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Water-promoted One-step Anodic Acetoxylation of Benzene to Phenyl Acetate with High Selectivity

Juan Pei, Song Qin, Gui-ying Li, Chang-wei Hu*

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China

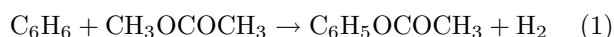
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One-step anodic acetoxylation of benzene to phenyl acetate was studied in acetic acid-water solution using a one-compartment electrochemical cell in galvanostatic mode. Compared to the anhydrous system, the addition of water improved the current efficiency for the electro-synthesis of phenyl acetate. The maximum efficiency reached 4.8% with the selectivity of 96% to phenyl acetate when the electrolysis was carried out under the optimal conditions. The investigation also indicated that the concentration of phenyl acetate increased linearly in 12 h and reached 1.07 g/L with the selectivity of 95%. Cyclic voltammetry experiments showed that the adsorption of benzene at Pt anode enhanced by the addition of water was critical to the formation of phenyl acetate. An activated benzene mechanism was proposed for the anodic acetoxylation, and the analysis of gas products demonstrated that Kolbe reaction was the main side reaction.

Key words: Anodic acetoxylation, Benzene, Acetic acid aqueous solution, Phenyl acetate, Mechanism

I. INTRODUCTION

Phenyl acetate, one of the important intermediates in organic synthesis, could be easily converted to other value-added chemicals, such as 2-hydroxyacetophenone (2-HAP) and 4-HAP which were widely used in pharmaceutical industry via Fries rearrangement [1–4]. Conventional routes [5, 6] to produce phenyl acetate were condensed reactions using phenol and acetic anhydride or acetyl chloride as the starting materials. However, those reactants were generally synthesized from benzene and acetic acid through complex processes, respectively [7, 8]. From the viewpoint of synthetic efficiency and atom economy [9–12], one-step acetoxylation of benzene to phenyl acetate was the way to shorten the reaction paths and reduce by-products, as:



Because of the limitation of thermodynamics ($\Delta G > 0$), this process was hardly to take place under normal temperature and atmospheric pressure. Therefore, electro-synthesis method was one of the useful routes to realize the process.

Electrochemical acetoxylation of aromatics aiming at obtaining the intermediate to yield phenols was previ-

ously investigated [13–15]. Linstead *et al.* firstly discovered the anodic acetoxylation by adding substituted-aromatics to the system of Kolbe acetate oxidation [13]. A 24% yield of 1-naphthyl acetate was obtained when naphthalene was added into a mixture of HOAc-NaOAc. The new procedure for the synthesis of 1-naphthyl acetate was carried out on the tonne scale at BASF Corporation after a series of improvements [16, 17]. Then Rhone-Poulenc corporation [18] used the method for the trifluoroacetoxylation of benzene in the presence of trifluoroacetic acid. The total current efficiency η of the reaction was 70%, but the yield of mono-substituted phenyl ester just reached 12% for a large amount of di-substituted phenyl esters with an *o*:*p*:*m*-proportion of 22:31:16 were generated.

To the best of our knowledge, although there were a few literatures involving the anodic acetoxylation of benzene an anhydrous liquid system [19–21], the efficiency was rather poor for the synthesis of phenyl acetate. Ross *et al.* investigated Kolbe reaction in the presence of benzene in glacial acetic acid and found the formation of phenyl acetate in electrolysis [19]. However, η just reached 0.64% at a current density of 400 mA/cm². In their procedure, a large amount of supporting electrolyte (0.85 mol/L) was needed because of the extremely low conductivity of glacial acetic acid. Recently, a novel solid electrolytic system for anodic acetoxylation was developed by Tajima *et al.* [20, 21], but no phenyl acetate was detected from benzene and glacial acetic acid in their system.

* Author to whom correspondence should be addressed. E-mail: gchem@scu.edu.cn, chwuhu@mail.sc.cninfo.net, Tel./FAX: +86-28-88835525

This work was to selectively synthesize phenyl acetate directly from benzene and acetic acid in term of electrolysis. The efficiency was improved by adding water in the electrolysis system. The electrochemical behaviors of benzene with or without water at Pt anode in the present electrolysis were discussed. The mechanism of the present anodic acetoxylation reaction was also investigated.

II. EXPERIMENTS

A. Materials

All chemicals in the experiments were of analytical grade and used without any further purification. C_6H_6 , HOAc, NH_4OAc , CH_3CN , and *o*-cresol were purchased from Chengdu Kelong Chemical Co., Ltd. All solutions were prepared with deionized water. Pt and graphite electrodes were purchased from Tianjin Aida Hengcheng Co., Ltd.

B. Electrolysis and analysis procedures

The galvanostatic electro-synthesis was performed using a direct current (DC) power supply (Huaian Yaguang electronics Co., Ltd.). A one-compartment electrochemical cell equipped with a pair of Pt (1 cm^2) anode and cathode (a separation of 1.0 cm) was used as the reactor. A desired amount of NH_4OAc as the supporting electrolyte was weighted and dissolved into the solution. The electrolysis was carried out at 283 K with constant current under atmosphere. The operation current density j was 100 A/m^2 .

All liquid products were identified by coupled gas chromatography and mass spectroscopy (GC-MS, Agilent 5973 Network 6890N). After electrolysis, the crude reaction mixture was diluted in acetonitrile and analyzed by HPLC (Waters 1525P) on a C18 dimethyloctadecylsilane (ODS) column with a UV detector at 190 nm. The main product and by-products were quantified using *o*-cresol as an internal standard. The current efficiency for the electro-synthesis of phenyl acetate was calculated by the ratio of the actual yield to that obtained theoretically according to the Faraday laws. The selectivity to phenyl acetate was calculated as (phenyl acetate)/(phenyl acetate+phenol).

Gas products generated in the reactor were introduced into gas chromatography (GC, Agilent 1790) with thermo-conductivity detector (TCD) to analysis the compositions of the gas. Argon was used as a carrier gas. It was found that argon had no effect on the target reaction.

C. Cyclic voltammetry

Cyclic voltammetry (CV) experiments were carried out on the CHI610D Model electrochemical workstation

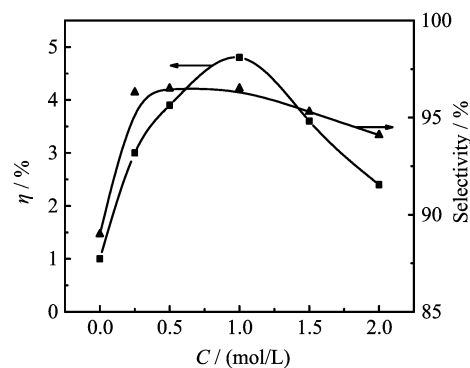


FIG. 1 Effect of water on η and selectivity to phenyl acetate. Reaction conditions: 10 mL HOAc, 1.6 mol/L C_6H_6 , 0.1 mol/L NH_4OAc , $j=100\text{ A/m}^2$, $T=283\text{ K}$, reaction time is 2 h.

(Shanghai Chenhua Instrument Co., Ltd.). A Pt disk or graphite, a platinum wire and a saturated aqueous calomel electrode (SCE) served as working, counter and reference electrodes, respectively. CV was recorded in a constant sweep rate of 50 mV/s and at a constant temperature of 283 K. All solutions were thoroughly deoxygenated with high purity nitrogen for 5 min before executing the voltammetric experiments.

III. RESULTS AND DISCUSSION

A. Effect of water

The effect of water in the electrolysis was tested and the results were shown in Fig.1. Under the anhydrous condition, it was found that η was about 1% with a selectivity of 89%, which was consistent with the results of Ross *et al.* [19]. In the presence of water, both η and the selectivity to phenyl acetate increased. When the concentration of water increased from 0.25 mol/L to 1.0 mol/L, η increased from 3.0% to 4.8%, while the selectivity to phenyl acetate stabilized at about 96%. With further addition of water to 2.0 mol/L, η decreased to 2.4% gradually, which might be due to the increase of oxygen evolution reaction (OER) at anode [22–24]. Meanwhile, the main by-product phenol was detected, and the selectivity to phenyl acetate slightly decreased to 94%.

B. Influence of the concentration of the supporting electrolyte NH_4OAc

Since the presence of water favored the electro-synthesis, the following reactions were performed in acetic acid-water solution. NH_4OAc was used as the supporting electrolyte to enhance the conductivity and diminish the voltage of the cell. The influence of the concentration of NH_4OAc on η and selectivity to phenyl acetate was investigated. As shown in Fig.2,

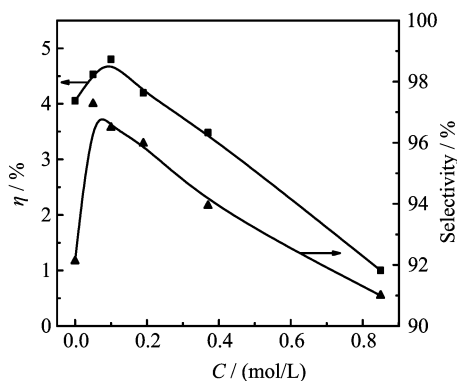


FIG. 2 Influence of concentration of NH_4OAc on η and selectivity to phenyl acetate. Reaction conditions: 10 mL HOAc , 1.6 mol/L C_6H_6 , 1.0 mol/L H_2O , $j=100 \text{ A/m}^2$, $T=283 \text{ K}$, reaction time is 2 h.

with the increase of the concentration of NH_4OAc , both η and the selectivity to phenyl acetate increased firstly and then decreased. A large amount of NH_4OAc (0.85 mol/L) resulted in a poor efficiency and low selectivity in the electrolysis. It was found that the optimized concentration of NH_4OAc (0.1 mol/L) in the presence of water was much lower than that reported previously in glacial acetic acid ($>0.8 \text{ mol/L}$) [19]. This might be due to the fact that water enhanced the conductivity and therefore decreased the dosage of supporting electrolytes.

C. Mechanism analysis

Although η was increased by the addition of water, it should be emphasized that η was no more than 5% which meant that only 5% of the total current was used for the conversion of benzene to phenyl acetate. Therefore, analysis of gas products was conducted to investigate the side reactions. When electrolysis under optimal conditions without benzene was performed at $j=100 \text{ A/m}^2$, it was found that the main compositions of the gas products were ethane, carbon dioxide, and hydrogen with a proportion of 24:48:28, and the rate of gas evolution was a constant of 0.132 mL/min generally. The result meant that the balance of the current was used in the main side reaction known as the Kolbe reaction at Pt anode which was involved in attacking acetate ions to produce anodic gaseous products like ethane and carbon dioxide [25, 26].

When a certain amount of benzene (1.6 mol/L) was added, the compositions and proportion remained unchanged with the rate of gas evolution slightly decreased to 0.126 mL/min. The decrease of the rate for gas evolution might be ascribed to the adsorption of benzene at Pt, as pointed out by other researchers that the adsorption of aromatics compounds exerted an impact on the electrode processes [27]. Moreover, the results showed that benzene exerted little effect on the Kolbe reac-

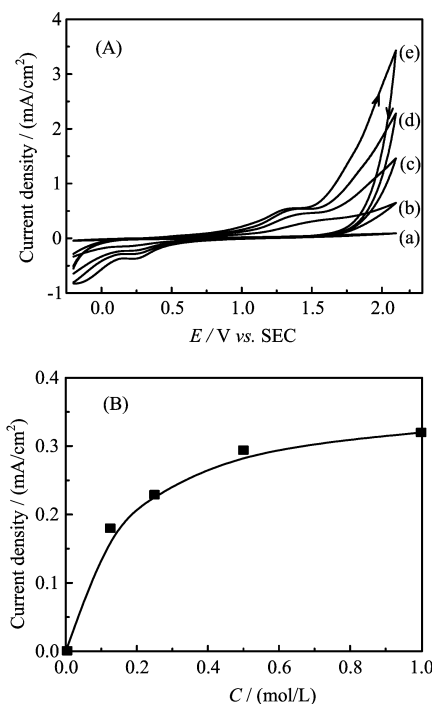


FIG. 3 (A) Cyclic voltammograms of 1.6 mol/L benzene at platinum in the absence (a) and presence (b) of 0.125 mol/L water with 0.1 mol/L NH_4OAc in HOAc solution. (c) 0.25 mol/L water, (d) 0.50 mol/L water, and (e) 1.0 mol/L water. Scan rate: 50 mV/s, $T=283\pm 1 \text{ K}$. (B) The peak current of oxidation of adsorbed benzene vs. 0.25 mol/L water.

tion, which was in accordance with the observation in Ref.[28].

As indicated in the above investigation, the presence of water was favorable for the formation of phenyl acetate. This result was quite different from the previous reports in trifluoroacetoxylation of benzotrifluoride [29], in which the presence of water led to poorer current efficiency for the generation of phenols. Therefore, experiments aiming at ascertaining the effect of water and evaluating the electrochemical behavior of benzene at anode in acetic acid aqueous solutions were performed. CV experiments at Pt anode were firstly carried out in a potential above the hydrogen-evolution region and the curves were shown in Fig.3. As shown in Fig.3(A), the anodic sweep in glacial acetic acid Fig.3(a) showed a slight increase in current at $E>2.0 \text{ V vs. SCE}$, which was related to Kolbe reaction at Pt anode [30, 31]. In contrast, when water was added in glacial acetic acid, there was an obvious increase of the peak in Fig.3 (b)–(e). This implied that the Kolbe reaction was significantly enhanced by the addition of water. A weak oxidative peak, assigned to the anodic oxidation of adsorbed benzene at the electrode surface [32], was observed at approximately 1.5 V vs. SCE in Fig.3 (b)–(e). It was found that the peak potential became more negative when the amount of water was increased, indi-

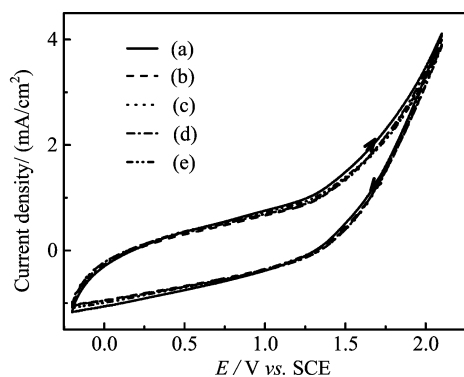
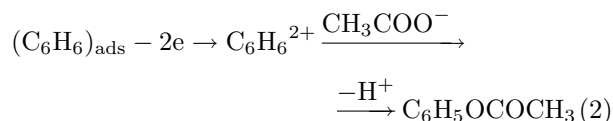


FIG. 4 Cyclic voltammograms at graphite in the absence (a) and presence (b) of 0.025 mol/L C_6H_6 with 0.1 mol/L NH_4OAc in $HOAc$ aqueous solution. (c) 0.05 mol/L C_6H_6 , (d) 0.1 mol/L C_6H_6 , (e) 0.5 mol/L C_6H_6 . Scan rate: 50 mV/s, $T=283\pm 1$ K.

cating electrochemical irreversibility. Furthermore, as shown in Fig.3(B), the peak current of oxidation of adsorbed benzene increased with the increasing of added water, suggesting that acetoxylation of benzene should be closely related to the oxidation of adsorbed benzene at anode and enhanced in the presence of water.

To further confirm the assumption that the adsorbed benzene played an important role in the electro-synthesis, a graphite electrode was comparatively used as anode in the electrolysis. Compared with the result of Pt-anode system, little amount of phenyl acetate ($\eta < 0.6\%$) was obtained when graphite was used. The investigations of electrochemical behaviors of benzene at graphite were also performed and illustrated in Fig.4. The peak of 2.0 V *vs.* SCE corresponding to Kolbe reaction at graphite anode could be found, but no adsorption of benzene was observed when benzene was added. This CV experiments at graphite further confirmed the above assumption that the reaction was related to the adsorption of benzene at Pt anode.

It was noteworthy that the present electrolysis was involved in two reactions which were the target reaction and the Kolbe reaction via $CH_3COO\cdot$ radical mechanism. The related investigation showed that the lifetime of $CH_3COO\cdot$ radical was very short, which might result in the formation of methylation products [33, 34]. However, no toluene was detected in the reaction products. Therefore, the above results could rule out the radical mechanism in the generation of phenyl acetate in this system. The mechanism was summarized in reaction (2):



Benzene was firstly adsorbed at the electrode, then two electrons transferred from benzene to platinum to form

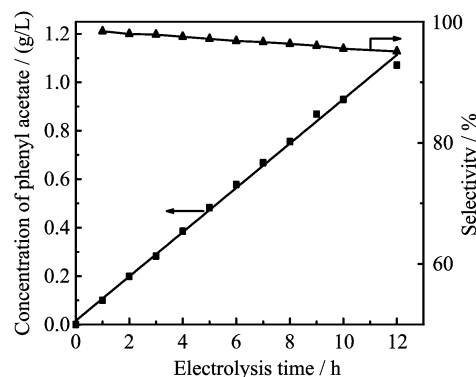


FIG. 5 Concentration of phenyl acetate and selectivity to phenyl acetate in 12 h reaction. Reaction conditions: 10 mL $HOAc$, 1.0 mol/L H_2O , 1.6 mol/L C_6H_6 , 0.1 mol/L NH_4OAc , $j=100$ A/m², $T=283$ K.

a dicationic intermediate, which reacted with acetate ion and then lost a proton.

For the main by-product phenol, it might be generated via two distinct paths in aqueous solution: (i) hydrolysis of the target product phenyl acetate [35, 36] and (ii) anodic hydroxylation of the substrate benzene [37]. A comparative experiment to detect the possible hydrolysis of phenyl acetate was carried out, where a certain amount of phenyl acetate (2.4 mg, the amount obtained in the electrolysis) was used to substitute benzene in the electrolysis. The results showed that the amount of phenol was approximately consistent with that obtained when benzene was used as the substrate. Therefore, it was reasonable to conclude that small amount of the phenyl acetate formed in the present electrolysis might be hydrolyzed, forming phenol.

D. Long time reaction in 12 h

Under the optimal conditions, the reaction time was prolonged to 12 h to obtain a larger amount of phenyl acetate, as shown in Fig.5. It was observed that the concentration of phenyl acetate showed a linear increment from the beginning of electrolysis and reached 1.07 g/L at 12 h with a good selectivity of about 95% to phenyl acetate. The amount of phenyl acetate yielded in 12 h was 15 mg. The results in the long time reaction indicated that the present method was practical to the synthesis of phenyl acetate from benzene and acetic acid.

IV. CONCLUSION

A "green" and simple method for the one-step production of phenyl acetate with high selectivity was presented by anodic acetoxylation of benzene in acetic acid-water mixtures at Pt anode. The process involved the target reaction and the Kolbe reaction, the latter being the major cause leading to low η . The addition

of water facilitated the formation of phenyl acetate accompanied by the decrease of the amount of supporting electrolyte. The adsorption of benzene at Pt anode was crucial for the synthesis of phenyl acetate. Small amount of added water favored the adsorption of benzene at the surface of Pt and enhanced the formation of phenyl acetate. The mechanism of anodic acetoxylation involving the activation of benzene at Pt anode was further confirmed. Furthermore, a considerable amount of phenyl acetate with a good selectivity could be obtained through a long operation time. This might be potential for the industrial applications.

V. ACKNOWLEDGMENTS

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