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# Electrochemical reduction of benzoyl chloride to benzil in ionic liquid BMIMBF<sub>4</sub>

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A new electrochemical procedure for the electrocatalytic dimerisation of benzoyl chloride in ionic liquid, 1-butyl-3methylimidazoliumtetrafluoborate, to benzil was investigated for the first time. The electrochemical behavior of benzoyl chlorides in BMIMBF<sub>4</sub> was studied by cyclic voltammetry with a reduction peak at -1.2 V (vs Ag). The electrolysis experiments were carried out in an undivided cell under mild conditions without any toxic solvents, catalysts and supporting electrolytes, creating benzil at a moderate yield (51%). The results showed that the yields were strongly affected by various factors: temperature, working potential, electrode material. Moreover, the ionic liquid was successfully recycled for this reaction. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: benzil; benzoyl chloride; electrocatalytic dimerisation; ionic liquid

# INTRODUCTION

The synthesis of benzil arouses a strong interest in many researchers because of its biochemical properties as insecticide agents to kill insects or its use as intermediates for the synthesis of various medicines, photosensitizers, odorants and other valuable chemical products.<sup>[1-3]</sup> Conventional synthesis has certain drawbacks, such as the use of hazardous chemicals including Cr(VI) reagents, high reaction temperatures, and poor yields.<sup>[4,5]</sup>

The direct electrochemical dimerisation of benzoyl chloride (BC) has attracted considerable interest as a method to obtain benzil.<sup>[6–8]</sup> Nevertheless, the use of toxic organic solvents, such as CH<sub>3</sub>CN and DMF, and large amounts of supporting electrolytes makes it more complex to recover the solvents. With the growing demand of environmentally friendly technologies, efforts should be devoted to avoid the use of volatile and damaging solvents and supporting electrolytes.

lonic liquids, molten salts with melting points close to room temperature, are obtained by the combination of large organic cations (*N*,*N*-dialkylimidazolium, phosphonium, pyridinium, quaternaryammonium, etc.) with a variety of anions, such as  $BF_{4'}$ ,  $PF_6^-$  and  $AlCl_4^{-.[9,10]}$  Recently, ionic liquids have been used as green reaction media in organic synthesis because of their wide electrochemical potential window, high ionic conductivity, good solvating ability and low vapour pressure. Up to now, several research groups have reported electrochemical reduction of various organic compounds in ionic liquid to obtain valuable products.<sup>[11-13]</sup>

Conversely, to our best knowledge, no investigation concerning the electrochemical dimerisation of BC in ionic liquids has been reported. Herein, we began studying the electrochemical dimerisation of BC in ionic liquid BMIMBF<sub>4</sub> (Scheme 1). The aim of this investigation was to set up an efficient and more environmentally friendly route for the synthesis of benzil under mild conditions without supporting electrolytes and catalysts.

# **EXPERIMENTAL**

#### Chemicals and apparatus

The ionic liquid BMIMBF<sub>4</sub> (with a purity of more than 99%) was dried under vacuum at 120 °C, until the cyclic voltammogram result indicated that there was no detectable water (the presence of water would narrow the potential window of the ionic liquid BMIMBF<sub>4</sub>).<sup>[14,15]</sup> Unless otherwise noted, other reagents and solvents were used as received from commercial suppliers.

## Typical electroanalytical and electrolysis procedure

The electroanalytical experiments were carried out using a CHI660B electrochemical station (Shanghai Chenhua Instrument Company, Shanghai, China) in an undivided cell, with a metallic cathode (area =  $0.2 \text{ cm}^2$ ) as the working electrode, a platinum (Pt, area =  $1 \text{ cm}^2$ ) as the counter-electrode and an Ag wire as the pseudoreference electrode. Prior to the experiments, all the electrode surfaces were polished mechanically with sandpaper and then sonicated (KQ-50DE, Kunshan Libo Ultrasonic equipment company, Kunshan, China) with ethanol for 5 min to remove any microparticulates. Finally, all the electrodes were cleaned with diluted hydrochloric acid and doubly distilled water and then dried with Ar gas.

The potentiostatic electrolysis experiments were performed by using the CHI660B electrochemical station with a metallic cathode (area =  $2 \text{ cm}^2$ ) and a magnesium rod (Mg, d = 0.5 cm) sacrificial anode, with Ag wire as the pseudoreference electrode. The sacrificial magnesium rod anode was placed down the middle of a ringed cathode. Prior to each test, BMIMBF<sub>4</sub> (2 cm<sup>3</sup>) with 0.1 mol dm<sup>-3</sup> of BC was bubbled with Ar for 20 min. After that, a suitable potential was applied. When a 1.0 F charge had been supplied to the electrode, the electrolysis was interrupted.

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Scheme 1.

Then the reaction mixture was extracted with diethyl ether (Et<sub>2</sub>O,  $3 \times 5$  cm<sup>3</sup>), and the combined organic layers were dried over anhydrous MgSO<sub>4</sub>. After evaporation of the Et<sub>2</sub>O under reduced pressure, the crude product was obtained. The product was purified through a silica gel column with petroleum ether/ethyl acetate as eluents.

Gas chromatography–mass spectrometry (GC-MS) was conducted with an HP 6890/5973 GC-MS Agilent 1100 series (Agilent Technologies Company, California, American). H-NMR spectra were obtained with a Varian INOVA-300 spectrometer (Varian Medical systems company, California, American) using tetramethylsilane as the internal standard and deuterated chloroform (CDCl<sub>3</sub>) as the solvent.

GC-MS: (*m/z*, %) 210(M<sup>+</sup>, 5), 105(100), 77(48), 51(18). H-NMR (CDCl<sub>3</sub>): 7.20–7.86(m, Ar-H)

## **RESULTS AND DISCUSSION**

#### Cyclic voltammogram of BC and benzil in BMIMBF<sub>4</sub>

Cyclic voltammograms (CV) of BC and benzil in BMIMBF<sub>4</sub> on the Ag electrode were recorded at the scan rate of 0.01 Vs<sup>-1</sup> in an undivided cell with platinum (Pt, area = 1 cm<sup>2</sup>) as counter electrode and an Ag wire as the pseudo-reference electrode. Fig. 1 and 2 show the typical curves.

As can be seen from Fig. 1(a), there is no reduction peak in the sweeping region -0.3 to -2.3 V in neat BMIMBF<sub>4</sub>. It should be noted that the current began to increase at around -2.2 V because of the reduction of BMIMBF<sub>4</sub>.<sup>[16]</sup>



Figure 1. Cyclic voltammograms recorded with Ag electrode: (a) neat  $BMIMBF_4$  and (b)  $BMIMBF_4$  containing 20 mmol·dm<sup>-3</sup> BC

After addition of BC (20 mmol dm<sup>-3</sup>) to neat BMIMBF<sub>4</sub>, the current starts to increase at around -0.9 V (Fig. 1(b)), and a distinct reduction peak appears at -1.2 V; this peak is attributed to the one-electron reduction of BC to acyl radicals, two of which quickly couple to produce benzil.<sup>[7,17]</sup> In the course of a potential scan to the more negative potential, the CV displays two weak waves in the region from -1.5 V to -1.8 V, which corresponds to the reduction of benzil and to the product of its further reactions. Moreover, another irreversible reduction peak appears at -2.0 V, which is ascribed to the decay of the BC anion radical. These CV characteristics of BC reduction in BMIMBF<sub>4</sub> appeared qualitatively similar to those in the organic solvent.<sup>[7,8]</sup>

To further demonstrate that the two weak waves were reduction peaks of the products, the CV of benzil was also investigated. Fig. 2(a) shows that a reduction peak appears at -1.6 V, which is attributed to the one-electron reduction of benzil to its anion radical.<sup>[17–19]</sup> Furthermore, the effect of the temperature on the CV behavior of benzil in BMIMBF<sub>4</sub> was examined. Fig. 2 shows that the reduction peak shifted towards the negative values, and the peak current was enhanced with the increase in temperature.

To examine the electrocatalytic properties of the Ag electrode towards the reduction of BC in BMIMBF<sub>4</sub>, the CVs of BC were also investigated at the most commonly used cathodes, for example, copper (Cu), nickel (Ni) and stainless steel (SS). This cathode had the same geometric surface and shape. The results are presented in Fig. 3. As shown in this figure, a peak corresponding to the one-electron reduction of BC was observed at  $-1.1\,V$  and -1.3 V at the Cu and SS electrodes, respectively. With the SS electrode, however, a single irreversible reduction peak of BC was obtained at -1.5 V. Fig. 3 also demonstrates that the current of the BC reduction on the Ag electrode is much higher than that on the Cu electrode, while the benzil reduction current on the Cu electrode is much higher than on the Ag electrode. The difference in currents of the first reduction peak of BC at the four electrodes could be ascribed to the fact that the Ag electrode's catalytic surface is more reproducibly activated.

The CVs of BC on the Ag electrode were also recorded during and at the end of the electrolysis. As can be seen from Fig. 4(a), during the electrolysis, the CV characteristics were similar to those in Fig. 1(b), recorded before electrolysis, confirming that the solution contained the unconverted BC. At the end of the



**Figure 2.** Cyclic voltammograms recorded of benzil with Ag electrode in BMIMBF<sub>4</sub>: (a) 25 °C; (b) 50 °C; and (c) 75 °C



**Figure 3.** Cyclic voltammograms recorded at Cu (a), Ag (b), SS (c) and Ni (d) electrode in BMIMBF<sub>4</sub> containing 20 mmol·dm<sup>-3</sup> BC,  $v = 0.01 \text{ V s}^{-1}$ ,  $T = 25 \degree \text{C}$ 



**Figure 4.** Cyclic voltammograms recorded with Ag electrode during (a) and at the end (b) of the electrolyses in BMIMBF<sub>4</sub>,  $v = 0.01 \text{ V s}^{-1}$ , T = 25 °C

electrolysis, the reduction peak at -1.2 V disappeared, indicating that at this time the BC was converted completely and this reduction does, indeed, involve  $1e^{-/BC}$  molecule.

#### Influence of reaction conditions

To optimize the experimental conditions, the influence of temperature, working potential and electrode material on the yield was investigated. The results are summarized in Table 1. The yields are based on the starting material BC.

## Influence of temperature

The viscosity of ionic liquids is very high, which has an effect on the rate of mass transport within a solution, so the temperature effect on the reaction yield was investigated first.<sup>[11,12]</sup> Electrolysis were carried out under constant potential at 25 °C, 50 °C and 75 °C. The results in Table 1 (entries 1–3) show that an increase in the temperature from 25 °C to 50 °C brings about a remarkable increase in the yields of benzil from 14% to 51%. However, the yield is hardly changed from 50 °C to 75 °C.

Table	1.	Electrochemical	dimerisation	of	BC	to	benzil	in
$BMIMBF_4$								

Entry	Electrode	T /°C	E/V	l/mA Time/h		Yield (%)		Conv.
						1	2	
1	Ag/Mg	25	-1.2	1.0–1.5	4.1	14	9	29
2	Ag/Mg	50	-1.2	2.5-3.0	2.0	51	21	80
3	Ag/Mg	75	-1.2	2.8-3.5	1.8	9	36	51
4	Ag/Mg	50	-0.9	1.0-1.3	4.6	38	12	56
5	Ag/Mg	50	-1.0	1.5–2.1	3.2	45	18	67
6	Ag/Mg	50	-1.4	3.2-3.5	1.6	24	20	48
7	Ag/Mg	50	-1.50	3.7-4.0	1.4	23	32	61
8	SS/Mg	50	-1.2	2.0-2.5	2.5	11	13	33
9	Cu/Mg	50	-1.2	2.4–2.8	2.1	29	41	72
10	Ni/Mg	50	-1.2	2.0-2.7	2.3	13	25	45
11	Ag/Al	50	-1.2	2.4–2.9	2.1	49	22	78
12	Ag/Zn	50	-1.2	2.6-3.2	1.9	48	20	75

It is well known that the viscosity of BMIMBF<sub>4</sub> displays an essential Arrhenius behavior.<sup>[11]</sup> Increasing the temperature leads to a decrease in viscosity and an increase in conductivity, which is helpful to this reaction. However, increasing the temperature is unfavourable to the electrocatalytic dimerisation because it also readily leads to a side reduction reaction of the benzil. Therefore, the optimal temperature is 50 °C based on the above two factors.

## Influence of working potential

The influence of working potential on the yields of benzil was also studied. As shown in Fig. 1, the potential of the BC reduction peak was at -1.2 V. Around -0.9 V, the values of -1.0, -1.2, -1.4 and -1.5 V were chosen as working potentials for this reaction. Table 1 (entry 2, 4–7) shows that the yields of the product increased from 38% to 51% with the potential becoming negative from -0.9 to -1.2 V. However, the yield of the target product declined when the potential was more negative than -1.2 V.

The more negative the potential is, the larger the current will be. When the potential was raised from -0.9 to -1.2 V, the current between the anode and the cathode arose, and more electrogenerated intermediates were produced, which led to an increase in the yield.<sup>[20]</sup> However, benzil reduction competed with the BC reduction when the potential was more negative than -1.2 V. Under this condition, some of the supplied energy was consumed by benzil reduction instead of being used for the reduction of BC, resulting in a lower yield.<sup>[10,11]</sup> An optimized potential of -1.2 V was finally chosen.

## Influence of electrode material

During electrolysis, the reduction of BC takes place on the surface of the electrode. Thus, the choice of electrode material is quite of importance. Contrast tests were performed by using Ag, Cu, Ni and SS as cathodes under otherwise identical experimental conditions. Table 1 (entries 2, 8–10) shows that the Ag cathode gives a good yield of benzil (51%, entries 2), whereas the Cu cathode created the product at a low yield (29%, entry 9). The result for the Ni cathode is almost the same as that of SS cathode (entry 8, 10). The excellent result of the Ag cathode may be associated with its electrocatalytic activation towards organic halides. Organic halides (RX) tend to specifically adsorb on Ag electrodes. Then the RX is activated and the reaction reaches the transition state where an activated complex interacting with the Ag electrode surface is formed. In the activated complex, the C–X bond has been considerably weakened because of the X...Ag and R...Ag interactions.<sup>[21,22]</sup>

Also, the effect of the sacrificed anode was studied, and the results suggested that no obvious difference was observed between Mg, Al and Zn (entries 2, 11,12). It indicates that the property of the sacrificed anode has less impact on this reaction.

In conclusion, based on the experimental results, the optimized condition for the electrosynthesis in BMIMBF<sub>4</sub> are 0.1 mol dm<sup>-3</sup> BC, with Ag as the cathode with a -1.2 V potential and Mg as the anode at a temperature of 50 °C.

#### Recycling of ionic liquid

Following extraction by ether, dichloromethane  $(CH_2Cl_2, 20 \text{ cm}^3)$  was added to BMIMBF<sub>4</sub>. Then the solvent was washed with 0.5 cm<sup>3</sup> deionized water six times. The obtained aqueous solution was tested with silver nitrate until no precipitate formed, indicating that no chloride was present. Then the organic layer containing BMIMBF<sub>4</sub> was evaporated to remove the CH<sub>2</sub>Cl<sub>2</sub>. The obtained BMIMBF<sub>4</sub> was dried under vacuum. This recycled BMIMBF<sub>4</sub> can be used for at least three cycles.

#### **Reaction mechanism**

Mass spectrometric analysis of the electrolysis products showed that only two major products were formed in the electrolysis. By comparison with the chromatographic (GC-MS) and voltammetric characteristics, the major products were identified as 210 m/e benzil and 316 m/e stylbenolbenzoate, which is consistent with the results of the electrochemical reduction of BC in acetonitrile and acetone.<sup>[18]</sup>

As previously reported, silver not only catalytically activates the RX bond, but also favours radical coupling as a consequence of the high local concentration of incipient radicals.<sup>[7,8,17,23]</sup> On the basis of literatures and experimental results, a proposed pathway is outlined in Fig. 5. Initially, the BC molecule approaches and makes contact with the Ag electrode surface through weak adsorption. Then the BC molecule is activated and the reaction reaches the transition state **A** where an activated complex interaction is formed. In this transition state, the C-Cl bond has been considerably weakened because of the Cl...Ag and C...Ag interactions. Then electron transfer from the Ag electrode to BC leads to acyl radicals, two of which quickly couple to produce benzil.<sup>[7]</sup>

Cyclic voltammetry (Fig. 2) indicates that the reduction of benzil to its anion radical can occur at the potential employed in the BC electrolysis. The reduction of benzil (the second wave, Fig. 1(a)) leads to the formation of an anion radical, and coupling of the intermediate anions with benzil chloride produces the observed product mixture. Further study on this is needed in the future.



Figure 5. The possible reaction mechanism

# CONCLUSIONS

The important organic chemical industry intermediate benzil was synthesized in  $BMIMBF_4$  from available BC by electrocatalytic dimerisation using some common electrode materials. Cyclic voltammetry showed that  $BMIMBF_4$  could act as a medium for the electrochemical dimerisation of benzoyl chloride. The electrolysis was carried out in an undivided cell under mild conditions, without resorting to the use of toxic solvents and catalysts. The influence of temperature, working potential and electrode material on the yield was investigated, and the target benzil could be prepared at a moderate yield (51%) under an optimized condition. Efforts are underway to explore more electrochemical dimerisation systems. This research may contribute to the start of a new research field in the application of ionic liquids to organic synthesis aimed at 'green chemistry'.

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