Adipic Acid Production from Biomass Derivatives

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Introduction

While adipic acid (AA) is an essential precursor in Nylon 66 production, its synthesis relies heavily on petroleum feedstocks, producing nitrous oxide (N_2O), a potent greenhouse gas, as a byproduct.[1] In effort to alleviate these concerns and break dependence on nonrenewable carbon sources, C_6 sugars derived from biomass provide an alternative to petrochemical fuels for AA production.[2] One such pathway requires selective hydrogenolytic ring opening of 2,5-tetrahydrofurandicarboxylic acid (THFDCA), which can be synthesized through sequential oxidation and hydrogenation reactions of 5-hydroxymethylfurfural (HMF).[3]

Selective ring opening of THFDCA to AA has been sparsely studied with the exception of a patent from Rennovia which claims that metal catalysts (Pd/SiO_2) work together with hydriodic acid (HI), molecular H_2, and an acetic acid solvent to selectively form AA from THFDCA (99% yield).[3] Though selective, the underlying reaction mechanism remains elusive. With an ultimate goal to design a heterogeneous catalytic system, we herein compile mechanistic insights through a combination of experimental and computational contributions, observing that ring opening from THFDCA proceeds through the formation of a ring-opened ester prior to C-O bond scission to AA. In this work, we provide strong evidence that HI plays a multifaceted role in the ring opening chemistry where it acts as a strong Brønsted acid to facilitate ring opening through protonation of the cyclic ether, and it activates molecular H_2 to drive hydogenolysis reactions. Based on our understanding, we propose several directions for catalyst design.

Materials and Methods

All reactions were conducted in liquid-phase in a 50 mL stainless steel Parr reactor in a temperature range of 100 to 160 °C, pressurized by H_2. Stainless steel reactors are employed with glass inserts and thermocouple Teflon sheaths to prevent corrosion by acid. After reaction, products were analyzed in both HPLC (Waters Alliance e2695) and HPLC-MS (Agilent 6120), both equipped with a Bio-Rad Aminex HPX-87H (300 mm × 7.8 mm) column.

Results and Discussion

Though metal catalysts are typically needed to activate molecular H_2 in hydrodeoxygenation reactions, our study indicates that the hydrogenolysis of THFDCA occurs readily at 160 °C to form >85% yield of AA after 3 h in the absence of any metal catalyst. In this case, 0.3 M HI was employed in propionic acid under 500 psi H_2, where the interplay between molecular H_2 and HI likely drives the ring opening reaction. This is evidenced by experimentally determined reaction orders with respect to THFDCA, HI, and H_2, all of which maintain a reaction order of one (Figure 1a and 1b). When the concentration of HI or H_2 partial pressure drops to 0, THFDCA conversion drops to 0%, suggesting that both H_2 and HI play key roles in ring opening.

In addition to HI and H_2's importance, the organic acid solvent (propionic acid) plays a critical role on the ring opening chemistry. When the reaction was carried out in water or alcohol solvents under otherwise identical conditions (0.3 M HI, 500 psi H_2 at 160 °C for 3 h), minimal AA formation was observed; moreover, varying the water concentration in propionic acid resulted in a drastic decrease in ring opening activity. Based on experimental and computational evidence, we propose that the ring opening step is mediated by addition of HI

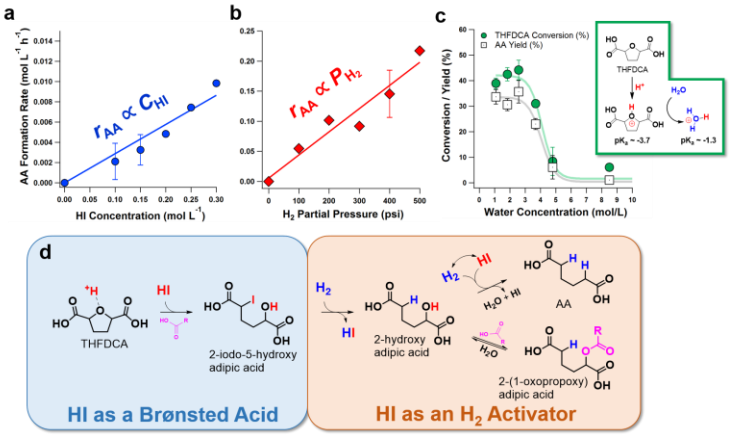

Figure 1. AA formation rates versus HI concentration (A) and H_2 pressure (B), as well as water's detrimental effect on AA yield and THFDCA conversion (C). (D) shows the proposed reaction pathway from THFDCA to AA, whereby HI acts to donate protons and activate H_2.

across the C-O bond, where water's basicity severely inhibits the protonation and subsequent ring opening of THFDCA (Figure 1c and 1d). An additional role of propionic acid might be to stabilize the intermediate hydroxyl species (2-hydroxyadipic acid) by formation of an ester (Figure 1d) which is the only observed reaction intermediate in the reaction.

By employing a commercially available substrate, e.g., malic acid (C_4 hydroxylated diacid), as a model compound to probe the hydrogenolysis step from 2-hydroxyadipic acid to AA, kinetic insights demonstrate that the C-OH bond occurs significantly faster via the combination of H_2 and HI than by HI alone. While HI can act alone to remove C-OH bonds through sequential dehydration and hydrogenation steps, employment of H_2 and HI together cleaves C-OH bonds directly, suggesting that HI activates H_2 either through a redox cycle thereby creating hydride species or through an iodine-mediated radical mechanism subsequently creating hydrogen radicals. Thus, we propose two key roles for HI: 1) to protonate the ether group in THFDCA to facilitate ring opening; and 2) to activate hydrogen to remove C-O bonds.

Significance

Mechanistic insights revealed in this study lay the groundwork for the design of effective heterogeneous materials that can be used to renewably synthesize AA. In addition, this work reveals that HI's effectiveness stems from its ability to act as both a strong Brønsted acid and a mild hydrogenation catalyst, where the cyclic ether can be reduced without losing AA's carboxylic acid groups. This study further provides a general strategy for the removal of C-O bonds in biomass derivatives without the use of expensive noble metals.

References

[1] Oppenheim, D. *Encyclopedia of Chemical Technology* 2014. [2] Van de Vyver, S. and Roman-Leshkov, Y. *Catal. Sci. Tech.* **2013**, *3*, 1465. [3] Boussie et al. US Patent 0317822, Dec. 16, 2010.