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### Supramolecular Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/gsch20</u>

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To cite this article: Zu-Jin Yang , Hong-Guo Jiang , Xian-Tai Zhou , Yan-Xiong Fang & Hong-Bing Ji (2012) β-Cyclodextrin polymer promoted green synthesis of cinnamaldehyde to natural benzaldehyde in aqueous solution, Supramolecular Chemistry, 24:6, 379-384, DOI: <u>10.1080/10610278.2012.688119</u>

To link to this article: <u>http://dx.doi.org/10.1080/10610278.2012.688119</u>

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### β-Cyclodextrin polymer promoted green synthesis of cinnamaldehyde to natural benzaldehyde in aqueous solution

Zu-Jin Yang<sup>a</sup>, Hong-Guo Jiang<sup>b</sup>, Xian-Tai Zhou<sup>a</sup>, Yan-Xiong Fang<sup>b</sup> and Hong-Bing Ji<sup>a</sup>\*

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(Received 17 December 2011; final version received 20 April 2012)

An environmentally benign synthesis of natural benzaldehyde from cinnamaldehyde under mild conditions has been investigated with sodium hypochlorite as oxidant and  $\beta$ -cyclodextrin polymer as phase-transfer catalyst. The polymer showed excellent catalytic activity exhibiting 92% conversion and 62% selectivity to benzaldehyde at ambient pressure and at 70°C. This catalyst could be recovered and reused six times, and the catalyst efficiency remained unchanged, which suggests that the catalyst is an efficient and green catalyst for oxidation of cinnamaldehyde. The results reported herein may be a promising method in industry for the synthesis of natural benzaldehyde.

Keywords: phase-transfer catalyst; benzaldehyde; sodium hypochlorite;  $\beta$ -cyclodextrin polymer; mechanism

### 1. Introduction

Benzaldehyde is the second most utilised flavour compound in the world, and it is widely used in cosmetics, perfumery, food and pharmaceutical industries (1-3). With more care about food quality, consumers prefer natural products, and the demand for natural benzaldehyde is increasing rapidly. Because of the limited supply and high price of the natural product, synthetic benzaldehyde produced from natural cinnamon oil, which contains more than 80% of cinnamaldehyde, under mild conditions is often used as an alternative (4). Conventionally, preparing natural benzaldehyde is mostly from alkaline of *Laetrile*. However, toxic hydrocyanic acid is produced, which must be removed thoroughly from benzaldehyde and the rest of the oil prior to use. In this way, the natural benzaldehyde could be obtained at high cost.

Other techniques for producing natural benzaldehyde from alkaline hydrolysis of cinnamaldehyde or natural cinnamon oil (5-7) are known. However, these techniques produce natural benzaldehyde in a low yield because cinnamon oil or cinnamaldehyde are poorly soluble in water, making the resulting process less economical. In order to promote the reaction in aqueous solution, phase transfer or surfactants (8-10) have been utilised to increase the contact between the two phases. However, there are also some drawbacks, e.g. many by-products and toxic phasetransfer catalysts remained. Cyclodextrins (CDs) have been introduced into many organic reactions in aqueous solution (11-14). CDs are cyclic oligosaccharides composed of 6-8 glucopiranose units (namely  $\alpha$ -,  $\beta$ - and  $\gamma$ -CDs) linked

Sodium hypochloride is an effective, inexpensive and non-toxic oxidant, which has been reported in the liquidphase oxidation (27, 28). In this work, the catalytic oxidation of cinnamaldehyde to natural benzaldehyde using  $\beta$ -CDP as a phase-transfer catalyst and sodium hypochloride as an oxidant has been investigated for the first time (Scheme 1). This methodology might provide promising opportunity for industrial applications in the field of natural benzaldehyde.

ISSN 1061-0278 print/ISSN 1029-0478 online © 2012 Taylor & Francis http://dx.doi.org/10.1080/10610278.2012.688119 http://www.tandfonline.com

by glycosidic bonds. They are water soluble, non-toxic and hydrophobic in the central cavity. The most significant characteristic of the CDs is the ability to form inclusion complexes with different guest molecules in aqueous solution or in the solid state through host-guest interactions (15-17).  $\beta$ -CD is the cheapest among the CD family and has been widely used in separation, catalysis, and in organic reactions (18-21). And it has played a vital role in activating substrate and improving its selectivity (22-24). Although  $\beta$ -CD exhibits good catalytic activity in liquid-phase oxidation, the separation of  $\beta$ -CD from the homogeneous system is very difficult. Therefore,  $\beta$ -CD was immobilised on appropriate supports, e.g. organic, polymeric and mineral materials due to its recyclability, easy recovery and cost-effectiveness (25). Immobilised  $\beta$ -CD not only shows mechanical properties but also completely retains molecular recognition and catalytic properties of cyclodextrins. One way for producing immobilised  $\beta$ -CD (abbreviated as  $\beta$ -CDP) is through the reaction of  $\beta$ -CD molecules with bifunctional crosslinking agents such as epichlorohydrin (EPI) (26).

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Scheme 1. Oxidation of cinnamaldehyde to benzaldehyde catalysed by  $\beta$ -CDP.

#### 2. Results and discussions

# 2.1 Fourier transform infrared spectroscopy (FTIR) characterisation

FTIR spectra of  $\beta$ -CD (a) and  $\beta$ -CDP (b) are shown in Figure 1. FTIR spectrum of  $\beta$ -CDP is similar to that of  $\beta$ -CD, indicating that the frame of  $\beta$ -CD does not change. The peaks of  $\beta$ -CDP at 3446 and 2876 cm<sup>-1</sup> are stronger than those of  $\beta$ -CD, and the increased intensity may be attributed to the presence of more -OH and -CH<sub>2</sub> groups in the  $\beta$ -CDP. The spectrum of  $\beta$ -CDP showed the characteristic peak at 1260 and 720 cm<sup>-1</sup>, indicating the formation of the expoxy group onto  $\beta$ -CDP. The peak at  $1030 \text{ cm}^{-1}$  in the  $\beta$ -CDP was assigned to the C–O or C-O-C stretching in the  $\beta$ -CDP. The increase in the band intensity at around  $1030 \text{ cm}^{-1}$  might be  $\beta$ -CD. In addition, the peak at  $890 \text{ cm}^{-1}$  in the  $\beta$ -CDP was the characteristic bands of  $\alpha$ -(1,4)-glucopyranose in  $\beta$ -CD (29). Therefore, it could be concluded that  $\beta$ -CD had been immobilised successfully onto B-CDP.

### 2.2 Effect of stirring speed

Stirring speed has a great influence on the oxidation of cinnamaldehyde by  $\beta$ -CDP catalysis. The effect of stirring speed was investigated in the range of 100–600 rpm in Figure 2. The results showed the conversion of cinnamaldehyde significantly increased with increasing



Figure 1. FTIR spectra of  $\beta$ -CD (a) and  $\beta$ -CDP (b).



Figure 2. Stirring speed on the oxidation of cinnamaldehyde. Reaction conditions: cinnamaldehyde (1 mmol),  $\beta$ -CDP (1 g), NaClO [4 ml, 7.5% (w/w)], H<sub>2</sub>O (25 ml), 70°C and 2 h.

in stirring speed. When the speed is 400 rpm, the conversion is up to 92%, which was much higher than 50.5% at the stirring speed of 100 rpm. Furthermore, there is no significant influence on the conversion of cinnamaldehyde with an increase in the stirring speed beyond 400 rpm. The results indicated that the conversion of cinnamaldehyde was strongly dependent on the dispersed extent of organic phase in aqueous phase, which promoted the mass transfer between the two phases to improve the selectivity of natural benzaldehyde. The optimal stirring speed is 400 rpm. Siva and Murugan (*30*) reported similar behaviour displayed by reactions with a real 'phase transfer'.

### 2.3 Effect of amount of catalyst

The effect of amount of  $\beta$ -CDP on the yield of natural benzaldehyde and the conversion of cinnamaldehyde was investigated by varying its amount from 1 to 5 g. As shown in Figure 3,  $\beta$ -CDP exhibited higher catalytic activity for the oxidation of cinnamaldehyde to natural benzaldehyde comparing with that in blank experiment, in which only 51% cinnamaldehyde could be converted. The conversion of cinnamaldehyde increased with the amount of catalyst, which should be attributed to the increase in the number of hydrophobic cavity in  $\beta$ -CDP. As reported by Ji et al. (31), it is well known that  $\beta$ -CDP and substrate can form hostguest inclusion complex, resulting in enhancing the solubility of cinnamaldehyde in water and promoting the reaction of cinnamaldehyde compared with experimental result blank. Maximal conversion (ca. 92%) was obtained when using 1.0 g of  $\beta$ -CDP. The excess amount of the catalyst caused decrease of selectivity to benzaldehyde. It could be attributed to further oxidation of benzaldehyde to benzoic acid. The optimal amount of  $\beta$ -CDP is 1.0 g.



Figure 3. Amount of catalyst on the oxidation of cinnamaldehyde. Reaction conditions: cinnamaldehyde (1 mmol), NaClO [4 ml, 7.5% (w/w)], H<sub>2</sub>O (25 ml), 70°C, 2 h and 400 rpm.

### 2.4 Effect of reaction temperature

The effect of reaction temperature on the oxidation of cinnamaldehyde to benzaldehyde by  $\beta$ -CDP was investigated under the temperature range of 30–80°C with other parameters being kept constant, and the results are shown in Figure 4.

As shown in Figure 4, the conversion of cinnamaldehyde increased with increasing the reaction temperature from 30 to 80°C. Nearly, 100% conversion of cinnamaldehyde was achieved at 80°C. It seems that the selectivity for benzaldehyde was closely related to the reaction temperature. The selectivity for benzaldehyde increased from 32% to 62% with rising temperature from 30 to 70°C. The selectivity for benzaldehyde decreased when the temperature was beyond 70°C due to the undesirable side reaction. As shown in Figure 4, the optimal reaction temperature for oxidation of cinnamaldehyde is 70°C.

### 2.5 Effect of molar ratio of NaClO to cinnamaldehyde

The amount of NaClO used in the system is another important factor influencing the oxidation of cinnamaldehyde. The effect of NaClO/cinnamaldehyde molar radio on the oxidation of cinnamaldehyde to benzaldehyde was studied, and the results are shown in Table 1. The conversion increased with increasing the molar ratio of NaClO/cinnamaldehyde. About 92% conversion of cinnamaldehyde and 62% selectivity of benzaldehyde were obtained when the molar ratio of NaClO/cinnamaldehyde reached 4:1. When the ratio was increased, cinnamaldehyde was completely converted. However, the selectivity for benzaldehyde decreased when the ratio was above 4:1. It could be attributed to that benzaldehyde was further oxidised to benzoic acid at higher molar ratio of NaClO/cinnamaldehyde. As shown in Table 1, optimal ratio of NaClO/cinnamaldehyde was 4:1.

### 2.6 Large-scale experiment

Furthermore, in order to verify the efficiency of the catalytic system, a large-scale experiment for oxidation of cinnamaldehyde to benzaldehyde catalysed by  $\beta$ -CDP in the presence of NaClO in water under the above optimum reaction conditions was carried out as shown in Scheme 2. The isolated yield of benzaldehyde was 57%. Comparing with other ways of preparing benzaldehyde from cinnamaldehyde (22), this process realised the clean



Figure 4. Temperature on the oxidation of cinnamaldehyde. Reaction conditions: cinnamaldehyde (1 mmol),  $\beta$ -CDP (1 g), NaClO [4 ml, 7.5% (w/w)], H<sub>2</sub>O (25 ml), 2 h and 400 rpm.

Table 1. Effect of molar ratio of NaClO to cinnamaldehyde on the oxidation of cinnamaldehyde.<sup>a</sup>

| Entry | NaClO:cinnamaldehyde<br>(mol:mol) | Conversion<br>(%) | Selectivity<br>(%) |
|-------|-----------------------------------|-------------------|--------------------|
| 1     | 0.5:1                             | 31                | 50                 |
| 2     | 1:1                               | 48                | 52                 |
| 3     | 2:1                               | 60                | 54                 |
| 4     | 3:1                               | 74                | 59                 |
| 5     | 4:1                               | 92                | 61                 |

<sup>a</sup> Reaction conditions: cinnamaldehyde (1 mmol),  $\beta$ -CDP (1 g), H<sub>2</sub>O (25 ml), 70°C, 2 h and 400 rpm.



Scheme 2. Large-scale oxidation of cinnamaldehyde to benzaldehyde catalysed by  $\beta$ -CDP in the presence of NaClO.

synthesis of natural benzaldehyde and provided middle yield for natural benzaldehyde under mild conditions which is very important to preserve natural essence of benzaldehyde during the reaction process.

## 2.7 Plausible mechanism for oxidation of cinnamaldehyde to benzaldehyde

The progress of the oxidation of cinnamaldehyde to benzaldehyde catalysed by  $\beta$ -CDP in the presence of NaClO in a batch was carried out by measuring reaction samples using GC-MS with naphthalene as an internal standard. The plots of the conversion of cinnamaldehyde and the yields of the products versus reaction time were shown in Figure 5. The conversion of cinnamaldehyde was greatly increased by the addition of NaClO with extending the reaction time, and 92% conversion was obtained at the time of 30 min. And the yield of benzaldehyde reached 57% at the time of 120 min and decreased a little due to further oxidation to benzoic acid beyond 120 min. However, the yield of epoxide almost simultaneously reached up to 40% at the time of 15 min and then gradually decreased to 8%. At the same time, the yield of phenylacetaldehyde gradually increased to 12% and decreased to 9% at the time of 180 min. According to the previous reports (27, 28), sodium hypochloride is an effective, inexpensive and non-toxic oxidant. It can efficiently promote epoxide and phenylacetaldehyde to benzaldehyde in the system. The above results suggest that epoxide and phenylacetaldehyde are intermediates in the reaction. Therefore, the mechanism has been proposed for β-CDP-catalysed oxidation of cinnamaldehyde by sodium hypochloride based on above experimental results, as shown in Figure 6. Firstly,  $\beta$ -CD in the  $\beta$ -CDP and cinnamaldehyde can form the inclusion complex via



Figure 5. Plots of conversions and yields of the products versus reaction time for the cinnamaldehyde/ $\beta$ -CDP/NaClO oxide system at 70°C: (a) conversion of cinnamaldehyde; (b) yield of benzaldehyde; (c) yield of epoxide; (d) yield of phenylacetaldehyde and (e) yield of benzoic acid.

intermolecular hydrogen bonding O—H···O at the second rim of  $\beta$ -CD. Small amount of the complex can directly react with NaClO to produce benzaldehyde. Secondly, the non-covalent intermolecular interaction between  $\beta$ -CD and cinnamaldehyde also promotes the nucleophilic oxidation. Larger amount of cinnamaldehyde is converted into two intermediates including epoxide and phenylacetaldehyde. Thirdly, the corresponding intermediates are further oxidised to benzaldehyde by hypochlorite ion. Finally, a small amount of benzaldehyde produced slowly diffuses into bulk of aqueous solution and is further oxidised into benzoic acid.

### 2.8 Reusability of the catalyst

The insoluble  $\beta$ -CDP could be easily recycled by centrifugation after the reaction. The filtered  $\beta$ -CDP was washed with ethanol and deionised water. After drying, the catalyst was reused for the next run under the same condition. As shown in Figure 7, the results indicated that the catalytic activity was not affected significantly. Similar conversion and selectivity were obtained when the recovered  $\beta$ -CDP was reused six times.

#### 3. Conclusions

In conclusion, natural benzaldehyde has been successfully obtained using  $\beta$ -CDP as phase-transfer catalyst in aqueous solution. The  $\beta$ -CDP catalyst is found to be recyclable and efficient for selective oxidation of cinnamaldehyde to natural benzaldehyde with sodium hypochloride as an oxidant, and 92% cinnamaldehyde conversion and 57% benzaldehyde selectivity could be





Figure 6. The mechanism of the oxidation of cinnamaldehyde and the by-product formed.

obtained within 2 h. This method is bestowed with merits such as high yield, cost-effectiveness, biomimetic, neutral aqueous-phase conditions and environmentally benign nature. These are beneficial for keeping the natural essence of natural benzaldehyde. Furthermore, the solid  $\beta$ -CDP



Figure 7. Catalyst ( $\beta$ -CDP) recyclability data. Reaction conditions: cinnamaldehyde (1 mmol),  $\beta$ -CDP (1 g), H<sub>2</sub>O (25 ml), NaClO [4 ml, 7.5% (w/w)], 60°C, 2 h and 400 rpm.

can be conveniently used in continuous operation. These advantages of the catalyst made it referential for the synthesis of natural benzaldehyde in industrial process.

### 4. Experimental

### 4.1 Chemicals

 $\beta$ -CD was obtained from Shanghai Boao Biotechnology (Shanghai, China). EPI was supplied from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Cinnamaldehyde (>99%) was obtained from Sinopharmacy Chemical Reagent (Shanghai, China). Other chemicals were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). All reagents and solvents were of analytical grade and used without further purification unless indicated.

### 4.2 Catalyst preparation

According to the previous report (32), a typical procedure for preparing  $\beta$ -CDP was described as follows:  $\beta$ -CD (5 g, 0.44 mmol) was mixed with 8 ml NaOH (50%, w/w) solution and mechanically stirred for 20 min till  $\beta$ -CD was dissolved completely. Then, 15 ml EPI was slowly added into the mixture. The reaction mixture was heated to 65°C and kept at the same temperatureduring polymerisation. After stirring (200 rpm) for about 2 h, the insoluble polymers were poured into water and washed until it becomes neutral. The resulting product was filtrated and further washed with acetone in a Soxhlet extractor for 24 h. After drying in vacuum at 60°C for 12 h, the product was crushed and granulated to  $160-250 \,\mu\text{m}$  in diameter. The content of  $\beta$ -CD immobilised on  $\beta$ -CDP according to the previous report (*33*) was 50%.

### 4.3 Catalyst characterisation

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The FTIR spectra of samples were measured by KBr pellet. All the infrared spectra were recorded on a Bruker TENSOR 37 FTIR spectrometer with wavenumber ranging from 400 to  $4000 \text{ cm}^{-1}$  and a resolution of  $4 \text{ cm}^{-1}$ .

### 4.4 Catalyst evaluation

For a typical reaction run, 1 mmol cinnamaldehyde was dissolved in 25 ml of deionised water at 70°C, and 1 g of  $\beta$ -CDP was added into a 100-ml three-necked flask fitted with a reflux condenser and magnetic stirrer. The mixture was heated to 70°C in an oil bath with electric heater and then 4 ml of 7.5% NaClO was slowly dropped in. The resulting system was stirred with magnetic stirrer at 70°C for 2 h. After reaction, the mixture was extracted by ethyl acetate and then centrifuged. The extracted liquid mixture was analysed by GC-MS with naphthalene as an internal standard. The reproducibility for the data was within 5%.

### 4.5 Large-scale experiment

The large-scale reaction experiment was performed under the following optimum reaction conditions: a mixture of  $\beta$ -CDP (10g) and 250 ml deionised water was stirred at 70°C. Subsequently, cinnamaldehyde (10 mmol) was added. After 1 h, 40 ml of 7.5% NaClO was added in drops to the reaction system and then stirred for 2 h. After the reaction, the solution was extracted by ethyl acetate, and benzaldehyde was obtained by distillation.

#### Acknowledgements

The authors thank the National Natural Science Foundation of China (Nos 21036009 and 21176268), Guangdong provincial universities for higher-level talent project and the Fundamental Research Funds and the Central Universities for providing financial support to this project.

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