

Comparison of “on water” and solventless procedures in the rhodium-catalyzed hydroformylation of diolefins, alkynes, and unsaturated alcohols



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ABSTRACT

Catalytic systems containing $\text{Rh}(\text{acac})(\text{CO})_2$ or Rh/PAA ($\text{PAA} = \text{polyacrylic acid}$) and hydrophobic phosphine (PPh_3) were used in the hydroformylation of diolefins, alkynes, and unsaturated alcohols under solventless and “on water” conditions. The total yield of dialdehydes obtained from 1,5-hexadiene and 1,7-octadiene reached 99%, and regioselectivity towards linear dialdehydes was higher in the “on water” system. The tandem hydroformylation-hydrogenation of phenylacetylene led to the formation of saturated aldehydes (3-phenylpropanal and 2-phenylpropanal) at 98% conversion with a good regioselectivity towards the linear aldehyde in the “on water” reaction. In contrast, solventless conditions appeared better in the hydroformylation of 1-propen-3-ol. 4-Hydroxybutanal, formed in this reaction with an excellent selectivity, was next transformed to tetrahydrofuran-2-ol via a ring-closure process. Cyclic products were also obtained in hydroformylation of 1-buten-3-ol. In reaction of undec-1-ol and 2-allylphenol linear aldehydes were formed with the yield 69–87%. The hydroformylation of 3-buten-1-ol performed under “on water” conditions showed very good regioselectivity towards a linear aldehyde, 5-hydroxypentanal. Further cyclization of the aldehyde to tetrahydropyran-2-ol was observed.

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1. Introduction

The hydroformylation of olefins is one of the most important homogeneously catalyzed industrial processes with about nine million tons of aldehydes produced annually. Hydroformylation was discovered by Otto Roelen in 1938. However, this reaction is still extensively studied as a highly attractive process to produce aldehydes and alcohols [1].

“On water” and solventless methods of performing catalytic reactions are gaining significant attention in green chemistry due to their advantages as environmentally friendly procedures. In most cases, reactions occur smoothly giving pure products with high selectivity and a high reaction rate. These procedures are also very attractive from the economic point of view because they enable the elimination of environmentally harmful, toxic, and flammable organic solvents [2–7].

The term “on water” means catalytic reactions performed with reactants insoluble in water [5,36].

It was shown that hydrophobic effect, observed when water was used as a solvent, could enhance the rate of organic reactions [8–10].

The hydroformylation of diolefins produces a mixture of mono- and dialdehydes, saturated and unsaturated, linear and branched [11,12]. Dialdehydes are valuable intermediates for the production of a range of commercially significant products such as diamines [13], bicarboxylic acids and their derivatives [14,15], alicyclic and heterocyclic compounds having different structures, [16] and cross-linking agents for polymers, such as proteins, polysaccharides, and other functionalized macromolecular compounds [17–21]. The hydroformylation of diolefins has been carried out in organic solvents [11,22–28] and in scCO_2 [29]. However, attempts to hydroformylate diolefins under “on water” or solventless conditions have not been reported till now.

In contrast to the hydroformylation of alkenes, studies on the hydroformylation of alkynes are still underdeveloped. [1,30–33]. The hydroformylation of phenylacetylene, carried out by Goettmann et al. [31] in an organic solvent with a zirconia-silica catalyst, gave 23% conversion to enals. The same reaction was reported in a patent [34], $\text{Rh}(\text{acac})(\text{CO})_2$ in scCO_2 being used as a catalyst. Here, the reaction products were 3-phenylpropanal (62%), 2-phenylpropanal (18%), and styrene (20%) at 80% conversion.

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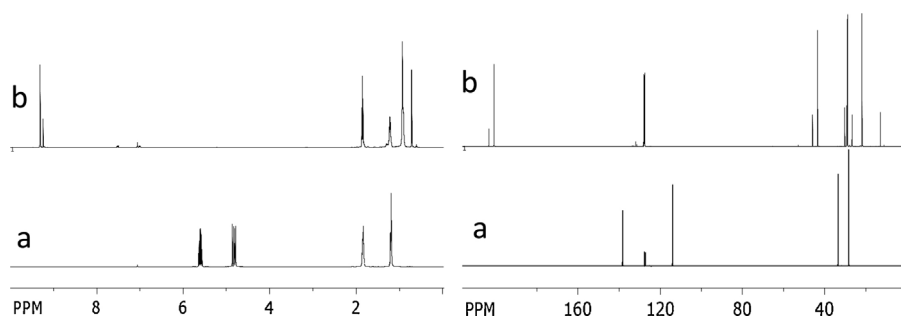


Fig. 1. ¹H NMR and ¹³C NMR spectra (C₆D₆) of a) 1,7-octadiene and b) post-reaction mixture after the hydroformylation of 1,7-octadiene under solventless conditions.

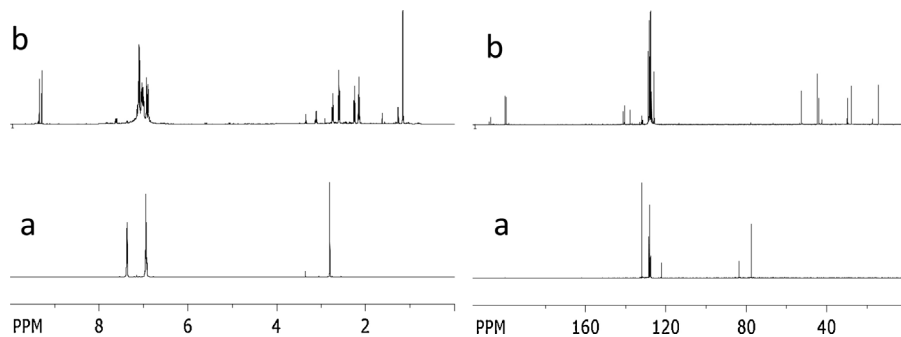


Fig. 2. ¹H NMR and ¹³C NMR spectra (C₆D₆) of a) phenylacetylene and b) solution obtained after the hydroformylation of phenylacetylene under solventless conditions.

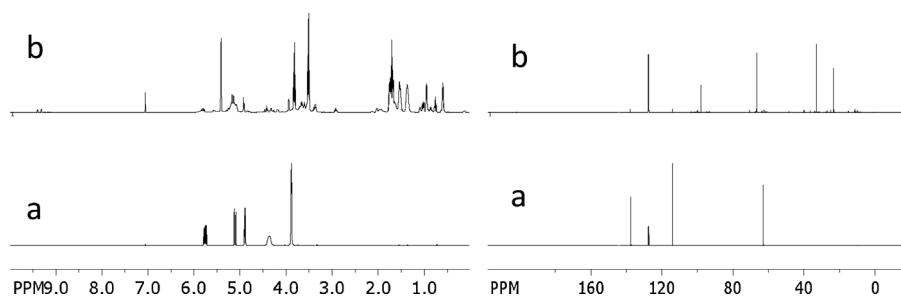


Fig. 3. ¹H NMR and ¹³C NMR spectra (C₆D₆) of a) allyl alcohol and b) products after the hydroformylation of allyl alcohol under solventless condition at substrate to rhodium ratio 600.

4-Hydroxybutanal could be obtained by the hydroformylation of allyl alcohol. It could next be reduced to 1,4-butanediol, an important component in the synthesis of plastics. Often, 4-hydroxybutanal undergoes cyclization to substituted 2-hydroxytetrahydrofuran [35–37].

We have recently developed protocols for the hydroformylation of olefins “on water” and under solventless conditions which give excellent selectivity to aldehydes at a very high activity of Rh catalyst [38].

In this paper, we would like to report the application of these two protocols to the hydroformylation of diolefins, alkynes, and unsaturated alcohols. The catalytic systems contained a water-soluble immobilized catalyst, Rh/PAA, or a water-insoluble complex, Rh(acac)(CO)₂, with an excess of hydrophobic phosphine, PPh₃. The substrates, diolefins, phenylacetylene, and 1-hexyne, are insoluble in water, while allyl alcohols are miscible with water.

2. Experiment section

2.1. The general procedure of hydroformylation

Hydroformylation experiments were carried out in 100 mL (or 50 mL) stainless steel autoclaves provided with a manometer, a

thermostat, a magnetic stirrer, and a gas inlet/outlet system. The catalyst, Rh(acac)(CO)₂ or Rh/PAA, and PPh₃ were placed in the autoclave. Then, 1.5 mL of substrate were introduced into the autoclave under a nitrogen atmosphere. In the case of experiments carried out on water, 1.5 mL of twice distilled water was added. The autoclave was closed, flushed with hydrogen (5 bar) three times, and thereafter pressurized with a synthesis gas (H₂: CO = 1:1) to 10 bar (or 14 bar) and heated to 80 °C (or 60 °C). After the reaction was finished, the autoclave was cooled to room temperature and the residual gases depressurized. The product mixture was immediately analyzed by NMR spectra, the catalyst was removed by Stratospheres™ Spe, and the obtained products were identified by means GC and GC–MS.

Selected reaction mixtures were analyzed additionally using ¹H and ¹³C NMR (Figs. 1–3).

3. Results and discussion

3.1. Hydroformylation of 1,7-octadiene

The hydroformylation of 1,7-octadiene was carried out in “on water” and solventless conditions, using rhodium precursors, Rh(acac)(CO)₂ (water-insoluble) and Rh/PAA (water-soluble), as

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