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Evidence for isomerizing hydroformylation of butadiene. A combined experimental and computational study

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ABSTRACT

The (DIOP)rhodium-catalyzed hydroformylation of butadiene has been shown to give among the highest selectivities for formation of adipaldehyde, which is useful for the synthesis of nylon. Herein, isomerizing hydroformylation is shown to be a mechanism that is partially responsible for this selectivity and density functional theory studies are used to reveal the detailed pathway for the requisite alkene isomerization.

1. Introduction

Transition-metal-catalyzed hydroformylation of olefins is one of the most important homogeneous processes for industrial production of aldehydes [1]. Hydroformylation, also known as the "oxo process" was discovered by Otto Roelen in 1938 and subsequently became a highly efficient and widely utilized industrial process for the production of oxo chemicals globally [2]. The resulting aldehydes and aldehyde-derived compounds such as alcohols, amines, carboxylic acids, and esters are also equally valuable for the synthesis of bulk chemicals [3]. As such, hydroformylation of butadiene has been suggested as an ideal process for the production of adipaldehyde.

Adipaldehyde is a potentially valuable intermediate for producing adipic acid and hexamethylene diamine (HMDA) which are key monomers for nylon-6,6 synthesis [4,5]. Currently, nylon-6,6 synthesis relies mainly on two processes [6–12]. First, adipic acid is synthesized by the oxidation of KA oil, utilizing harsh oxidizing agents such as concentrated sulfuric and nitric acids. These strong acids produce large quantities of N_2O gas as a side product, which is a significant environmental concern [6–8]. The resulting adipic acid is subsequently polymerized with hexamethylenediamine (HMDA) to form nylon-6,6. HMDA is predominantly produced by Ni-catalyzed hydrocyanation, which requires extremely careful handling of toxic HCN gas [9–12].

On the basis of the environmental concerns associated with these processes, hydroformylation has emerged as a desirable alternative for adipic acid and HMDA synthesis. Interestingly, both monomers can be synthesized from a common adipaldehyde intermediate by oxidation and reductive amination. Moreover, reduction of adipaldehyde to hexane-1,6-diol would produce a third high-valued monomer for the synthesis of polyesters (Scheme 1) [1,2,13–15]. Therefore, the efficient synthesis of adipaldehyde via hydroformylation of butadiene has significant potential to become industrially valuable. [16–23]

Several groups have reported the atom-economic synthesis of adipaldehyde via the hydroformylation of 1,3-butadiene [16–23]. However, the reactions suffer from limited selectivity to the desired adipaldehyde. For example, the Ohgomori group reported 31% selectivity of adipaldehyde with a catalyst formed from rhodium(I) and the commercially available DIOP ligand [13]. In 2011, the Hofmann group reported that selectivities of up to 50% could be achieved with rhodium(I) combined with bulky bisphosphite ligands [17]. More recently, they have utilized isomerizing hydroformylation to achieve up to 73% yield of an adipaldehyde bis-acetal derivative [24]. However, for industrial practicality the selectivity and activity of the catalysts needs further improvement.

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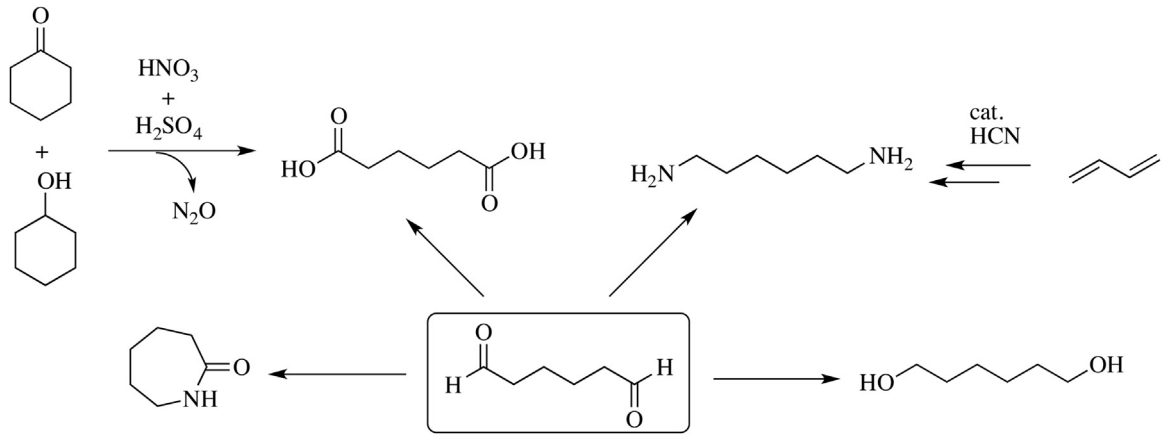


Scheme 1. Versatile utility of adipaldehyde.

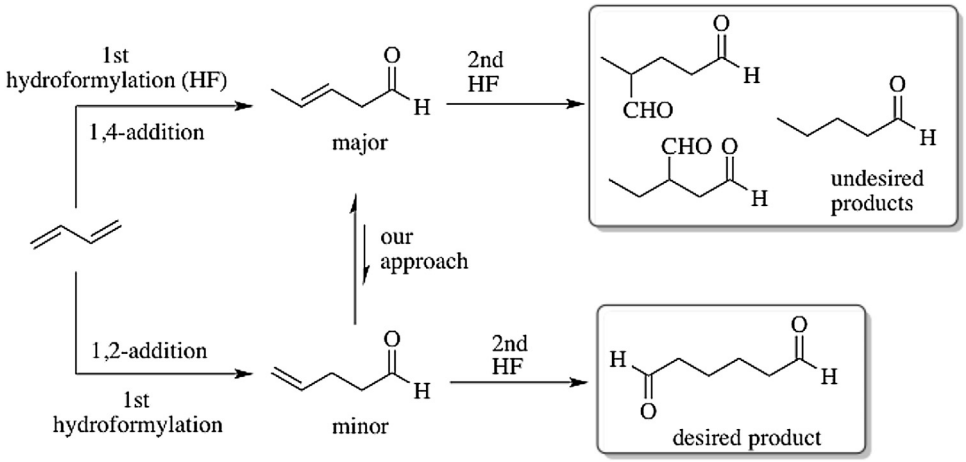
The hydroformylation of butadiene to produce adipaldehyde requires two sequential hydroformylation reactions. Ideally, butadiene would react with syn-gas via 1,2-addition to produce pent-4-enal (Scheme 2), which is known to undergo rapid hydroformylation to form adipaldehyde [16,17]. However, the poor selectivity in hydroformylation of butadiene typically arises from the predominance of 1,4-addition in the first hydroformylation to produce pent-3-enal (Scheme 2). This product is preferentially hydroformylated to produce undesired branched aldehydes and also undergoes hydrogenation. Unfortunately, the formation of pent-3-enal is usually strongly favored both kinetically and thermodynamically. For example, dppe-ligated rhodium provides pent-3-enal with 94% selectivity [16]. Since pent-3-enal can be formed with high efficiency, we became curious whether a catalyst, or catalysts, could effect the isomerization-hydroformylation of pent-3-enal to form adipaldehyde ("our approach", Scheme 2) [25–27]. Such a process would require the development of a catalyst that is highly active for isomerization and highly selective for hydroformylation of the terminal olefin of pent-4-enal.

According to the previous report of the Ohgomori group [16], there is no indication of this type of kinetically controlled *in situ* isomerization of pent-3-enal to pent-4-enal. Hofmann, however, has recently found evidence for such a kinetic pathway with rohodium *phosphite*-catalyzed bis-hydroformylation of butadiene [24], which has been studied extensively (computationally and experimentally). Since the related reaction with the simple DIOP ligand has not been explored in detail from a mechanistic point of view, though it exhibits significant selectivity for adipaldehyde, it was of interest to study whether *phosphine*-ligated rhodium can engage in isomerizing hydroformylation.

Herein, we report the results of a combined experimental and computational study of the hydroformylation-isomerization of butadiene. It is shown that the (DIOP)Rh catalyst does indeed facilitate conversion of pent-3-enal to adipaldehyde via isomerizing hydroformylation, albeit to a limited degree. Density functional theory studies are then used to illuminate the mechanistic features of the critical olefin isomerization.

2. Experimental

Hydroformylation reactions were conducted using a Parr Series 5000 Multiple Reactor System. 1,3-Butadiene was obtained as a solution (20 wt.% in toluene) from Sigma-Aldrich. A typical hydroformylation of butadiene is performed in the following manner. $Rh(acac)(CO)_2$ (4.77 mg, 0.0184 mmol), DIOP (46 mg, 0.092 mmol) and 5 g of butadiene solution (20 wt.% in toluene) were added to an autoclave in the glove box. The autoclave was sealed and removed from the glove box. The autoclave was flushed by syngas (CO/H_2 = 1:1) at 5–6 bar pressure. The procedure was repeated three times at the same pressure to ensure the complete replacement of the Ar by syngas, and then charged by the syngas to 20 bar. The solution was stirred by 1000 rpm while being heated at 80 °C. The heating was continued for 3 h. After 3 h the autoclave was cooled to room temperature and the pressure was



Scheme 2. *In situ* isomerization-hydroformylation concept.