Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

A new approach for the aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid without using transition metal catalysts☆

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A R T I C L E I N F O

Article history:
Received 16 January 2017
Revised 11 April 2017
Accepted 24 April 2017
Available online xxx

Keywords:
Aerobic oxidation
5-Hydroxymethylfurfural
2,5-Furandicarboxylic acid
Sodium hydroxide
Transition metal catalyst-free

A B S T R A C T

The organic compound 2,5-furandicarboxylic acid (FDCA) has been identified by the US Department of Energy (DOE) as a valuable platform chemical for a wide range of industrial applications. Currently, the most popular route for FDCA synthesis is reported to be the oxidation of 5-hydroxymethylfurfural (HMF) by O_2 over the catalysis of noble metals (e.g., Au, Pt, Ru, and Pd). However, the high costs of noble metal catalysts remain a major barrier for producing FDCA at an industrial scale. Herein, we report a transition metal-free synthesis strategy for the oxidation of HMF to FDCA under O_2 or ambient air. A simple but unprecedented process for the aerobic oxidation of HMF was carried out in organic solvents using only bases as the promoters. According to the high performance liquid chromatography (HPLC) analysis, excellent product yield (91%) was obtained in the presence of NaOH in dimethylformamide (DMF) at room temperature (25°C). A plausible mechanism for the NaOH-promoted aerobic oxidation of HMF in DMF is also outlined in this paper. After the reaction, the sodium salt of FDCA particles were dispersed in the reaction mixture, making it possible for product separation and solvent reuse. The new HMF oxidation approach is expected to be a practical alternative to current ones, which depend on the use of noble metal catalysts.

1. Introduction

There has been growing interest in sustainable development, particularly in the production of fuels and chemicals from renewable resources. Lignocellulosic biomass is not only the most abundant biomass on earth, but is considered to be a renewable and carbon neutral resource that has net-zero greenhouse gas emissions [1]. Over the past decades, numerous studies have been carried out on the conversion of non-edible lignocellulosic biomass into biobased chemicals, which can be used as substitutes for petroleum-based chemicals. Among these biobased chemicals, 5-hydroxymethylfurfural (HMF) has been recognized as a versatile platform chemical that has applications in a diverse range of industries [2–4]. HMF consists of a furan ring substituted with a hydroxyl and an aldehyde group in the 2,5-position. The synthesis of HMF involves the dehydration of fructose or glucose which can be obtained from the depolymerization of cellulose [5,6]. As one of the oxidized derivatives of HMF, 2,5-furandicarboxylic acid (FDCA) is a symmetrical furanic diacid which is considered to be a promising build block for the production of sustainable polymeric materials [7,8]. Specifically, FDCA is found to be a biobased and environmentally friendly substitute for terephthalic acid, which is widely used in the plastics industry as a monomer for the manufacture of polyethylene terephthalate (PET) bottles and films [9]. It has been reported that the FDCA-based poly(ethylene-2,5-furandicarboxylate) (PEF) products outperformed the traditional PET ones in many aspects [10]. Besides PEF, researchers have been experimenting on using FDCA for the production of a variety of biobased polyesters, polyamides, and polyurethanes [11,12]. Due to its high potential for industrial applications, FDCA was listed as one of the twelve top biobased value-added chemicals by the US Department of Energy (DOE) in 2004 [13]. Since then, the studies on the production of FDCA have received significant attention in both academia and industry.

Although efforts have been made to directly convert carbohydrates (e.g., fructose, glucose, and cellulose) into FDCA over multifunctional catalysts, unsatisfactory performance of direct conversion methods limits their application. One major drawback of

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☆ This work was supported by the SEEDS grant from the Ohio Agricultural Research and Development Center (OARDC) of the Ohio State University, Ohio, USA [grant number 2016-105].

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http://dx.doi.org/10.1016/j.jechem.2017.04.020
2095-4956/

Please cite this article as: L. Zhang et al., A new approach for the aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid without using transition metal catalysts, Journal of Energy Chemistry (2017), http://dx.doi.org/10.1016/j.jechem.2017.04.020

direct conversion methods is the occurrence of the unwanted oxidation of carbohydrates, resulting in the generation of large amounts of byproducts [14]. Currently, most studies on FDCA production use a two-step conversion process in which carbohydrates are firstly dehydrated to HMF, and then oxidized to FDCA [15]. When using HMF as a starting material, nearly 100% yields of FDCA can be obtained in various catalytic oxidation systems [14]. The conversion of HMF to FDCA is an oxidization process in which both the hydroxyl and aldehyde groups are oxidized to carboxylic acid groups [16]. While the selective oxidation of primary alcohols into aldehydes has been intensively studied in recent years, the direct oxidation of primary alcohols to carboxylic acids is still confined to a limited number of methods [17,18]. In early studies, FDCA was produced from HMF by using HNO_3 or N_2O_4 as a terminal oxidant, but the product selectivity was relatively low due to the generation of byproducts [19,20]. In later reports, FDCA was produced from HMF by using stoichiometric amounts of $KMnO_4$ as a terminal oxidant, but the product yield was still not satisfying and large amounts of heavy metal waste were produced at the same time [21]. Recently, *tert*-butyl hydroperoxide (*t*-BuOOH) was reported to be a suitable terminal oxidant for the oxidation of HMF into FDCA over the catalysis of transition metal catalysts [22]. However, this “transition metal/*t*-BuOOH” system also had a few drawbacks, such as low product yields and difficulties in catalyst recycling and product purification [14]. Nowadays, emphasis has been placed on using O_2 as an economical and environmentally friendly terminal oxidant for the oxidation of HMF to FDCA. In the past few years, a large number of aerobic oxidation systems have been successfully applied on the oxidation of HMF to FDCA. In most cases, supported noble metal catalysts (e.g., Au, Pt, Ru, and Pd) were essential in these oxidation systems for the activation of O_2 to obtain high oxidation efficiency of HMF [23–25]. Although high yields and efficiency could be achieved, these procedures often required elevated temperatures (50–100°C), relatively long reaction times, and the use of expensive catalysts [26].

Due to the growing awareness of environmental issues, the development of transition metal-free oxidation procedures has received more and more attention [27]. Recently, the aerobic oxidation of alcohols to corresponding ketones or carboxylic acids under transition metal-free conditions was unexpectedly discovered in several experiments. For example, in a 2009 experiment attempting to prepare a sodium alkoxide salt of a 4-dimethylaminopyridine-derived benzylic alcohol using NaH in tetrahydrofuran (THF), Wang et al. [28] was surprised to find that a high yield of ketone was produced from the benzylic alcohol due to the oxidation of its secondary hydroxyl group. A couple of years later, the same research group developed a protocol for the NaH-promoted aerobic oxidation of secondary alcohols in THF and systematically explored the mechanism of this oxidation method [29]. Inspired by this work, another research group reported the aerobic oxidation of a number of primary alcohols to carboxylic acids promoted by NaOH or sodium *tert*-butoxide (*t*-BuONa) in THF [17]. According to a very recent study on a “Na^+/azobenzene” aerobic oxidation system, a primary benzyl alcohol was unexpectedly over-oxidized to its corresponding carboxylic acid in the presence of NaOH in 1,4-dioxane [30]. These discoveries led to our hypothesis that HMF can be oxidized to FDCA in the presence of a base in an organic solvent. Within this context, the viability of using different bases to promote the aerobic oxidation of HMF to FDCA in organic solvents was investigated.

2. Experimental

2.1. Materials

All the reagents (HMF, NaOH, NaH and *t*-BuONa), solvents (THF, 1,4-dioxane and DMF), and reference standards (FDCA, 2,5-bis(hydroxymethyl)furan, 5-hydroxymethyl-2-furancarboxylic acid, 5-formyl-2-furancarboxylic acid and 2,5-diformylfuran) were purchased from Sigma–Aldrich (St. Louis, MO, USA) or Fisher Scientific (Hampton, NH, USA) and used without further purification.

2.2. Typical reaction procedure for HMF oxidation

All the oxidation experiments were carried out in test tubes (15 mL) fitted with balloons. In a typical HMF oxidization reaction, HMF solution and solid base were loaded into a test tube. The test tube was then connected to a balloon, which was filled with O_2 or ambient air at about atmospheric pressure. The resulting mixture was then stirred continuously at a fixed temperature of 25°C, 50°C, 70°C, or 90°C. After the indicated reaction time, the reaction mixture was neutralized using an aqueous H_2SO_4 solution.

2.3. Analytical procedures

The HMF conversion and the product selectivity were determined by a Shimadzu high-performance liquid chromatography (HPLC) (Kyoto, Japan) equipped with a Rezex RFQ column (100 × 7.8 mm) and a refractive index detector (Model No. RID-6A). After the completion of each oxidation reaction, the neutralized reaction mixture was diluted with water and then filtered through a 0.2 µm PTFE filter prior to HPLC analysis. An aqueous solution of H_2SO_4 (2.5 mM) was used as mobile phase at a flow rate of 0.2 mL/min. The column temperature and injection volume were fixed at 60°C and 10 µL, respectively. The commercial reference standards were used for the qualitative and quantitative analyses of the reaction products. Fourier transform infrared spectroscopy (FT–IR) analysis was conducted using a PerkinElmer Spectrum Two IR spectrometer (PerkinElmer, Waltham, MA, USA) at a spectral resolution of 2 cm^{-1}.

3. Results and discussion

3.1. Oxidation of HMF in the presence of different bases in THF

Initially, the aerobic oxidation of HMF in the presence of different loadings of NaH, *t*-BuONa, and NaOH was performed in THF under O_2 atmosphere at 25°C for 24 h. In addition, a control experiment was carried out under the same conditions but without using any base. As expected, no oxidized product was observed in the control experiment, confirming that the base played a crucial role in the aerobic oxidation of HMF (Table 1, entry 10). HMF is known as an unstable compound that may undergo degradation [31]. However, the result of the control experiment also indicated that HMF was stable in THF without the addition of any base. In general, *t*-BuONa showed the highest activity in THF with 32%–74% yields of FDCA, which might be attributed to its high basicity due to the *tert*-butoxide ion (Table 1, entries 4–6). On the other hand, NaH and NaOH had a limited effect on promoting the oxidation of HMF with only 8%–35% yields of FDCA (Table 1, entries 1–3, 7–9). Since there is no consensus about the optimum amount of base that should be used, the effect of base loading on the oxidation of HMF in this oxidation system was also investigated. The results showed that the FDCA yield increased with an increase of base loading when NaOH and *t*-BuONa were used as promoters (Table 1, entries 4–9), which probably increased the pH of the solutions, and thus was favorable for the oxidation of alcohol and aldehyde groups of HMF. However, the NaH loading increases did not dramatically influence the FDCA yield, and the optimum NaH loading was found to be 1.0 mmol (Table 1, entry 2). The decreased FDCA yields in the presence of 2.0 mmol NaH loading could be explained by the generation of larger amounts of byproducts (data not shown), which were induced by the increased NaH content.

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