

Hydroformylation of propylene to butyraldehyde using dichloro-bis(salicylaldehyde)-*o*-phenylenediiminato ruthenate(III)

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Abstract

Butyraldehyde is obtained by the hydroformylation of propylene in aqueous medium catalysed by Ru^{III}-saloph-CO complex at 27 atm CO+H₂ (1:1) syn gas with C₃H₆:syn gas ratio 1:5 and 120 °C with a turnover rate of 17 mol product per mol catalyst per hour.

Synthesis of aldehydes by the hydroformylation of olefins under milder conditions has been of great interest in recent years [1-5]. The usual catalysts involve the metal complexes of cobalt such as cobalt carbonyl [6, 7] and phosphine-coordinated cobalt carbonyl [8], which act at ~130-160 °C and 100-200 atm CO+H₂ (1:1). The commercial preparation of butyraldehyde by the hydroformylation of propylene uses rhodium complexes as catalysts [9, 10]. The advantages [10] of the rhodium complex are low temperature (80-120 °C), low pressure of CO+H₂ (7-30 atm) and the higher selectivity for the more valuable hydroformylation product butyraldehyde.

There are reports in the literature in which hydroformylation of propylene to butyraldehyde was achieved using ruthenium complexes as catalysts at 150 °C and 150 atm CO+H₂ (1:1) [11]. In the present paper we report the hydroformylation of propylene to butyraldehyde using [Ru^{III}(saloph)CO] complex at 120 °C and 27 atm CO+H₂ (1:1).

Experimental method and results

The complex [Ru(saloph)CO] was prepared by the reported method [12]. The hydroformylation of propylene was studied in aqueous medium in a 300 ml pressure reactor using [Ru(saloph)CO] complex. The bomb, containing C₃H₆ at 4 atm, was pressurized by CO+H₂ (1:1) to the desired value when the desired temperature was attained. The reaction was continued for 4 h; liquid samples were withdrawn from the reactor at specified time intervals and analysed by GLC (Shimadzu GC - 9A) using a 10% Carbowax column. It was observed that up to 4 h only butyraldehyde was formed, after which minor amounts of isobutyraldehyde began to form. The n:i ratio was found to be 10:1. On continuing the reaction for a longer contact time (>6 h) the formation of the corresponding alcohols of butyraldehyde and isobu-

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tyraldehyde was also observed. The product butyraldehyde was further confirmed by taking ^{13}C NMR spectra of ether extract of the reaction mixture. The spectrum of the reaction mixture showed peaks corresponding to n-butyraldehyde (^{13}C δ 206 ppm for C=O) and some unreacted propylene (^{13}C δ 115 and 136 ppm for alkene carbons and 18.7 ppm for CH_3 protons). The conversion of propylene to butyraldehyde after a contact time of 4 h was found to be 60%, and the turnover rate for butyraldehyde formation is 17 mol product per mol catalyst per hour. The reaction was also conducted at atmospheric pressure of $\text{CO} + \text{H}_2$ (1:1) with C_3H_6 :syn gas ratio 1:5 and 50 °C. The yields of butyraldehyde were reduced to half as compared to the yields obtained at 120 °C and 27 atm $\text{CO} + \text{H}_2$ (1:1).

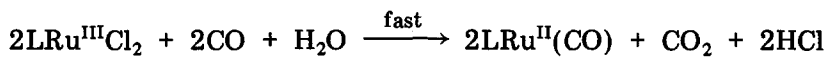
The hydroformylation of propylene to butyraldehyde was also carried out using $[\text{Ru}(\text{EDTA})\text{CO}]$ complex at 120 °C and 27 atm $\text{CO} + \text{H}_2$ (1:1) with C_3H_6 :syn gas ratio 1:5. It was observed that along with butyraldehyde, isobutyraldehyde also formed from the second hour onwards. The yield of butyraldehyde was found to be about 15 times less as compared to the $[\text{Ru}(\text{saloph})\text{CO}]$ complex. The n:i ratio for $[\text{Ru}(\text{EDTA})\text{CO}]$ complex was found to be 3.0, and the overall turnover rate in terms of formation of both normal and isobutyraldehyde was 16 mol products per mol catalyst per hour.

Discussion

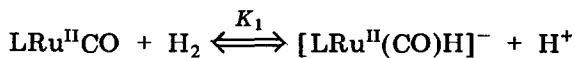
The mechanism for the $[\text{Ru}^{\text{II}}(\text{saloph})\text{CO}]$ complex catalysed hydroformylation of propylene to butyraldehyde is shown in Scheme 1.

In the proposed mechanism, in the presence of $\text{CO} + \text{H}_2$ the $\text{Ru}(\text{III})$ Schiff base complex $[\text{LRu}^{\text{III}}\text{Cl}_2]^-$ is reduced to $\text{LRu}^{\text{II}}(\text{CO})$ species **1**, which is the actual catalyst in the reaction. Complex **1** reacts with H_2 with a heterolytic cleavage of the latter to form the monohydrido species **2** in a pre-equilibrium step. In a second pre-equilibrium step K_2 , the hydrido complex **2** forms an intermediate mixed ligand olefin complex **3** with a rate-determining transfer of H to the olefin to form the alkyl complex **4**. Fast inserting CO in **4** results in the formation of acyl complex **5**, which undergoes hydrogenolysis in the presence of CO in a fast step to form the hydride **2** and the product butyraldehyde. Transfer of the hydride in step **4** to the β -carbon atom results in the formation of isobutyraldehyde. In the catalysis by complex **1**, Markownikoff's addition of the hydride to the α -carbon atom is however favoured over the transfer to β -carbon atom; the latter however picks up slightly with the progress of the reaction. The formation of carbonyl complex **1** is supported by the IR spectrum of the complex in solution, which shows a peak at 1970 cm^{-1} and also a LMCT band in the electronic spectrum of the complex at 370 nm [13–15]. The proton NMR of the hydride **2** gives a multiplet in the region -20.0 to -30.0 ppm. The insertion of CO in the alkyl intermediate and the hydrogenolysis of the acyl intermediate are the usual fast steps in the hydroformylation catalysed by cobalt and rhodium complexes [16–18].

The values of equilibrium constants K_1 and K_2 and the rate constant k obtained at 120 °C are:

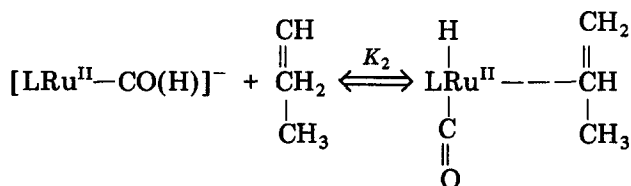


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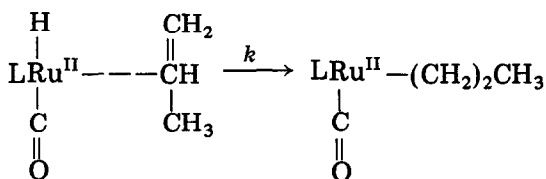
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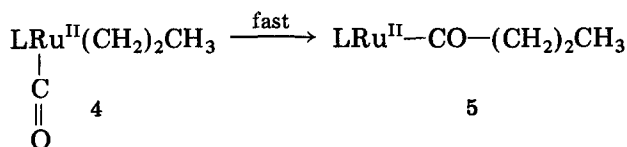
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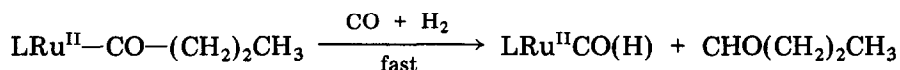
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5



5

L = bis(salicylaldehyde)-*o*-phenylenediimine

Scheme 1.

$$K_1 = 18.0 \text{ M}^{-1}$$

$$K_2 = 27.0 \text{ M}^{-1}$$

$$k = 8.3 \text{ min}^{-1}$$

The turnover rate for the reaction is 17 mol butyraldehyde per mol catalyst per hour.

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