

# Gas–liquid–liquid reaction engineering: hydroformylation of 1-octene using a water soluble rhodium complex catalyst

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## Abstract

Hydroformylation of 1-octene was studied in a two-phase system using  $[\text{RhCl}(1,5\text{-COD})]_2$  complex catalyst and the trisodium salt of tri(*m*-sulfophenyl) phosphine (TPPTS) as a water soluble ligand. The reaction was carried out in a batch reactor at pressures between  $1.5$  to  $2.5 \times 10^3$  kPa and temperatures of 333 and 343 K. Ethanol was added as a cosolvent to enhance the octene solubility in the aqueous phase and a buffer solution of sodium carbonate and bicarbonate was used to eliminate the formation of acetals. The hydroformylation products were *n*-nonanal and 2-methyl nonanal with a selectivity to linear aldehyde of about 80%. The reaction is first order with respect to octene and catalyst concentrations. The dependence on the carbon monoxide pressure was found to be complex with an enhancement at low partial pressures and an inhibition rate at high pressures. The reaction rate increased with the hydrogen partial pressure. A thermodynamic analysis concerning the solubilities of octene and gases in the reaction medium was studied and a semiempirical kinetic model was used to describe the rate of reaction.

## 1. Introduction

Hydroformylation of olefins is an important commercial process for the production of aldehydes and alcohols. Homogenous catalysts are widely used for this reaction. An important drawback of this process is the difficulty of separating the products from the catalyst and from any solvent. Therefore the use of a heterogeneous catalyst is preferred to overcome this difficulty. One method of preparing such a catalyst is to heterogenize a homogeneous catalyst onto an insoluble polymer support [1]. However, this approach has found no application in major industrial processes because of problems of catalyst leaching and deactivation. The other alternative is the use of a two-phase system (aqueous–organic) with a water

soluble complex catalyst. This method provides a suitable means by separating the reaction product in the organic phase from the catalytic aqueous phase immediately after the reaction [2].

Kuntz [3] prepared the trisodium salt of tri(*m*-sulfophenyl) phosphine (TPPTS) by sulfonation of triphenylphosphine with oleum followed by neutralization. The complex  $[\text{RhCl}(1,5\text{-COD})]_2$  (where 1,5-COD is 1,5-cyclo-octadiene) is highly insoluble in water, however, displacement of the COD ligand with the TPPTS affords a new complex  $[\text{RhCl}(\text{TPPTS})_n]$  which is actually soluble in water. This complex is successfully used as a catalyst precursor for the preparation of butyraldehyde from propylene by Ruhrchemie [4]. This biphasic process requires a low pressure of syngas but is limited to the hydroformylation of lower olefins.

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