl]-4-yl(phenyl)methanol; dimer = 1,2-di([1,1'-biphenyl]-4-yl)-1,2-diphenylethane-1,2-diol.

[f] The alcohol yield determined by HPLC was slightly less than that determined by GC-MS in identical conditions in another study (97%)[28].

For the electroreduction of acetophenone, based on HPLC analysis, a small amount of dimer was obtained, no carboxylic acid was detected and the major product (>90%) was 1-phenylethanol in all three ionic liquids, which is consistent with a proton coupled electron transfer providing the major reaction pathway. These results are consistent with those in our previous study, which suggested 97% of the product was 1-phenylethanol from the electrolysis of acetophenone in [Bmim][BF_4] based on GC-MS analysis[16, 28]. Small differences in reaction yields (91% *vs* 97%) reported in these two studies could result from systematic differences between these different analytical techniques.

No dimer products were detected by HPLC analysis after the electroreduction of benzophenone and 4-phenylbenzophenone in any of the ionic liquids under a CO_2 atmosphere. As reported in studies in molecular organic solvents[12], this difference may result from steric hindrance associated with the larger size of these substrates. Furthermore, in contrast to acetophenone reduction, the target products (carboxylic acids) were obtained in all ionic liquids, although alcohols were still the major products. In the case of benzophenone, the reduction product distribution of ~15% carboxylic acid and ~85% alcohol is essentially independent on the identity of ionic liquid anion. In contrast, in the case of 4-phenylbenzophenone, an ionic liquid anion dependent reduction product distribution is clearly evident in that the yields of carboxylic acid obtained in [Bmim][TfO] and [Bmim][FAP] are considerably larger than in [Bmim][BF_4].

When reaction products and their yields are compared, the influence of the ketone substituent on the product distribution clearly emerges. Alcohols are the major product and dimers are the minor product for the electroreduction of acetophenone. In contrast, dimers are absent in the electroreduction of either benzophenone or 4-phenylbenzophenone. While alcohols remain the major products, substantial yields of carboxylic acid are now also obtained with these latter two aromatic ketones. The reduction of 4-phenylbenzophenone produces a higher yield of carboxylic acid and lower yield of alcohol than benzophenone. This could be due to the fact that the 4-phenylbenzophenone radical anion is a weaker base than benzophenone radical anion (diphenyl is a stronger electron withdrawing group than phenyl). Consequently, the driving force for protonation to form an alcohol is weaker in the case of the 4-phenylbenzophenone radical anion.

As shown in **Table 2**, with 4-phenylbenzophenone, the highest yield of acid and lowest yield of alcohol were obtained in [Bmim][FAP]. This anion dependent product distribution is unlikely to be a consequence of differences in CO_2 concentration since the solubility of CO_2 in all ionic liquids at room temperature and 1 atm is comparable (approximately 100 mM).[46, 47] Although the concentration of CO_2 is close to the stoichiometric amount required for electrocarboxylation of 50 mM aromatic ketones (**Scheme 1**), depletion of CO_2 during electrolysis is unlikely, due to the faster diffusion of smaller sized CO_2 and the fact that a constant CO_2 stream was employed in all bulk electrolyses. The above discussion is based on the assumption that the molecular form of CO_2 is the reactive CO_2 species in all three ionic liquids. This should be a reasonable assumption, since the chemical interaction between CO_2 and $[FAP]^-$, though unique among the ionic liquids under investigation, is rather weak.[48] It should also be noted that the yields of carboxylic acid and alcohol remain essentially unchanged when a lower concentration of 4-phenylbenzophenone, 25 mM instead of 50 mM, was used in the electrolysis (results not shown). This observation again confirms that the amount of CO_2 is adequate.

To explain this experimental observation on ionic liquid anion dependent product distribution, we refer to the NMR study of Cremer *et al.*[36] who showed that the bonding strength of C2-H of imidazolium and hence its acidity depends on the ionic liquid anion. In their work, with ten imidazolium-based ionic liquids having different anions ($[Cl]^-$, $[Br]^-$, $[I]^-$, $[NO_3]^-$, $[BF_4]^-$, $[TfO]^-$, $[PF_6]^-$, $[TFSI]^-$, $[FAP]^-$ and $[Pf_2N]^-$) NMR data showed that the C2-H donating ability increases when the size of the anions increases, and the basicity and coordinating strength of the anions correspondingly decrease. Of the anions investigated, the ionic liquid containing the $[FAP]^-$ anion exhibited the lowest ability to donate C2-H. Furthermore, since C2-H only becomes sufficiently active under electrocarboxylation conditions as a result of NHC-CO_2 interaction, the activity of C2-H should also depend on the stability of this complex. Feroci *et al.*[33] investigated the reactivity of electrogenerated NHC towards CO_2 in $[Bmim]^+$-based ionic liquids containing anions, such as $[BF_4]^-$, $[PF_6]^-$, $[CF_3CO_2]^-$, $[TfO]^-$ and $[TFSI]^-$. The results of this study using voltammetry, infrared spectroscopy and thermogravimetric analysis suggested that the kinetics of the NHC-CO_2 reaction are dependent upon the ionic liquid anion, with the slowest rate being observed in [Bmim][TfO]. This result implies that [Bmim][TfO] should have the weakest proton donating ability in the presence of CO_2 of all the ionic liquids investigated in this study. On these bases, higher yields of acid product may be expected with 4-phenylbenzophenone from imidazolium-based ionic liquids containing $[TfO]^-$ and $[FAP]^-$ anions. However, the product distribution for acetophenone and benzophenone reduction does not depend on the identity of the anion. This may be a result of the basicity of acetophenone and benzophenone radical anions being so much stronger than that of the 4-phenylbenzophenone radical anion.

Consequently, differences in proton availability in the ionic liquids may be inadequate to significantly alter the reaction pathway, hence leading to an anion independent product distribution.

Conclusion

Electrochemical reduction of the aromatic ketones acetophenone, benzophenone and 4-phenylbenzophenone under a CO_2 atmosphere in imidazolium-based [Bmim][BF_4], [Bmim][TfO] and [Bmim][FAP] ionic liquids reveal bulk electrolysis product distribution is influenced by the nature of substrate and the anion of the ionic liquid. The yields of carboxylic acids were found to be dependent on both the nature of the substrate and the anion of the ionic liquid, with the highest yield obtained *via* reduction of 4-phenylbenzophenone in [Bmim][FAP]. Formation of alcohol as a side reaction through a proton coupled electron transfer pathway is least favourable in this system since the 4-phenylbenzophenone radical anion is the weakest base and C2-H in [Bmim][FAP] is the weakest acid. Although higher yields of carboxylic acid may be obtained in imidazolium-based ionic liquids if an optimal combination of aromatic ketone and ionic liquid anion are selected, the results obtained in this study confirm the unsuitability of imidazolium-based ionic liquids for electrocarboxylation of aromatic ketones reported in our previous study[28].

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