

AN EFFICIENT WATER-SOLUBLE RUTHENIUM HYDROFORMYLATION CATALYST FOR THE EXCLUSIVE FORMATION OF 1-HEPTALDEHYDE FROM 1-HEXENE

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Summary

Hydroformylation of 1-hexene was carried out in a high pressure reactor using water soluble [Ru(III)-EDTA] catalyst, synthesis gas (1:1) CO + H₂ at 50 atm, in 80:20 ethanol-water mixture and at 130 °C. The reaction proceeds with a turnover rate of 11.83 mol product per mol catalyst per hour with the conversion of 1-hexene exclusively (100%) to linear 1-heptaldehyde.

Introduction

Recently, much attention has been devoted to water-soluble catalysts in order to achieve a high conversion of terminal olefins to the linear aldehyde by the hydroformylation reaction [1 - 5]. The use of water-soluble phosphine ligands, especially the sulphonated phosphines [2 - 4], offer a simple biphasic system where the Rh(I) catalyst is maintained in an aqueous phase, while the organic phase contains the reactants and products. The organic products are then separated from the catalyst phase. In the hydroformylation of propylene catalyzed by sulphonated phosphine complexes of Rh(I), a linear:branched aldehyde ratio of 96:4 was achieved [2, 3]. With different water-soluble Rh(I) catalysts and 1-hexene as substrate, a linear: branched aldehyde ratio ranging from 9:1 to 18:1 was obtained [4] at 80 °C and CO pressure of 8 atm in a contact time of 15 h. Water-soluble cobalt carbonyl complexes [5] gave even much smaller ratios of linear:branched aldehydes in the hydroformylation of 1-hexene.

The present work reports an efficient water-soluble Ru(III)-EDTA catalytic system for the hydroformylation of 1-hexene to yield 100% 1-heptaldehyde in a homogeneous system at 130 °C and 50 atm of syn gas in a contact time of 12 h. The catalyst can be recycled many times without any degradation.

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Experimental

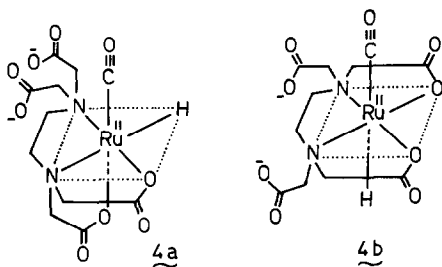
The complex $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ (EDTA = ethylenediaminetetraacetic acid) was prepared according to the procedure described elsewhere [6]. Synthesis gas 1:1 ($\text{CO}:\text{H}_2$) was procured from Indian Oxygen Limited, Bangalore, India. 1-Hexene was obtained from Aldrich Chemical Company, Inc., USA and ethanol was twice distilled before use.

Apparatus and procedure

The hydroformylation of 1-hexene was carried out in a 300 ml stainless steel pressure reactor (Parr Inst. Co.) provided with automatic temperature control and a thorough gas-liquid mixing agitator system. The operating procedure has been described in an earlier communication [10]. The $[\text{Ru}(\text{III})-\text{EDTA}]$ complex 3×10^{-3} M and 0.426 M 1-hexene substrate were mixed in 142 ml of 80:20 ethanol-water solvent mixture; the bomb was pressurised to 50 atm of ($\text{CO} + \text{H}_2$) gas when the desired temperature of 130 °C was attained. The reaction was continued and liquid samples were withdrawn at different time intervals and analyzed for reactant and products by GLC (Shimadzu, Japan) using a TCD detector. The column used for analysis was 2.0 m long 10% Carbowax 20M on 90/100 mesh Anakrom-As acid washed and silanized. Carrier gas (H_2) flow rate 20 ml min^{-1} was used in the temperature programming in the range 60 - 160 °C. Conversion of 1-hexene and selectivity for 1-heptaldehyde were calculated based on the peak areas of the synthetic mixture and the unknown sample. The reaction was continued until complete conversion of 1-hexene, ascertained by the complete disappearance of the 1-hexene peak in the GLC. Only the product peak corresponding to 1-heptaldehyde was obtained during GLC analysis. The product was further separated by vacuum distillation and characterized by IR and NMR techniques. The contact time required for complete conversion of 1-hexene was found to be 12.0 h, yielding exclusively linear product 1-heptaldehyde; no isomeric/branched aldehydes were found.

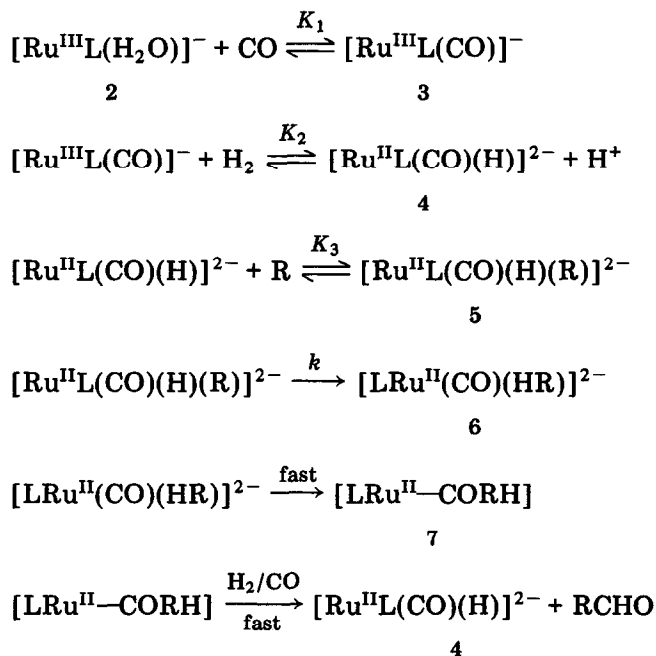
Results and discussion

The water-soluble $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA}-\text{H})\text{Cl}]$ 1 readily gives the *aquo* species $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA})(\text{H}_2\text{O})]$ 2 [7]. Reaction of 2 in the presence of CO results in the formation of the paramagnetic carbonyl complex $\text{K}[\text{Ru}^{\text{III}}(\text{EDTA})(\text{CO})]$ 3 by displacement of the coordinated water molecule [8]. Complex 3 is paramagnetic with a μ_{eff} of 1.92 BM, corresponding to one unpaired spin of a $(t_{2g})^5 \text{Ru}(\text{III})$ configuration. The $\nu(\text{CO})$ in complex 3 is observed at 1960 cm^{-1} . In the presence of hydrogen, complex 3 undergoes reduction to the Ru(II) hydridocarbonyl species $[\text{Ru}^{\text{II}}(\text{H})(\text{CO})(\text{EDTA})]^{2-}$ 4 [9], with the hydride peaks at -20.07 ppm and -8.11 ppm corresponding to the formation of isomers 4a and 4b in solution, respectively, the *cis* hydride 4a being the predominant form. Thus 4a is considered to be the active catalytic species in the hydroformylation of 1-hexene.



The hydroformylation of 1-hexene conducted at 50 atm of CO + H₂ (1:1) syn-gas, a catalyst concentration of 3×10^{-3} M and substrate concentration of 0.426 M proceeds with 100% conversion to 1-heptaldehyde in a contact time of 12.0 h. This corresponds to a turnover rate of 11.83 mol product per mol catalyst per hour. Isomeric products of hydroformylation of 1-hexene other than the exclusive linear product 1-heptaldehyde were not observed. Escaffre *et al.* [4] have recently reported a turnover rate of 28 mol product per hour in the hydroformylation of 1-hexene based on the dinuclear species $\text{Rh}_2(\mu\text{-SBU}^t)_2(\text{CO})_2(\text{LS})_3$ (LS = trisulphonated phosphine, $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$) with a linear to branched ratio of 18:1.

Based on the kinetic observations, the probable mechanism of 1-hexene hydroformylation catalyzed by **3** is given in Scheme 1.



L = EDTA-H, R = 1-hexene

Scheme 1.

The first step in the hydroformylation mechanism is the formation of a carbonyl complex 3, which reacts with hydrogen to form the mixed ligand Ru(II) hydridocarbonyl complex 4. Complex 4, which is the active catalytic species, combines with the olefin to form the unstable mixed ligand olefin complex 5. The rate-determining step of the reaction is the transfer of hydride to the olefinic bond of 1-hexene, giving an alkyl complex 6. The insertion of CO in the metal-carbon bond of the alkyl complex 6 to give acyl [10 - 12] complex 7, and a further reaction with one mole of CO and H₂ takes place in two fast reaction steps, giving back the catalytic species 4 and the product aldehyde.

From the mechanism shown in Scheme 1 and kinetic observations, the following rate equation is derived for the hydroformylation of 1-hexene:

$$\text{rate} = kK_1K_2K_3[\text{Ru}^{\text{III}}(\text{EDTA})][\text{CO}][\text{H}_2][\text{R}] \quad (1)$$

where $[\text{Ru}^{\text{III}}(\text{EDTA})]$ = catalyst concentration, $[\text{CO}]$ = carbon monoxide concentration, $[\text{H}_2]$ = hydrogen concentration and $[\text{R}]$ = 1-hexene concentration. K_1 , K_2 and K_3 are the equilibrium constants and k is the rate constant for the reaction. The equilibrium constant K_2 also combines a rate constant for the reduction of Ru(III) to Ru(II) by molecular hydrogen. If $[\text{Ru}^{\text{III}}(\text{EDTA})]$ is expressed in terms of its total concentration $[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}$, the final rate laws are:

$$\text{rate} = \frac{kK_1K_2K_3[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}[\text{CO}][\text{H}_2][\text{R}]}{1 + K_1[\text{CO}] + K_1K_2[\text{CO}][\text{H}_2] + K_1K_2K_3[\text{CO}][\text{H}_2][\text{R}]} \quad (2)$$

$$\frac{[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}}{\text{rate}} = \left[\frac{1}{kK_1K_2K_3[\text{CO}][\text{H}_2]} + \frac{1}{kK_2K_3[\text{H}_2]} + \frac{1}{kK_3} \right] \frac{1}{[\text{R}]} + \frac{1}{k} \quad (3)$$

From eqn. (3), the value of the rate constant k was obtained from the intercept of a straight line obtained by plotting $[\text{Ru}^{\text{III}}(\text{EDTA})]_{\text{T}}/\text{rate}$ vs. $1/[\text{R}]$. From the slope of the above straight line, the value of the equilibrium constant K_3 was calculated by substituting the known values K_1 , K_2 obtained separately [9], and k , $[\text{CO}]$ and $[\text{H}_2]$. The values of the constants obtained for the hydroformylation of 1-hexene reactions are:

$$K_1 = 4.9 \text{ M}^{-1}, K_2 = 190.6 \text{ M}^{-1}, K_3 = 5.33 \text{ M}^{-1}, k = 0.322 \text{ min}^{-1}.$$

Conclusions

Hydroformylation of 1-hexene using syn-gas and water-soluble $[\text{Ru}^{\text{III}}(\text{EDTA})]$ catalyst in a mixed ethanol-water solvent system gave exclusively a linear product, 1-heptaldehyde. This is the first report of its kind wherein 100% conversion of an olefin gave only linear aldehyde. The high specificity of the reaction to linear aldehyde may be due to the steric constraints imposed on the coordinated olefin due to the presence of coordinated EDTA in 4.

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