

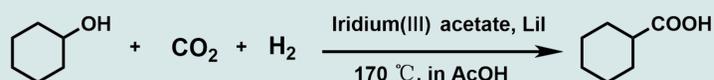
Synthesis of Carboxylic Acids via Hydrocarboxylation of Alcohols with CO₂ and H₂

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01 Introduction

Carbon dioxide (CO₂) is an abundant, easily available and renewable C1 building block. The utilization of CO₂ is of great scientific and social significance to alleviate the environment and energy crisis. Carboxylic acids are important basic chemicals that are widely used in industry and everyday life. Synthesis of carboxylic acids using CO₂ as a C1 synthon is an interesting topic. Most classical examples of creating C-C bonds with CO₂ are limited to high-energy or air/water sensitive starting materials, including alkenes, alkynes, aromatic halides or organometallic reagents. Herein, we provided a protocol of synthesizing higher carboxylic acids via the hydrocarboxylation of alcohols with CO₂ and H₂ (Scheme 1). The simple catalytic system consisting of Iridium(III) acetate and LiI was very efficient in accelerating the reaction in the AcOH solvent.



Scheme 1 Synthesis of higher carboxylic acids via alcohol, CO₂ and H₂.

02 Results and discussion

The hydrocarboxylation of cyclohexanol with CO₂ and H₂ to synthesize cyclohexanecarboxylic acid was selected as the model reaction. To optimize the catalytic system, we screened the type of catalysts, promoters, solvents, and other reaction conditions. The results indicated the catalytic system consisting of Iridium(III) acetate catalyst and LiI promoter is fit for the reaction. Figure 1 shows the yield of product at different temperatures, suggesting that 170 °C is a suitable temperature at 6 MPa CO₂ and 1 MPa H₂. The yield based on cyclohexanol could reach 65.2%. The catalytic system could be applied to various ether substrates (Figure 2), such as primary and secondary alcohols, diols and triols.

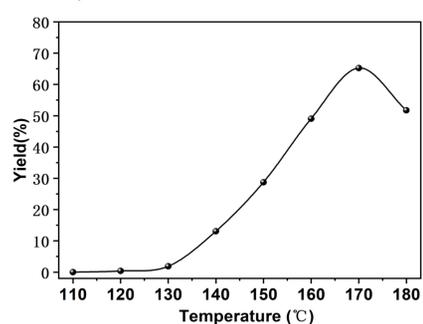


Figure 1 Effect of temperature on this reaction. Reaction conditions: 45 μmol Iridium(III) acetate (based on Ir), 2 mmol LiI and 0.5 mL AcOH, 2.25 mmol cyclohexanol, 6.0 MPa (68 mmol) CO₂ and 1 MPa H₂ (at room temperature), 16 h.

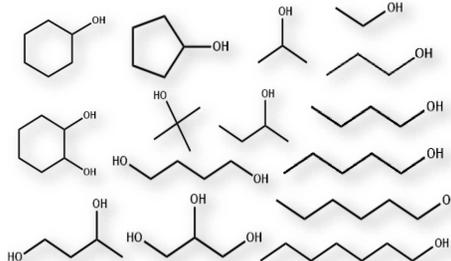


Figure 2 Various substrates.

The time course of the reaction is showed in Figure 3. Large amounts of cyclohexene were produced at 0-1 h, accompanied by rapid depletion of cyclohexanol. Meanwhile, cyclohexyl acetate and iodocyclohexane also increased with time. Then, cyclohexanol was completely consumed, and other intermediates decreased. Cyclohexanecarboxylic acid increased gradually, and almost no change until 16 h. It suggested that cyclohexanol was first converted to cyclohexene, cyclohexyl acetate and/or iodocyclohexane, and then cyclohexanecarboxylic acid was generated. Besides, CO progressively increased and then kept at a nearly constant level during the reaction. The CO pathway was further confirmed by tracer experiments using ¹³CO₂, H₂¹⁸O, D₂O and D₂ respectively. To our knowledge, this is the first work on alcohol hydrocarboxylation with CO₂ and H₂ using an iridium catalyst. Accordingly, we proposed the possible mechanism of the reaction (Figure 4).

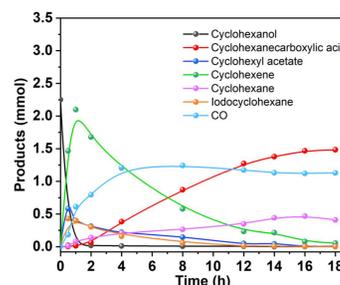


Figure 3 Time course of the reaction. Reaction conditions: 45 μmol Iridium(III) acetate (based on Ir), 2 mmol LiI, 0.5 mL AcOH, 2.25 mmol cyclohexanol, 6.0 MPa (68 mmol) CO₂ and 1 MPa H₂ (at room temperature), 170 °C.

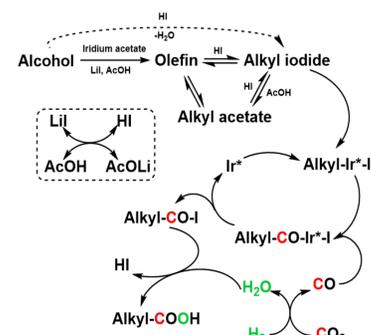


Figure 4 The proposed reaction mechanism.

03 Conclusion

In summary, we designed an effective catalytic system for synthesizing carboxylic acids from alcohols, CO₂ and H₂ under relatively mild conditions. The reaction can take place at over 120 °C catalyzed by the Ir catalyst with high selectivity and yield at optimal temperature. The catalytic system may apply to various alcohols and even polyols. The proposed mechanism indicates the production of higher carboxylic acids via tandem reactions. The alcohol rapidly generated olefin and then converted into alkyl iodides and/or acetates. The oxidative addition of alkyl iodide to active Ir species (Ir*) occurred, and CO, generated by RWGS reaction, insert between the alkyl and Ir. Subsequently, reductive elimination of alkyl-C=O (acyl) occurs with the participation of H₂O, and the C₁-elongated carboxylic acids were accordingly produced. This work provides a new strategy of higher carboxylic acids production and CO₂ utilization.

04 Reference

[1] Y. R. Zhang, Y. Wang, Q. L. Qian*, B. X. Han*. Synthesis of higher carboxylic acids via the hydrocarboxylation of alcohols with CO₂ and H₂[J]. In preparation.