Hydrogenation of Amino Acid Mixtures to Amino Alcohols: Renewable Building Blocks for Fine and Specialty Chemicals Production

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Introduction

Amino alcohols serve as intermediates for numerous pharmaceutical, insecticidal and surfactant applications. Catalytic hydrogenation of amino acids to amino alcohols[1-6] is a route that offers easy integration of readily available biorenewable feedstocks – amino acids derived from plant and animal proteins - into existing industrial manufacturing processes. Additionally, such hydrogenations have been found to be stereoretentive[4], considerably enhancing their utility The development of such routes to use renewables is desirable in light of the strain on petroleum derived feedstocks.

Catalytic hydrogenation of individual amino acids has been studied previously in our laboratory[1-4] and elsewhere[5,6]. Given the complex composition of most biorenewable feedstocks, it is important to study how increase in substrate complexity can affect rate of hydrogenations.. Hence the hydrogenation of a model system of three amino acids: alanine, serine and valine and their mixtures was studied to quantify reaction rates, understand interactions between the substrates and catalyst, and shed light onto the reaction mechanism. The understanding gained from this model system will aid in design of hydrogenation processes of more complex biorenewable feedstocks.

Materials and Methods

Aqueous catalytic hydrogenations were carried out in a Teflon-lined 300ml Parr high pressure reactor (Model 4560). Typical reaction conditions were 1.5 g of substrate in 100 ml water, 130^{o}C, 1000 psi hydrogen pressure, stirring at 1000 rpm, and 1gm of dry 5% ruthenium on carbon. Because hydrogenation of amino acids requires that they be present in the protonated form, a slight molar excess of phosphoric acid is added to the feed solution prior to reaction. Running an experiment involved first reducing the catalyst at 200 psi hydrogen overnight, and then introducing the feed solution to the reactor. Samples were withdrawn at regular intervals and analysed for change in concentrations on a Waters HPLC with UV and ELSD detectors using a reverse phase ion exchange column from Silec Technologies[4].

Results and Discussion

In general, the individual amino acids showed the following order of reactivity towards hydrogenation: Serine > Alanine > Valine. The effect of varying phosphoric acid concentration on the rate of hydrogenation has been studied previously[3] and was verified here in serine hydrogenation. To ensure H_3PO_4 didn't interfere with other effects, H_3PO_4 concentrations were maintained at a constant level in experiments for which rates were compared.

It was found that competitive adsorption between the amino acids influences the reaction rate. In the hydrogenation of serine, for instance, the effect of the presence of other amino acids in feed was studied. Serine at a concentration of 0.25M was hydrogenated a) alone, b)with 0.23M alanine and c) with 0.24M valine. In each of the three cases, H_3PO_4 was present at a concentration of 0.56M. The results are shown in Figure 1 below. The presence of other amino acids inhibits hydrogenation of serine.

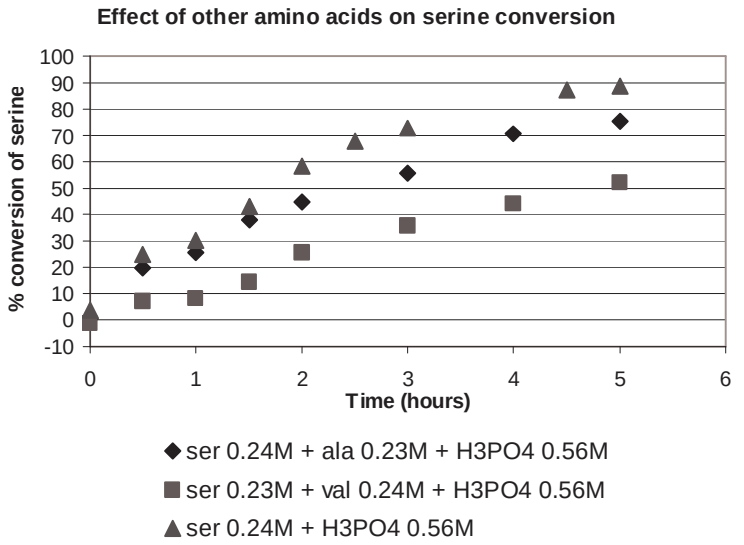

Figure 1. Effect of the other amino acids on the hydrogenation of serine. Reaction conditions : 130^{o}C, 1000 rpm, 0.71M H_3PO_4, 1gm (dry basis) 5% Ru/C, solution volume 100 ml, 1000 psi hydrogen.

The above results lead to the conclusion that adsorption on the catalyst surface, and competition between substrates, plays an important role in catalytic hydrogenation of amino acids on Ru/C catalyst. A Langmuir-Hinshelwood kinetic model to describe the behavior shown in Figure 1 is being developed.

References

1. Jere, F., Ph.D. Thesis, Michigan State University, 2003
2. Molengraft, A., M.S. Thesis, Michigan State University, 2006
3. Jere, F., Jackson, J., Miller, D., *I&EC Research* 43, 3297, 2004.
4. Jere, F., Miller, D., Jackson, J., *Org. Lett.* 5(4), 527, (2003)
5. Antons, S., Beitzke, B. U.S. Patent 5,536,879, 1996
6. Antons, S., Tilling , A., Wolters E., U.S. Patent 6,310,254, 2001