



## NOTE

### Electrocatalytic Carboxylation of Benzoyl Bromide with CO<sub>2</sub> in Ionic Liquid 1-Butyl-3-Methylimidazoliumtetrafluoroborate to Methyl phenyl glyoxylate

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A new electrochemical procedure for the electrocatalytic carboxylation of benzoyl bromide with CO<sub>2</sub> in ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF<sub>4</sub>), to methyl phenyl glyoxylate was investigated. The experiments were carried out in three electrodes undivided cell under mild conditions and the use of volatile and toxic solvents and catalysts, as well as any other additional supporting electrolytes, was avoided. The electrochemical reduction behavior of benzoyl bromide in BMIMBF<sub>4</sub> had been studied by cyclic voltammetry with a reduction peak at -1.6 V (vs. Ag). Methyl phenyl glyoxylate was obtained by typical electrolytic procedure.

**Keywords:** Ionic liquid, CO<sub>2</sub>, Benzoyl bromide, Methyl phenyl glyoxylate, Electrocatalysis.

Carbon dioxide is one of gases leading to the green house effect, the conversion and utilization of CO<sub>2</sub> have attracted extensively attention<sup>1</sup>. Carbon dioxide is an abundant, non-toxic and low-cost carbon source. It is well known that electrocarboxylation is a powerful pathway for the fixation of CO<sub>2</sub><sup>2</sup>. As reported in the literatures, the electrochemical reaction of CO<sub>2</sub> with various organic compounds, including benzyl chlorides, allylic halides and epoxides, could afford valuable carbamates and cyclic carbonates<sup>3-9</sup>.

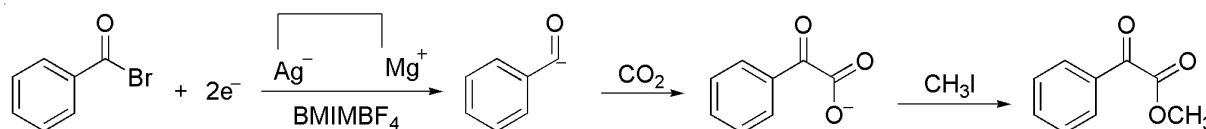
Nevertheless, the use of toxic organic solvents (CH<sub>3</sub>CN, DMF, etc.) and large amounts of supporting electrolytes, makes it more complex to recover the solvents. In addition, with the growing demand of environmental friendly technologies, the effort should be devoted to avoid the use of volatile and damaging solvents and supporting electrolytes.

Ionic liquids, the molten salts with melting points close to room temperature, are obtained by combination of large organic cations (N,N-dialkylimidazolium, pyridinium, phosphonium, quaternary ammoniums, etc.) with a variety of anions (AlCl<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, (CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>N<sup>-</sup>, etc.)<sup>10,11</sup>. In recent years, ionic

liquids have been the green reaction media in organic synthetic processes as the substitutes for conventional toxic and volatile solvents and supporting electrolytes, due to their low vapour pressure, high ionic conductivity and wide electrochemical potential window, solvating ability and ability to act as catalysts<sup>10-14</sup>.

To our best of knowledge, chemical fixation of CO<sub>2</sub> with benzoyl bromide (BB) in ionic liquids has not been reported. Herein, we reported the study of the reactivity of benzoyl bromide in CO<sub>2</sub>-saturated ionic liquid BMIMBF<sub>4</sub> (**Scheme-I**). The aim of this investigation was to set up an alternative methodology for electrocatalytic carboxylation of benzoyl bromide with CO<sub>2</sub> in BMIMBF<sub>4</sub> to methyl phenyl glyoxylate. The electrolyses were carried out in BMIMBF<sub>4</sub> under mild conditions without supporting electrolyte and catalysts.

The ionic liquid BMIMBF<sub>4</sub> (with a purity of more than 99 %) was dried under vacuum at 120 °C, until cyclic voltammogram result indicated that there was no detectable water. The purity of CO<sub>2</sub> and argon were 99.99 %. Unless otherwise noted, other reagents and solvents were used as received from commercial suppliers.



Scheme-I

**Cyclic voltammogram behavior of benzoyl bromide in BMIMBF<sub>4</sub>:** Cyclic voltammogram behavior of benzoyl bromide on Ag electrode (area = 0.3 cm<sup>2</sup>) at the scan rate of 10 mV s<sup>-1</sup> in BMIMBF<sub>4</sub> was measured in an undivided cell at 25 °C with platinum (Pt, area = 1 cm<sup>2</sup>) as the counter electrode. The reference electrode was Ag wire. All potentials are given with respect to this reference electrode. Fig. 1 shows the typical curves.

As can be seen from Fig. 1(a), in neat BMIMBF<sub>4</sub> there is no reduction peak in the sweeping region -0.4 to -2.3 V. It can also be observed that the cathodic current starts to increase at around -2.2 V, which is due to the polarization of the BMIMBF<sub>4</sub><sup>15,16</sup>. As shown in Fig. 1(b), in CO<sub>2</sub>-saturated BMIMBF<sub>4</sub>, a single irreversible reduction peak is observed at -2.0 V, which is attributed to the reduction of CO<sub>2</sub> to CO<sub>2</sub><sup>-</sup>. After addition of benzoyl bromide (20 mmol L<sup>-1</sup>) to neat BMIMBF<sub>4</sub>, the Fig. 1(c), shows a peak at -0.9 V, plus two waves in the more negative potential region -1.4 to -1.8 V. The first irreversible peak corresponds to the cathodic benzoyl bromide reduction and the second and third peaks can be ascribed to the reduction of benzoyl (formed in the initial benzoyl bromide reduction), as well as to the products of its further reaction.

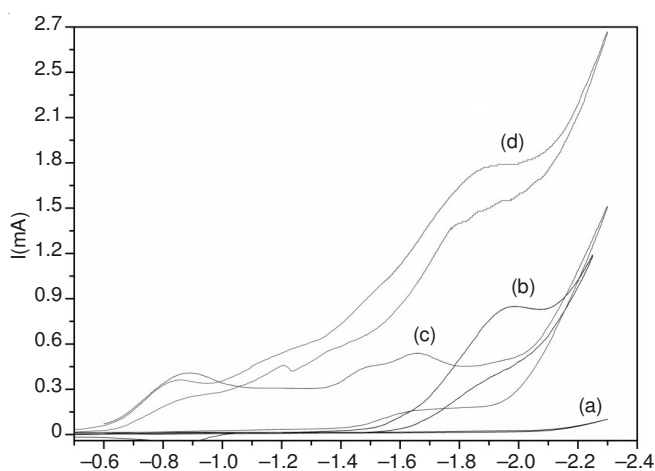


Fig. 1. Cyclic voltammograms recorded with Ag electrode: (a) neat BMIMBF<sub>4</sub>; (b) BMIMBF<sub>4</sub> saturated with CO<sub>2</sub>; (c) BMIMBF<sub>4</sub> containing 20 mmol L<sup>-1</sup> benzoyl bromide; (d) as (c) saturated with CO<sub>2</sub>

Bubbling of CO<sub>2</sub> to the solution of BMIMBF<sub>4</sub> containing benzoyl bromide, strongly modifies the voltammetric behavior. As shown in Fig. 1(d), after saturating with CO<sub>2</sub>, the second and third reduction peaks disappeared. This change indicates that the reduction of benzoyl and the further reaction products was suppressed with a new route emerging for consumption the active intermediates by a rapid carboxylation reaction with CO<sub>2</sub><sup>15,16</sup>. Another irreversible reduction peak appears at -1.9 V, which is attributed to the reduction of CO<sub>2</sub>. It is noteworthy that E<sub>p</sub> of benzoyl bromide is more positive than that of CO<sub>2</sub>, which provides a possible potential window to perform the electrocarboxylation of benzoyl bromide without any interference from reduction of CO<sub>2</sub>.

**Typical electrolyze procedure:** The potentiostatic electrolyses were performed in a standard three electrode undivided cylindrical glass cell equipped with a gas inlet and outlet. The

sacrificial magnesium rod (Mg, d = 0.5 cm) anode was placed down the middle of a ringed Ag (area = 3 cm<sup>2</sup>) cathode.

The reference electrode was Ag wire. Prior to experiment, BMIMBF<sub>4</sub> (5 mL) with definite concentration of benzoyl bromide was bubbled with CO<sub>2</sub> for 0.5 h after bubbling Ar gas for 0.5 h. After that the gas through the cell was closed and a constant potential applied. Until 2.0 F charge passed, the electrolyze was interrupted. Then CH<sub>3</sub>I (3-fold molar) were added, stirred at 55 °C for 12 h. Then, the reaction mixture was extracted with diethyl ether (3 × 5 mL) and the combined organic layers were dried over anhydrous MgSO<sub>4</sub> for 12 h. After filtration, the solvent was evaporated to yield melting point. The product was purified through silica gel column with petroleum ether/ethyl acetate (1:1 by volume) as eluents.

## Conclusion

The important pharmaceutical intermediate methyl phenyl glyoxylate was synthesized in BMIMBF<sub>4</sub> from inexpensive available benzoyl bromide and CO<sub>2</sub> by electrocarboxylation using the facile electrode materials. The experiments were carried out in three electrodes undivided cell under mild conditions, without resorting to the use of volatile and toxic solvents and catalysts. Cyclic voltammetry shows that BMIMBF<sub>4</sub> can act as a medium for benzoyl bromide reduction. Typical electrolyze procedure was investigated to prepare melting point. Efforts are underway to explore more optimized condition for electrochemical carboxylation benzoyl bromide to prepare melting point. This research may contribute to start a new research field in the application of ionic liquids to organic synthesis aimed at "green chemistry".

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## REFERENCES

1. M. Aresta and A. Dibenedetto, *Catal. Today*, **98**, 455 (2004).
2. D.H. Gibson, *Chem. Rev.*, **96**, 2063 (1996).
3. A. Jutand, *Chem. Rev.*, **108**, 2300 (2008).
4. H. Kamekawa, H. Senboku and M. Tokuda, *Electrochim. Acta*, **42**, 2117 (1997).
5. O. Scialdone, A. Galia, G. Errante, A.A. Isse, A. Gennaro and G. Filardo, *Electrochim. Acta*, **53**, 2514 (2008).
6. A.A. Isse and A. Gennaro, *Chem. Commun.*, **4**, 2798 (2002).
7. S. Rondinini, P.R. Mussini, P. Muttini and G. Sello, *Electrochim. Acta*, **46**, 3245 (2001).
8. O. Scialdone, A. Galia, A.A. Isse, A. Gennaro, M.A. Sabatino, R. Leone and G. Filardo, *J. Electroanal. Chem.*, **609**, 8 (2007).
9. O. Scialdone, M.A. Sabatino, C. Belfiore, A. Galia, M.P. Paternostro and G. Filardo, *Electrochim. Acta*, **51**, 3500 (2006).
10. M. Feroci, M. Orsini, L. Rossi, G. Sotgiu and A. Inesi, *J. Org. Chem.*, **72**, 200 (2007).
11. Z. Baan, Z. Finta, G. Keglevich and I. Hermecz, *Green Chem.*, **11**, 1937 (2009).
12. L. Zhang, D.F. Niu, K. Zhang, G.R. Zhang, Y.W. Luo and J.X. Lu, *Green Chem.*, **10**, 202 (2008).
13. R. Hagiwara and Y. Ito, *J. Fluor. Chem.*, **105**, 221 (2000).
14. L.E. Barrosse-Antle and R.G. Compton, *Chem. Commun. (Camb.)*, **25**, 3744 (2009).
15. V.G. Koshechko, V.E. Titov and V.A. Lopushanskaya, *Electrochem. Commun.*, **4**, 655 (2002).
16. G.T. Cheek and P.A. Horine, *J. Electrochem. Soc.*, **131**, 1796 (1984).