

# SOLVENT EFFECTS ON THE HYDROFORMYLATION OF LONG CHAIN OLEFINS

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## Abstract

The solvent effect on the rhodium-catalyzed hydroformylation of 1-dodecene in a thermomorphic multi-component solvent (TMS) system consisting of *N,N*-dimethylformamide (DMF), decane and 1-dodecene was studied experimentally. The Perturbed-Chain Statistical Associating Fluid Theory equation of state (PC-SAFT) was used to calculate the solvent dependent gas solubilities of carbon monoxide and hydrogen and the partial pressures needed to achieve an equal concentration of dissolved gases in all TMS systems. Kinetic experiments revealed a significant solvent influence of DMF content leading to an additional option to increase selectivity and yield of the desired *n*-aldehyde tridecanal.

## Keywords

Homogeneous catalysis, Solvent effects, Kinetics, Thermomorphic multicomponent solvent systems, Rhodium-catalyzed hydroformylation, 1-dodecene

## Introduction

Rhodium-catalyzed hydroformylation of olefins is one of the most important industrial applications in homogeneous catalysis to produce aldehydes with a world-wide production of over 12 million tons in 2012 (Frey, 2014).

In the Collaborative Research Center Transregio 63 supported by the German Research Foundation (DFG) the concept of thermomorphic multi-component solvent systems (TMS systems) with tunable properties is investigated for the Rh-BiPhePhos catalyzed hydroformylation of 1-dodecene (Kraume, 2013). For a fixed solvent mixture consisting of *N,N*-dimethylformamide (DMF), decane and 1-dodecene the reaction kinetics were investigated in detail (Kiedorf et al., 2014). The postulated

reaction network (see Figure 1) considers the hydroformylation ( $r_{hf,a}$ ,  $r_{hf,b}$ ,  $r_{hf,c}$ ) and hydrogenation rates ( $r_{hg,a}$ ,  $r_{hg,b}$ ) of 1-dodecene and the pseudo-component *iso*-dodecenes as well as the isomerization rate ( $r_{iso}$ ) of 1-dodecene to *iso*-dodecenes. Solvents are known to influence the kinetics, selectivities and yields of reactions (Reichardt; Welton, 2011). This aspect was already briefly studied for the hydroformylation of 1-dodecene (Brunsch, 2013). To evaluate, simulate and optimize the process in a broader range of operating conditions knowledge regarding the influence of the solvents on the reaction network is needed and studied in this contribution.

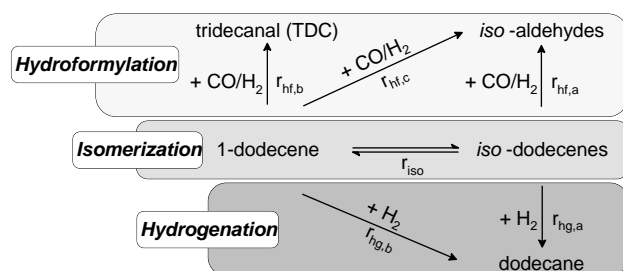


Figure 1: Reaction network of the Rh-catalyzed hydroformylation of 1-dodecene in TMS containing the hydroformylation, isomerization and hydrogenation reactions (based on Kiedorf, 2014).

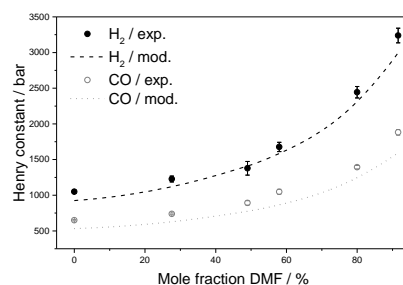


Figure 2: Experimental and PC-SAFT calculated gas solubilities in terms of Henry constant for carbon monoxide and hydrogen in TMS systems (DMF/decane/1-dodecene) with different amount of DMF at 378 K.

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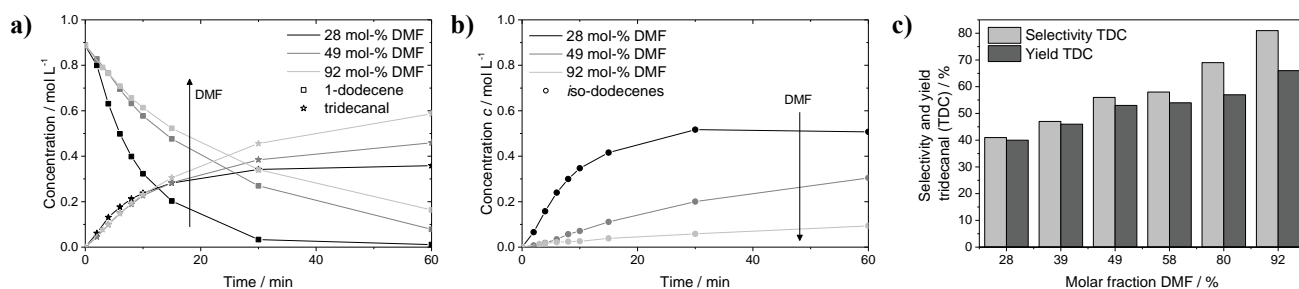


Figure 3: Solvent influence on the Rh-catalyzed hydroformylation of 1-dodecene in different thermomorphic solvent systems (DMF/decane/1-dodecene,  $c_{1-dodecene}^0 = \text{const.}$ ) at 378 K: Concentration profiles for 1-dodecene, tridecanal (a) and iso-dodecenes over time (b), selectivity and yields in tridecanal after 60 min (c).

## Gas Solubilities

To separate the solvent influence from the gas solubility of carbon monoxide and hydrogen in various mixtures of DMF/decane/1-dodecene the Perturbed-Chain Statistical Associating Fluid Theory equation of state (PC-SAFT) (Gross; Sadowski, 2001) was used to calculate gas partial pressures generating identical concentrations in the liquid phase for each solvent mixture. PC-SAFT was already successfully used to predict the gas solubility of carbon monoxide and hydrogen in DMF, decane and 1-dodecene as well as mixtures of that kind (Vogelpohl; Brandenbusch; Sadowski, 2013 and 2014). Results in Figure 2 show a higher solubility of carbon monoxide compared to hydrogen in all TMS systems under investigation. The solubilities of both gases decrease with increasing molar fraction of polar DMF.

## Experimental

Hydroformylation experiments were carried out in a high-pressure reactor system equipped with temperature and pressure controllers. The TMS system consisted of 1-dodecene, decane and DMF in six different compositions varying the molar fraction of polar and non-polar solvent DMF and decane, respectively. Rh(acac)(CO)<sub>2</sub> and BiPhePhos were used as catalyst precursor and ligand, respectively. The initial concentration of 1-dodecene and the reaction volume were kept constant in every experiment. The reactor was pressurized with synthesis gas with respect to the gas solubilities (see Figure 2) up to 39.2 bar at 378 K. Pressure and temperature were kept constant over the entire experiment (60 min). Samples were taken in discrete time steps and analyzed using standard gas chromatography.

## Results

The conducted hydroformylation experiments revealed a significant solvent effect on the hydroformylation of 1-dodecene for different solvent compositions considering the gas solubility of carbon monoxide and hydrogen in different TMS systems (see Figures 3a-c). Depending on the solvent composition the consumption rate of 1-dodecene strongly decreases with the molar fraction of DMF in the TMS system (see Figure 3a). In the same

manner the isomerization rate in Figure 3b decreases while the rate of hydroformylation in Figure 3a is nearly unaffected, leading to an increase in selectivity towards the desired *n*-aldehyde tridecanal (TDC) from 41 up to 74 % with increasing molar fraction of the polar solvent DMF (see Figure 3c). In the same manner the yields in TDC are significantly increased from 40 to 57 %.

The dominant isomerization in the reaction network of the hydroformylation seems to be inhibited by the polar solvent DMF. This inhibition could be further used in terms of process control and to intensify the hydroformylation using exclusively DMF at the beginning and a continuous dosing of decane to the reaction mixture over the time. Thus, the TMS system for product separation after reaction is realized (Kiedorf, 2014) and it is attempted to improve the selectivity and yield of TDC and the conversion of 1-dodecene.

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