Note

Electrochemical Reduction of Benzoylformic Acid in Ionic Liquid

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Ionic liquids possess a number of unique properties that make them ideal electrolytes. Electrochemical reduction of benzoylformic acid in room temperature ionic liquids as reaction media could be conducted with excellent performances without any additional supporting electrolyte. Electrolysis at glassy carbon electrode results in the formation of mandelic acid in 91% yield. And the electrochemical behavior of benzoylformic acid was investigated with the technique of cyclic voltammetry.

Keywords ionic liquid, electrochemical reduction, benzoylformic acid

Introduction

The chemical industry is under considerable pressure to replace many volatile organic compounds that are widely used as solvents in organic synthesis. The toxic and hazardous solvents combined with serious environmental issues, such as atmospheric emissions and contamination of aqueous effluents that making their use prohibitive. This is an important driving force in the quest for novel reaction media. Ionic liquids are gaining wide recognition as potential environmentally benign solvents, and they have been demonstrated as successful solvents for chemical reactions and seperation processes.[1-6] The use of ionic liquids as novel reaction media may offer a convenient solution to solvent emission and catalyst recycling in many organic reactions.[7] Organic electrosynthesis has been an important part of green chemistry. An attractive feature of the electrolytic method is that it has the possibility of controlling the activity of the reagent, the electron over a wide range. And electron undoubtedly is the cleanest reagent in the world. Electrosynthesis also have advantages such as mild condition, little side reactions and high rate of production. Ionic liquids are emerging as novel replacement for volatile organic compounds (VOC) traditionally used as industrial solvents. They also could be used as electrolytes in the process of electrochemistry.[8,9]

Although a lot of electrochemical processes have been studied in the ionic liquids, there have few precedent to go by electrosynthesis in ionic liquids. Deng *et al*.[10] have reported the first use of pure room temperature ionic liquids as reaction media in the electrochemical activation for the synthesis of cyclic carbonates through cycloaddition of CO_2 to epoxides without additional supporting electrolyte and catalyst. It illustrates that ionic liquids are effective reaction media in electrochemical synthesis. Here we investigated the electrochemical behavior of benzoylformic acid in ionic liquid of 1-ethyl-3-methylimidazolium bromine and got mandelic acid in 91% yield by electrolytic reduction of benzoylformic acid on glassy carbon electrode.

The 1,3-dialkylimidazolium salts revealed as attractive candidates since their reduction potentials were predicted to be about 0.8 V lower than those of 1-alkylpyridinium salts, and they could be prepared readily from commercially available starting materials.[9] 1-Ethyl-3-methylimidazolium bromine salts ([emim]Br), as a homologous series of 1,3-dialkylimidazolium salts, had more favorable physical and electrochemical properties and it was one of the easiest preparation.

The ionic liquid of [emim]Br was prepared by reacting of *N*-methylimidazole with ethyl bromine as decribed before.[11] The electrochemical experiments were performed using an EG&G PARC model 273 Potentiostat/Galvanostat and a CHI600 elecchochemical work station (CH instruments, USA). The undivided cell was fitted with a glassy carbon electrode. All electrochemical experiments were carried out under the protection of nitrogen gases. The electroreduction synthesis was carried at 80 ℃, 50 mL ionic liquid containing 28 mmol/L substrate with N_2 bubbling into the cell.

The working electrode was a rod of glassy carbon (area 0.67 cm^2) polished with 1.0, 0.3 and finally 0.05 μm alumina powders and cleaned by ultrasonic then dried in warm air. The reference electrode was SCE. The counter electrode was a Pt wire dipped directly into the ionic liquid.

Conductivity data were collected from 80 to 120 ℃ (Table 1), using an oil bath to control the temperature. Special conductivity of ionic liquid of [emim]Br was measured with a DDS-11A model conductivity apparatus, cell constant is 9.6 cm^{-1}.

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Table 1 Conductivities of 1-ethyl-3-methylimidazolium bromine salt

Temp. (℃)	80	90	100	110	120
κ^a ($s \cdot m^{-1}$)	1.41	1.70	1.92	2.17	2.45

[a] Specific conductivity.

As mentioned in the introduction, ionic liquids have excellent properties such as high conductivity, wide electrochemical window, which made them good electrolytes in electrochemical process. We investigated electrochemical behavior of the ionic liquid of [emim]Br at glassy carbon electrode. The electrochemical window of ionic liquid is usually much greater than that for aqueous electrolytes. Fig. 1 illustrates the electrochemical window of [emim]Br at glassy carbon electrode, which is about 2.2 V.

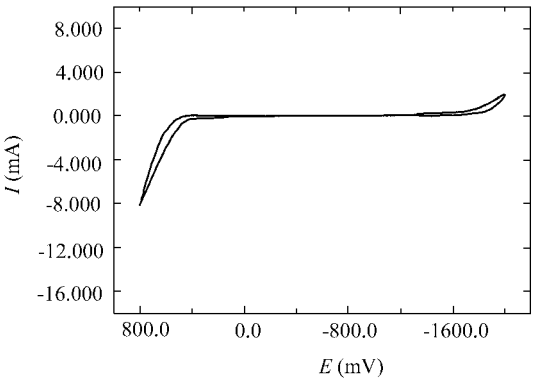

Fig. 1 Cyclic voltammetry of 1-ethyl-3-methylimidazolium bromine salt. Scan rate: 100 mV/s, temp.: 80 ℃.

Fig. 2 illustrates cyclic voltammograms obtained by scanning the solvent background to −2.0 V vs. SCE reference. On set of carbonyl of benzoylformic acid with glassy carbon electrode occurs at about −1.3—−1.6 V vs. SCE reference. No reverse oxidation currents could be detected on the return sweep, which would be the case that the electrode reaction is an inreversible process.

Preparation of benzoylformic acid by electrolysis at glassy carbon electrode was carried in the ionic liquid of [emim]Br, and the controlled potential was at −1.3 V vs. SCE reference. Products formed in electrolysis experiments in [emim]Br were detected with UV-vis spectrophotometer, and concentration analyses of electrolysis product were determined by HPLC.

During the electrochemical process, 91% chemical yield of mandelic acid was obtained, and the current efficiency was about 53.3%. The ionic liquid and electrochemistry reaction conditions could be further optimized.

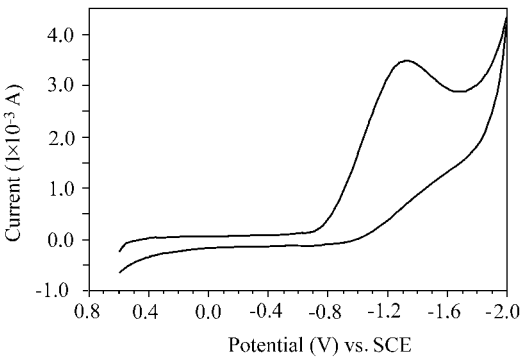

Fig. 2 Cyclic voltammogram of 48 mmol·L^{-1} benzoylformic acid in ionic liquid of [emim]Br at glassy carbon. Scan rate: 100 mV/s, Temp.: 80 ℃.

The higher conversion, selectivity and current efficiency could be achieved in the further study. It may state a new field in the application of ionic liquids to electrochemical reduction of carbonyl compounds.

As mentioned in the introduction, the electrochemical reduction of benzoylformic acid in ionic liquid of [emim]-Br accounts on the excellent properties of ionic liquids, which provides feasible electrochemical character, and could be used as an universal solvent in the field of electrolysis.

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