



Full Length Article

Electrochemical synthesis of anisole on platinum anode surface: Experiment and first-principle study

Zhengwei Zhang^{a,*}, Qiang Wang^{a,b}^a The Key Laboratory of Plant Resources and Chemistry of Arid Zones, The Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, 830011 Urumchi, China^b University of Chinese Academy of Sciences, 100049 Beijing, China

ARTICLE INFO

Keywords:

Phenol
Sodium phenate
Methylation
Tetramethyl ammonium chloride
Anisole

ABSTRACT

The anisole is synthesized by electrolyzing of phenol (or sodium phenate) and tetramethylammonium chloride (TMAC). The production forms on the Pt anode surface and not in the solution. There are adequate supplies of methyl radicals in all solutions. The phenoxy radical is difficult to form in phenol-TMAC solution, and thus the yield is low. The sodium phenate is easily oxidized into phenoxy radical, and hence there is high yield.

1. Introduction

The methylation process of phenol hydroxyl is widely investigated, such as synthesis of fine chemicals, modification of drug molecules and transformation of natural products. According to the reported methylation methods, there are five methyl sources: iodomethane, dimethyl sulfate, dimethyl carbonate, methanol and other rarely used reagents.

The iodomethane is a classical methylation reagent. For its exorbitant price and high toxicity, it is usually used to synthesize or modify drug. Fiamegos and co-workers [1] methylated a series of phenol derivatives with the assistance of microwave irradiation by employing the iodomethane as methyl source. Mohamed et al. [2] used iodomethane as methyl source to methylate phenol hydroxyl of quercetin, and acquired 3'-O-methyl quercetin with high yield. Li et al. [3] used iodomethane and synthesized 4'-O-methyl quercetin. Jurd [4] firstly successfully prepared 5-O-methyl quercetin through a complex method by using of iodomethane.

The dimethyl sulfate is another classical methyl source for the methylation of phenolic hydroxyl. Mouselmani and co-workers [5] used dimethyl sulfate to methylate the hydroxyls of phenol and beta-naphthol. When the reaction was catalyzed by Al₂O₃, its temperature was 130 °C; when there was no catalyst, the temperature was 200 °C, in gase phase. The authors found out that the process of dimethyl sulfate reacting with phenol derivatives have to be done at high temperature. Moreover, the dimethyl sulfate is classified as highly toxic compound. Other reagents should be considered for the methylation of phenol derivatives.

The dimethyl carbonate with low toxicity as methyl source is used in the methylation process of phenol derivatives. Because its low-activity, the methylation reaction has to be catalyzed at high temperature and high pressure. To find an effective catalyst is a key point for the reaction. Lee and co-workers [6] provided high temperature and high pressure by using of autoclave, and researched alkali carbonates as catalyst for the reaction. They believed that the best catalyst was Cs₂CO₃. The alkyl guanidine [7] was used as catalyst for the reaction, too. For the phenol derivative with highly steric hindrance, some tertiary amines and nitrogen-bearing heterocyclic compounds, such as 4-dimethylaminopyridine [8], are high efficiency catalyst. The yield of dimethyl carbonate reacting with 2,6-di-*tert*-butyl-4-methylphenol is higher than 95% by using of those catalysts. Ouk and co-workers [9] accomplished the reaction by employing of solid-liquid phase transfer catalyst in order to avoid using of high-pressure equipment. The methylation yield of phenol and p-cresol achieved 99%, when the catalyst of the reaction was tetrabutyl ammonium bromide combining with potassium carbonate [10]. If the tetrabutyl ammonium bromide was replaced by crown ether, the effect of catalyst would decline for the same reactants [11]. The methylation of catechol, dimethyl carbonate as methyl source, could be done in high-temperature gas phase, but the reaction need catalyst. The activated alumina as catalyst made the product of 1-hydroxy-2-methoxybenzene achieve a selectivity of 71% [11]. When the catalyst was LiOH supported with activated alumina, the selectivity of 1-hydroxy-2-methoxybenzene was 84% [12]. If KNO₃ was loaded on activated alumina as catalyst, the main product would be 1,2-dimethoxybenzene with selectivity of 97% [13].

* Corresponding author.

E-mail address: zww_dxj@sohu.com (Z. Zhang).<https://doi.org/10.1016/j.apsusc.2018.08.017>

Received 4 March 2018; Received in revised form 29 June 2018; Accepted 1 August 2018

Available online 02 August 2018

0169-4332/ © 2018 Published by Elsevier B.V.

The methanol as another low-activity methyl source is used at high temperature, too. Dang and co-workers [14] made a gas, containing of methanol and phenol, to pass through catalyst bed in order to get anisole. The catalyst was monopotassium phosphate loaded on activated alumina. The reaction temperature was 400–500 °C. The conversion of phenol was 75% and the selectivity of anisole was 90%. There was no anisole if the catalyst was other metal salts. Sad and co-workers [15] used a similar method to produce anisole. The catalyst of HZSM5 molecular sieves corresponded to the best selectivity.

Some rarely used reagents are employed to accomplish methylation reaction. Koirala and co-workers [16] synthesized 7-hydroxyl-8-methoxyl-flavone by using of methyltransferases. The reaction realized through molecular biology method, so its reaction temperature was 37 °C, and the conversion was 96%. Shadkani and co-workers [17] methylated catechins by using of tetramethylammonium hydroxide, trimethylsulfonium hydroxide and trimethylsilyldiazomethane the three methyl sources. The third one conveniently methylated hydroxyl at the 3', 4', 5, 7 positions. Even it could methylate the hydroxyl at the 3 position. This is a thorough methylation method, but the methyl source is expensive. It only fits to modify a small amount of sample before analysis.

The above methyl sources have some disadvantages, such as high toxicity, low activity and valuableness. In order to avoid those harsh reaction conditions caused by the disadvantages of methyl sources, and to realize a green synthesis route, the present paper proposes an electrolysis method for the methylation of phenol hydroxyl. There are two experimental facts supporting the proposed method. The first fact is that quaternary ammonium salts could be electro-reduced at a certain potential and produces alkyl radicals [18]. The electro-reduction of tetramethyl ammonium chloride (TMAC) could produce methyl

radicals. The TMAC can be taken as methyl source. The second fact is that the electro-oxidation of phenol hydroxyl could produce semi-quinone structure. This molecular structure has ability to bond with free radicals [19]. The semi-quinone would form chemical bond with methyl radicals. At present, there is no report about the methylation or alkylation method proposed by us.

2. Experiments and computation

2.1. Tests

The cyclic voltammetry (CV) of the phenol-TMAC and the sodium phenate-TMAC methanol solutions were performed by employing of Versatile Multichannel Potentiostat 2/Z (VMP2, Princeton Applied Research) with three electrodes cell. The platinum acted as the working electrode and the counter electrode, and Ag/AgCl was the reference electrode. The EPR spectra of electrolytes were measured by using of Bruker EMX-plus X-band EPR spectrometer. The solution samples were collected for EPR test when 0.5 times of theoretical amount of charge was supplied by the DC power. The concentration of phenols was 0.3 mol/L in all testing solutions.

2.2. Electrolysis

Phenol and TMAC were solved into methanol to form the first solution labeled as phenols-TMAC. Phenol, TMAC and NaOH were solved into methanol, and the NaCl was filtered after stirring for one hour, to get the second solution containing of phenoxyl anion, $(\text{CH}_3)_4\text{N}^+$ cation and/or TMAC. The second one was labeled as phenate-TMAC. The two kinds of solution were electrolyzed in a single-compartment cell by

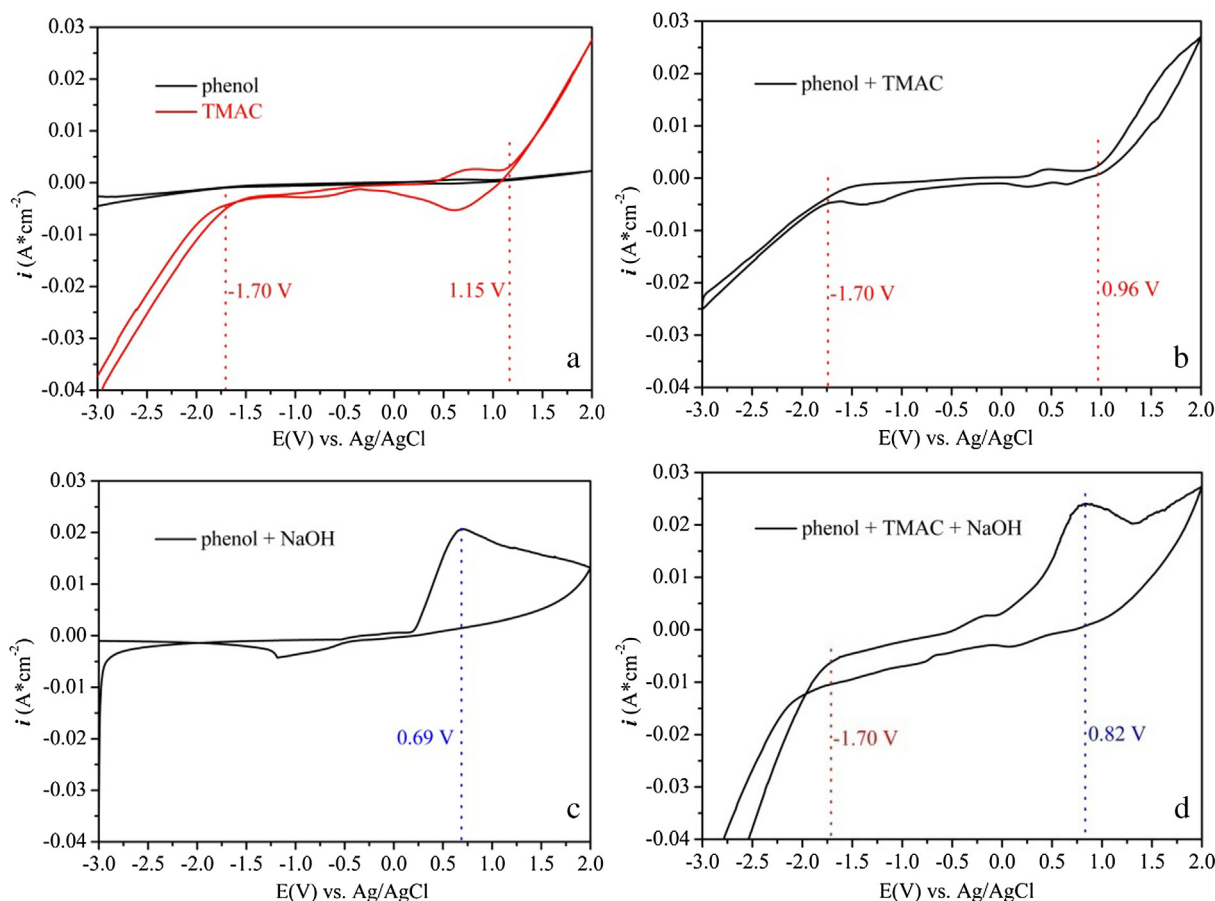


Fig. 1. The CV curves of (a) phenol and TMAC methanol solution, (b) phenol-TMAC methanol solution, (c) sodium phenate methanol solution, (d) phenate-TMAC methanol solution.

Download English Version:

<https://daneshyari.com/en/article/7832841>

Download Persian Version:

<https://daneshyari.com/article/7832841>

[Daneshyari.com](https://daneshyari.com)