

Short Communication

New Method for Electrochemical Activation of *N*-benzyl Ideneaniline to Dibutyl Phthalate in the Present of Carbon dioxide

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A new method for electrochemical activation of *N*-benzyl ideneaniline to dibutyl phthalate in the present of carbon dioxide was investigated. The electrochemical reduction behavior of *N*-benzyl ideneaniline was characterized by cyclic voltammetry used three electrode system with a reduction peak at -1.5 V (vs. Ag) on Pt electrode. The electrolysis experiments were carried out in an undivided cell containing *n*-Bu₄NBr-MeCN electrolyte with a constant current under mild conditions. The electrolytic study was conducted with an material cathode and magnesium anode, affording the dibutyl phthalate in a moderate yield (7.6%). The effect of operative parameters, such as temperature, charge passed, current density, substrate concentration, electrode material and supporting electrolyte, on the yield was also investigated.

Keywords: *N*-benzylideneaniline; CO₂; Dibutylphthalate; Electrochemical activation

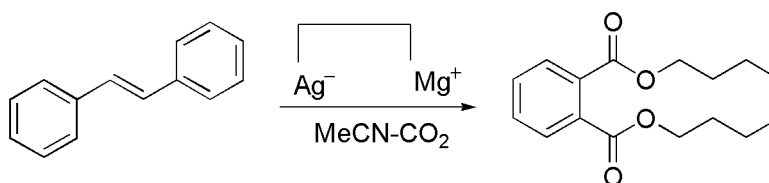
1. INTRODUCTION

Dibutyl phthalate (DBP) is a high production volume chemical that is used mainly as a plasticizer for nitrocellulose, polyvinyl acetate, and polyvinyl chloride, a lubricant, an antifoaming agent, and a skin emollient.[1-3] A variety of methods have been exploited to prepare DBP, the most important synthesis route is catalytic synthesis of phthalic anhydride (PA) with *n*-butanol using the batch stirred tank in the presence of sulphuric acid, but the yield and efficiency are not satisfactory. Moreover, the use of sulphuric acid in the reaction brings serious environmental pollution. It is very urgent to upgrade the synthesis process. [4]

Carbon dioxide (CO₂) is the green house gas, which is causing serious environmental problems. On the other hand, CO₂ is a source of recyclable carbon source that has attracted extensively attention in recent years. The direct reduction of CO₂ is far from satisfactory due to its low reaction activity.

Thus, new methods are constantly emerging. According to the literature, electrochemical method could provides efficient solutions to the activation and conversion of CO₂. [5] Electrochemistry technique use electron as reagent, which provides the possibility that CO₂ can either perform an electrophilic attack in the reaction of anionic species or a nucleophilic one via cathodic activation to the radical anion.[6-8] As reported in the literature, the direct electrochemical reduction of carbon dioxide could give some useful small molecules, such as CH₄, CH₃OH, HCOOH. In addition, the electrochemical reaction of CO₂ with various organic substances, could afford useful organic chemicals. For instance, many research groups have intensively studied the electrochemical reduction of CO₂ with alkenes, alkynes, benzylchlorides, carbonyl compounds, 2-amino-5-chloropyridine, vinyl triflates and epoxides, to prepare carboxylic acids or cyclic carbonates.[9-11] In contrast, this study uses electrochemical method for activation of *N*-benzyl ideneaniline to DBP in the present of CO₂.

We have done some work in the electrochemical conversion of CO₂ with 2-amino -5-bromopyridine and aromatic ketones in ionic liquid,[12,13] herein we began studying a new and highly efficient electrochemical route to activate *N*-benzyl ideneaniline in CO₂-saturated MeCN solvent (Scheme 1). This communication was devote to set up a simple route for synthesis dibutyl phthalate, under mild conditions, giving a safer and more environmental friendly process for CO₂ fixation. This technique is clean, easy to control and safe, indicating its great potential in the fixation of CO₂.



Scheme 1

2. EXPERIMENTAL

2.1. Chemicals

The acetonitrile (MeCN) is analytical pure, which was dried over by 4 Å molecular sieves before use. The purity of CO₂ and N₂ was 99.9%. Unless otherwise noted, the reagents and solvents were used as received without further purification.

2.2. Typical electroanalytical and electrolysis procedure

The electroanalytical experiments were conducted by CHI660B electrochemical station in an undivided cell equipped with three electrode system, platinum electrode (Pt, d = 3 mm) as cathode, Pt foil (area= 4 cm²) as anode and Ag wire as reference electrode. The study was carried out in a dried MeCN solution containing 0.1 M Tetra- Butylammonium bromide.

Prior to the experiments, all electrodes were polished mechanically with sand paper and then were sonicated in ethanol for 5 min to remove any microparticulates. Finally, all the electrodes were cleaned with diluted hydrochloric acid and double distilled water and then were dried with N_2 .

The electrolysis was carried out in a standard undivided glass cell fitted with a metal cathode (15 cm^2) and a magnesium rod (Mg, $d=2\text{ cm}$) sacrificial anode. The electrolysis was performed by CT2001C battery test system equipped with two electrodes. The electrolysis was carried out in MeCN (50 mL) solution containing TBAB as supporting electrolyte, certain concentration of *N*-benzyl ideneaniline as the standard material. Prior to each test, CO_2 was bubbled for 30 min to ensure that the solution was saturated, followed by charging of current into desired value. To ensure this electrolysis was conducted under CO_2 atmosphere, CO_2 flow was continuously fed into the system. After that, a constant current was supplied to the electrode until a certain amount of charge (Q) had been consumed. Then the electrolyzed solution was evaporated at reduced pressure, and the residue was cleaned with distilled water, and extracted with diethyl ether (3x5 mL), the crude product was obtained.

Gas chromatography–mass spectra (GC–MS) were recorded with HP 6890/5973 GC–MS an Agilent 1100 series. HNMR spectra were obtained with a Varian INOVA-300 spectrometer using tetramethylsilane (TMS) as internal standard and deuterated chloroform (CDCl_3) as solvent.^[12]

3. RESULTS AND DISCUSSION

3.1. Electroanalytical procedure

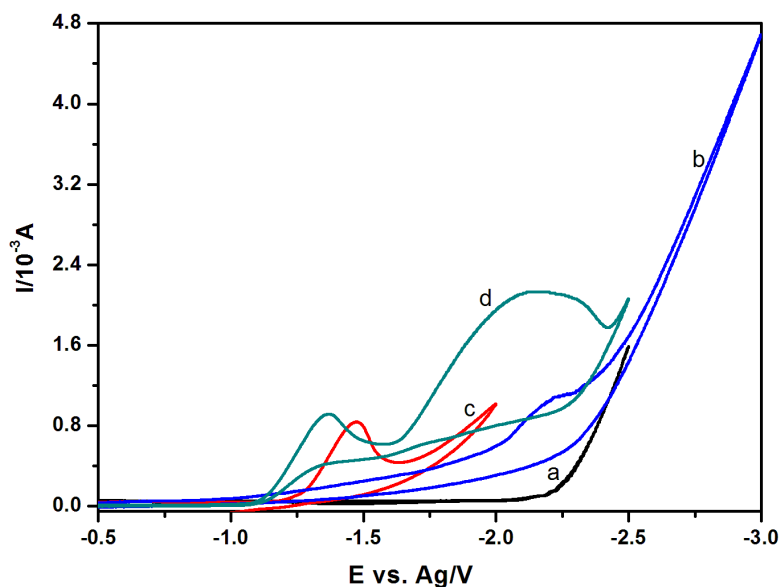


Figure 1. Cyclic voltammograms on Pt at a sweep rate of 0.2 Vs^{-1} : (a) MeCN with 0.1 M TBAB solvent; (b) MeCN with 0.1 M TBAB solvent saturated with CO_2 ; (c) MeCN with 0.1 M TBAB solvent containing 0.03 mol dm^{-3} *N*-benzyl ideneaniline; (d) as (c) saturated with CO_2 .

The electroanalytical experiments were carried out in MeCN solution containing 0.1 M Tetrabutylammonium bromide (TBAB) as the supporting electrolyte. As shown in Fig. 1a, under N_2

atmosphere, there was no any redox peak in the sweeping region from -0.5 V to -2.5 V without any substrate in electrolytic solution. It should be noted that the cathodic current began to increase at around -2.2 V, due to the polarization of the solvent.[12,13]

As shown in Fig. 1b, in CO₂-saturated MeCN with 0.1 M TBAB solvent, a single irreversible cathodic peak is observed at -2.2 V, which feature the reduction of CO₂ to its radical anion CO₂^{•-}. Fig. 1c illustrates that addition of *N*-benzylideneaniline (0.03 mol dm⁻³) to MeCN with 0.1 M TBAB solvent gave rise to a distinct reduction peak at about -1.5 V. This peak corresponded to the one electron reduction of *N*-benzyl ideneaniline to radical anion.[13]

When the voltammetric behavior was recorded after the solution of MeCN with 0.1 M TBAB containing *N*-benzyl ideneaniline was saturated with CO₂, two irreversible reduction peaks were observed at -1.3 V and -2.1 V. The peak potential was shift into positive region from -1.5 V to -1.3 V under CO₂, and the current of this peak increased (Fig. 1d). This observed changes indicated that a rapid chemical reaction between the electrogenerated *N*-benzyl ideneaniline anion radical and CO₂. Another irreversible reduction peak came up at -2.1 V ascribed to the reduction of CO₂. Fig. 1d presented that E_p of *N*-benzyl ideneaniline was about 0.7 V positively than CO₂ with E_p= -2.1 V, which provides a possible potential window to perform the electroreduction of *N*-benzyl ideneaniline without any interference from reduction of CO₂. [12,13]

The influence of scan rate on the cyclic voltammograms behavior of electrochemical reduction *N*-benzyl ideneaniline in MeCN with 0.1 M TBAB solvent was examined at room temperature. The results were summarized in Fig. 2. As shown, the reduction peak shifted into negatively potential region, the current of the cathodic peak enhanced with increasing the scan rate from 10 to 500 mVs⁻¹.

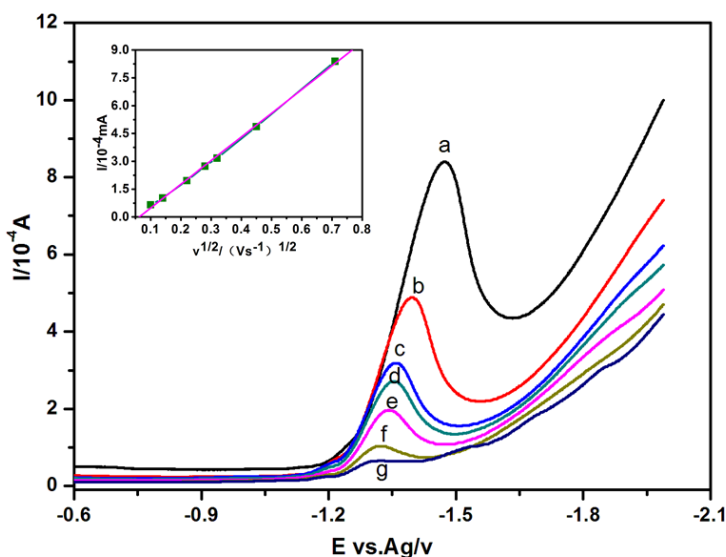


Figure 2. Cyclic voltammograms of *N*-benzyl ideneaniline (0.03 mol dm⁻³) in MeCN with 0.1 M TBAB solvent on Pt electrode: (a) $v=500 \text{ mVs}^{-1}$, (b) 200 mVs^{-1} , (c) 100 mVs^{-1} , (d) 80 mVs^{-1} , (e) 50 mVs^{-1} , (f) 20 mVs^{-1} and (f) 10 mVs^{-1} .

The peaks current varies linearly with $v^{1/2}$, showing that the electrochemical reduction process is controlled by diffusion rather than adsorption. [12,13]

3.2. Influence of reaction conditions

In order to optimize experimental conditions, the effect of numerous operative parameters, such as temperature, current density, charge passed, substrate concentration, supporting electrolyte and electrode material on the yield of main product dibutyl phthalate (DBP) was investigated under constant current condition. All experimental results are reported in Table 1. The yields were calculated on the basis of the *N*-benzyl ideneaniline. [12,13]

Dibutyl phthalate:

GC-MS (m/z, %): 223(M+, 5), 205(4), 150(9), 149(100), 57(6), 56(5), 41(8), 29(9).

¹HNMR δ : 7.6-7.7 (1H, -ArH), 7.4-7.5 (1H, -ArH), 4.2-4.3 (2H, -CH₂CH₂CH₂-), 1.6-1.8 (2H, -CH₂CH₂CH₂-), 1.3-1.5 (2H, -CH₂CH₂CH₂-), 0.8-1.0(3H, -CH₃).

Table 1. Electrochemical Reduction of *N*-benzyl ideneaniline to Dibutyl phthalate in the Present of Carbon dioxide under various conditios

Entry	T/°C	j/mA cm ⁻²	Q (Fmol ¹)	c/mol dm ⁻³	Electrode	supporting electrolyte	Yield (%)
1	20	4	2	0.03	Ag	TBAB	2.2%
2	30	4	2	0.03	Ag	TBAB	1.3%
3	40	4	2	0.03	Ag	TBAB	0.5%
4	30	3	2	0.03	Ag	TBAB	1.8%
5	30	1	2	0.03	Ag	TBAB	2.4%
6	30	4	3	0.03	Ag	TBAB	1.0%
7	30	4	4	0.03	Ag	TBAB	2.2%
8	30	4	2	0.02	Ag	TBAB	2.7%
9	30	4	2	0.04	Ag	TBAB	1.0%
10	30	4	2	0.03	Ag	TEAB	3.2%
11	30	4	2	0.03	Ag	TBAC	7.6%
12	30	4	2	0.03	Ni	TBAB	2.5%
13	30	4	2	0.03	Cu	TBAB	6.8%

3.2.1. Effect of temperature

To study the effect of temperature, a set of electrolyses were carried out under 20 °C, 30 °C and 40 °C, respectively. Electrolysis was conducted in a closed undivided cell with a magnetic stirrer under a constant current. An decrease in yield of DBP from 2.2% (entry 1) to 0.5% (entry 3) was obtained by increasing the electrolysis temperature from 20 °C to 40 °C. It indicated that lower temperature seemed to favors the reaction. [14,15]

3.2.2. Influence of current density, charge passed and substrate concentration

The effect of current density and charge passed on the electrolysis of DBP from *N*-benzylideneaniline was carried out under three different current density. As presented in Table 1 (entries 2, 4-5), changing the current density from 1 to 4 mAcm⁻² affected the yield of DBP from 2.4% to 1.3%. This is one possible reason for this, the large the current density is, the more negative the potential would be. Under this condition, many unexpected reduction reaction would be carried out on the electrode surface, such as the reduction of CO₂ and the dissolved of Mg²⁺, this reaction competed with the *N*-benzyl ideneaniline reduction, and some of the supplied energy was consumed by CO₂ reduction instead of being used for the reduction of *N*-benzyl ideneaniline, resulting in a lower yield. A similar current density effect has been reported. [12,13,16]

Also, the charge passed have impact on the yield of DBP. Table 1 (entries 2, 6-7) showed that a shift of the yield from 1.0% to 2.2% was achieved by increasing the charge passed. As can be seen from Table 1 (entries 2, 8,9), a drastic increase of the yield was obtained by decreasing the substrate concentration. [13]

3.2.3. Influence of the supporting electrolyte

To study the influence of supporting electrolyte on the reaction yields, a set of electrolysis process was performed under different supporting electrolyte. The results are reported in Table 1 (entries 2 and 10,11). The yield of DBP increased in the following order: TBAC (7.6%)>TEAB (3.2%)>TBAB (1.3%). The best yield was obtained with TBAC. This is one possible reason for this, that with the same anion of Br⁻, the electrolysis conducted with Et₄N⁺ cation gave target compound yield superior to n-Bu₄N⁺. Et₄N⁺ cation behave more easily to associate with the electrogenerated radical anion and consequently reduced the nucleophilicity towards CO₂. When the experiments are conducted with TBAC supporting electrolytes, it was found that anion of Cl⁻ gave more promising results. The phenomena were similar to some previously reported results [8,17,18]

3.2.4. Influence of cathode material

The nature of electrode materials have important effect on the yield of target product, since the electroreduction of *N*-benzyl ideneaniline takes place on the surface of the electrode. Electrolysis experiments were carried out by Cu, Ni and Ag electrode under other identical

conditions. Table 1 (entries 2, 12 and 13) show the results. A better DBP yield was obtained by Cu cathodes (entry 13), whereas the Ag and Ni cathode gave the desired product in even lower yield (entries 2, 12). Different cathodes led to different DBP yields, indicating that electrode materials had different adsorption and catalytic activities to the substrate. [12,13]

4. CONCLUSIONS

This paper describes a simple and efficient electrolysis route to prepare extensively used chemistry dibutyl phthalate from available *N*-benzyl ideneaniline and CO₂. This electrolysis were carried out in an undivided cell under mild conditions by common electrode materials in MeCN with 0.1 M TBAB solution. The electrochemical behavior was detected by cyclic voltammetry on Pt electrode, results showed that MeCN with 0.1 M TBAB solution could used as a electrolyte for electroreduction of *N*-benzyl ideneaniline. The electroreduction of *N*-benzyl ideneaniline gives rise to different yields of DBP under CO₂. The electrolysis process depend on temperature, current density, supporting electrolyte and electrode material. Efforts are underway to investigate the reduction mechanism. This work is helpful to extend more electrochemical systems to covert CO₂ into useful chemicals.

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