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Iodine Catalyzed Oxidation of Alcohols and Aldehydes to Carboxylic Acids in Water: A Metal-Free Route to Synthesis of Furandicarboxylic Acid and Terephthalic Acid

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A metal-free iodine/NaOH-catalyzed oxidation of alcohols and aldehydes has been developed for the practical synthesis of a wide range of carboxylic acids using water as the solvent. This transformation involves dehydrogenation of alcohol, followed by a fast attack of water on the aldehyde. This method is mostly free from chromatographic purification, which makes it suitable for large-scale synthesis. The iodine species formed during the reaction as the active oxidation catalyst has been deduced as  $IO_2^$ by control experiments. We also demonstrate a 10 gram scale synthesis of furandicarboxylic acid (FDCA) from HMF in good yield by our method.

Selective oxidation of alcohols is an essential step in organic synthesis as it can be used to produce aldehydes, acids, amides, acetals and esters.<sup>1-5</sup> Among all the oxidized feedstocks, carboxylic acids are needed as bulk chemicals in large amounts in various fields including fine chemicals, polymers and many commercial products.<sup>6</sup> The global production of aryl carboxylic acids was estimated as 480 kilotons in 2014 and is likely to exceed 620 kilotons by 2023.<sup>7a</sup> Terephthalic acid (TPA), the monomer for the polyester PET, used extensively for the manufacture of mineral water and beverage bottles has a worldwide demand of 12.6×10<sup>6</sup> tons.<sup>7</sup> 2, 5- Furandicarboxylic acid (FDCA) has been identified by the US Department of Energy as one of the twelve priority chemicals for establishing the "green" chemistry industry of the future.<sup>8</sup> However, large-scale syntheses of these carboxylic acids are still being carried out by oxidizing aldehydes and alcohols with stoichiometric amounts of routine oxidants, such as permanganate and chromate. Often these reactions take place in unsafe organic solvents, generating copious amount of used solvents and harmful side products.<sup>9</sup> The recent demand for highly efficient and environmentally benign syntheses of

+ Electronic Supplementary Information (ESI) available: For full experimental techniques, X-ray data, UV-visible spectroscopic studies, see DOI: 10.1039/x0xx00000x fine chemicals and pharmaceuticals has encouraged the development of mild, safe, and highly chemoselective oxidizers. Iodine based reagents are now increasingly being used in organic synthesis as an alternative to transition metal based reagents.<sup>10</sup>



During the last decade hypervalent iodine(V) reagents, namely Dess-Martin periodinane (DMP), 2-iodoxybenzoic acid (IBX) and iodosobenzene have emerged as highly selective reagents for the stoichiometric oxidation of alcohols to carbonyl compounds and for many synthetically useful oxidative transformations.<sup>10,11</sup> In spite of the utility and popularity of DMP and IBX which are relatively expensive, a serious disadvantage is their explosive nature restricting their usage in larger quantities.<sup>10f-g</sup> Thus, a facile and efficient use of the readily available and relatively stable molecular iodine I2, in place of iodine(V) reagents has been long desired. Recently,  $I_2/$ aqueous tertiary-butyl hydrogen peroxide (TBHP) system has become a powerful methodology to construct new C-C, C-N and C-O bonds. <sup>11</sup> However, almost all of these reactions were carried out in organic solvents. With its abundance and inherent greener characteristics, water has been the most desirable and ideal solvent for chemists.<sup>12</sup> Biological oxidations

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in water using enzymes or microorganisms are well known. In 2000, Sheldon and co-workers established an aqueous-phase homogeneous catalytic aerobic oxidation of alcohols, thus mimicking the nature.<sup>1g</sup> Following this pioneering work, several groups have reported oxidation of alcohols to carboxylic acids in water (Scheme 1).<sup>1,2</sup> Recently, research group of Li and Wei independently reported aerobic oxidation of aldehydes to carboxylic acids using water as the solvent (Scheme 1).<sup>13</sup> Yet, all these methods require transition metals or their salts as catalysts and in some cases high pressure and large excess of additives. So, the development of a transition metal free methodology to oxidize alcohols and aldehydes to their corresponding carboxylic acids using a greener oxidant in water medium is highly desirable. Here, we report a highly efficient, I<sub>2</sub>/NaOH catalyzed oxidation of a wide range of alcohols and aldehydes using only water as the solvent with TBHP as the co-oxidant.

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As demonstrated by Bera and co-workers<sup>2f</sup>, one pot conversion of alcohols to carboxylic acids can be accomplished by two consecutive reactions: (1) acceptorless dehydrogenation (AD) of alcohol to aldehyde, and (2) subsequent "aldehyde–water shift" (AWS) reaction (Scheme 2).



An ideal catalyst system should facilitate both the reactions simultaneously. Although, molecular iodine has been used for the dehydrogenation of alcohols to aldehydes and CDC coupling reactions, 10,11 similar iodine catalyzed "aldehydewater shift" reactions have not been explored. We were keen to study whether water could play the role of both an oxygen donor and reaction medium in a catalytic coupling between alcohols and water under mild reaction conditions. We began our investigation by examining the oxidation of 4methoxybenzylalcohol in water medium using iodine and sodium hydroxide. We observed 12% conversion to the desired carboxylic acid in presence of 4 equiv. of NaOH. Modern organic synthesis uses oxidants which are highly selective, efficient, and environmental friendly. Therefore, we explored the effect of external oxidants for the reaction and after several reactions it was found that aq. TBHP improved the yields of the desired carboxylic acids (See SI Table-S4). This finding prompted us to explore the scope of the reaction by using catalytic amounts of iodine and base. We carried out the reaction by varying reaction parameters and after detailed exploration (see SI Table S2, S3 and S4), it was found that 10 mol% of iodine, 20 mol% of NaOH and 4 equiv. of aq. TBHP are best suited for the reaction (Scheme 3).



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After optimizing the reaction conditions, we explored the substrate scope for the reaction (Figure  $\mathfrak{P}$ ).  $\mathfrak{P}$  is  $\mathfrak{P}$  is  $\mathfrak{P}$  is  $\mathfrak{P}$  is a substrate scope for the reaction (Figure  $\mathfrak{P}$ ).  $\mathfrak{P}$  is  $\mathfrak{P}$  is  $\mathfrak{P}$  is a substrate scope for the reaction (Figure  $\mathfrak{P}$ ).  $\mathfrak{P}$  is  $\mathfrak{P}$  is a substrate scope for the reaction (Figure  $\mathfrak{P}$ ).  $\mathfrak{P}$  is  $\mathfrak{P}$  is a substrate scope for the reaction (Figure  $\mathfrak{P}$ ).  $\mathfrak{P}$  is  $\mathfrak{P}$  is a substrate scope for the reaction donating as well as electron withdrawing substituents on the aryl ring of alcohols and aldehydes. Both gave > 85% yields of carboxylic acids. Under identical conditions, aliphatic alcohols showed lower percentage of conversion (50-57%). Therefore, with a view to increase the yield by promoting homogeneity, a small amount of CH<sub>3</sub>CN as a co-solvent was added. Unfortunately, there was no improvement in yields even after using a water and acetonitrile (1:1) mixture and yield further decreased when we used pure acetonitrile as the solvent.



**Figure 1**: Substrate scope for the oxidation of alcohols and aldehydes to carboxylic acids. (% yields in parenthesis are for alcohol substrates). Reaction Conditions: Alcohols or aldehydes (5 mmol),  $l_2$  (0.5 mmol), NaOH (1 mmol), TBHP (70% in water; 20 mmol),  $H_2O$  (2 mL), 70 °C, 10-16h. <sup>a</sup>For compound 19 and 20,  $l_2$  (20 mol%), NaOH (0.5 equiv.), TBHP (70% in  $H_2O$ ; 8 equiv.) were used.

This methodology is highly selective towards primary alcohol and aldehyde groups for oxidation. To probe the selectivity, we used 4-methyl benzylalcohol and 2, 4, 6 –trimethyl benzylalcohol as substrates and these were separately treated with aq. KMnO<sub>4</sub> as oxidant as well as employing  $I_2$ /NaOH



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catalytic system. Terephthalic acid 19 was obtained in 55% yield when aq. KMnO<sub>4</sub> was used as oxidant but 4-toluic acid 5 was obtained in 90% yield when I<sub>2</sub>/TBHP was used. We also obtained 2, 4, 6-trimethyl benzoic acid 13 in 82% yield using our methodology but a mixture of partially oxidized products was obtained when aq. KMnO<sub>4</sub> was used (Scheme 4). Similar results were obtained when substituted aldehydes were used as substrates (Scheme 4).

To illustrate a potential application, we used our methodology to convert fructose from biomass into FDCA, a highly desired bio-based feedstock with numerous applications. Simultaneous or successive oxidation of both the functional groups (-CH<sub>2</sub>OH and -CHO) of hydroxymethylfurfural (HMF) has been a challenge for deriving polyester building-block chemicals of commercial importance. Enormous efforts are being undertaken for the production of FDCA by an economically acceptable way that could be scaled up at the industrial level. Partenheimer et. al. described the synthesis of 2,5-furandicarboxylic acid by catalytic air-oxidation of 5hydroxymethylfurfural with Co/Mn/Br in acetic acid at temperatures ranging from 50 to 125° C, commonly known as the Amoco process. Using this catalyst, FDCA was obtained with a maximum yield of 35.2 %.8d



There are few reports on the oxidation of HMF to FDCA using transition metal based heterogeneous catalysts in aqueous medium.<sup>8</sup> However, a major limitation of these reported methods is the requirement of dilute conditions to avoid polymerization or degradation of intermediates.<sup>8g</sup> Hence, most of the reactions were carried out only in milli-gram scale. The use of  $I_2/NaOH$  catalyst in our system enables efficient oxidation of HMF to FDCA in gram scale synthesis (Scheme 5). To understand the reaction mechanism and to identify the active iodine species for these transformations, several control experiments were carried out (Scheme 6). The addition of TEMPO (2, 2, 6, 6-tetramethylpiperidine-N-oxyl) and BHT (butylated hydroxytoluene) had no effect on the yield of the reaction (Scheme  $6_{a-b}$ ), suggesting that the free radical pathway is not involved in the present oxidation reaction. Recently, Wan and co-workers have reported synthesis of an ester from aldehyde by employing n-Bu<sub>4</sub>NI/TBHP catalyst system in water. <sup>111</sup> One can consider that esters as intermediates susceptible to hydrolysis in the presence of base to carboxylic acid. However, no ester was detected under our reaction conditions and it was also observed that there was no



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iodite  $(IO_2^{-})$  (eqn (1), Scheme 7). The iodite  $(IO_2^{-})$  species oxidizes the primary alcohol to aldehyde and gets itself reduced to IO<sup>-</sup>. Next, water molecule attacks the carbonyl centre under this reaction condition i.e. AWS reaction and results in the formation of a tetrahedral intermediate **IM1** (Scheme 7). Following this,  $IO_2^{-}$  oxidises **IM1** to the corresponding carboxylic acid and regenerates IO<sup>-</sup> and water. It may be noted that a reaction of 4-methoxybenzyl alcohol with anhydrous TBHP in anhydrous CH<sub>3</sub>CN as solvent resulted only the formation of 4-methoxybenzaldehyde supporting the AWS reaction.

## Conclusion

In conclusion, we have for the first time developed an efficient, metal free,  $I_2$  / NaOH catalyzed synthesis of carboxylic acids from alcohols and aldehydes in water as the solvent. Our studies indicate that  $IO_2^-$  is the most likely active catalyst which is formed and regenerated by oxidation of IO<sup>-</sup> by TBHP. Operational simplicity, broad substrate scope and ease of scaling up are additional features of this green oxidation method.

## **Conflicts of interest**

There are no conflicts of interest to declare.

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