

Letter

Hydroformylation of Allyl Alcohol Catalyzed by Ru(III)-EDTA Complex using Carbon Monoxide and Water as a Source of Hydrogen

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Introduction

In recent years many attempts have been made to use water as a source of hydrogen using CO [1], which is a good hydroxyl acceptor. The large-scale production of hydrogen is generally carried out by the water-gas shift reaction of CO and H₂O using metal oxide catalysts at a pressure of 200 atm and at 450 °C [2]. This reaction is of major economic importance, since it represents one of the largest industrial exploitations of carbon monoxide. With the increasing demand for fertilizer (urea), the production of hydrogen through the water-gas shift reaction has become important. Several attempts using soluble transition metal carbonyls [3, 4] as catalysts for water-gas-shifts have been made and have met with poor yields.

The present study reports an indirect generation of hydrogen using CO and water catalysed by K[Ru^{III}(EDTA-H)Cl]·2H₂O complex, creating hydroformylation conditions *in situ* for the transformation of allyl alcohol into γ -hydroxy-butyraldehyde. This compound, on further hydrogenation, gives 1,4-butanediol, a chemical required in polymer application [5, 6].

Experimental

The reagents allyl alcohol A.R. grade and carbon monoxide gas procured from BOC, U.K. purity > 99.9%, verified by GLC, were used in the carbonylation experiments. Ruthenium(III) chloride was obtained from Johnson Matthey Inc. The disodium salt of ethylenediaminetetraacetic acid (EDTA) was of A.R. grade. The complex 1 K[Ru^{III}(EDTA-H)Cl]·2H₂O was prepared according to the procedure described elsewhere [7].

Allyl alcohol carbonylation was carried out in a 300 ml pressure reactor (Parr Instrument Co., USA), the standard operating procedure has been described in an earlier paper [8]. The products of carbonylation were anal-

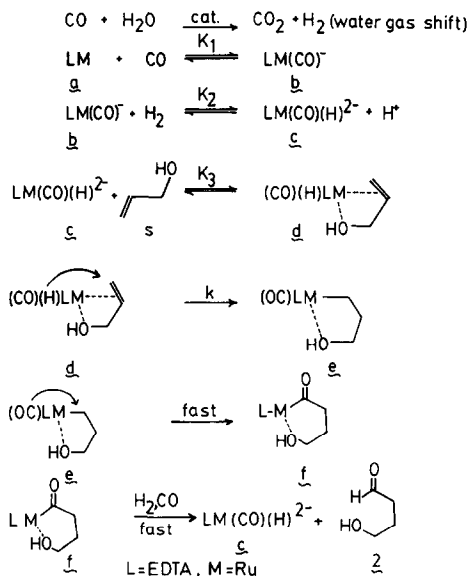
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used by TLC techniques and the rates of carbonylation were calculated by observing moles of allyl alcohol consumed *vs.* time. The allyl alcohol was analysed by GLC (Shimadzu GC 9A, Japan) using a Porapak-Q stainless steel column. A thermal conductivity detector (TCD = 300 °C, injection = 200 °C, column temperature = 150 °C and carrier gas H₂ flow rate = 30 ml min⁻¹) was used for the analysis.

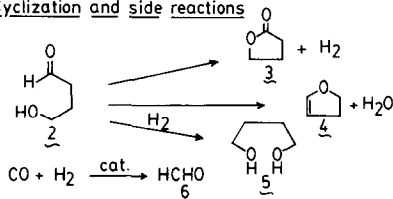
Results and discussion

The allyl alcohol carbonylation catalyzed by complex 1 using CO and water conducted at CO pressures between 10 - 40 atm and in the temperature range 110 - 130 °C gave γ -hydroxybutyraldehyde (2, 35%) as the major product and γ -butyrolactone (3, 25%), dihydrofuran (4, 25%), 1,4-butanediol (5, 1%) and a small amount of formaldehyde (6) as the side products.

The product distribution of allyl alcohol, which is the same as the hydroformylation of allyl alcohol catalysed by complex 1 under identical conditions using (CO + H₂) 1:1 gas mixture [8], reveals that the water-gas shift reaction must have taken place under carbonylation conditions, generating H₂ in a parallel step faster than hydroformylation, as shown below:



Cyclization and side reactions



Scheme 1.



The hydrogen gas thus produced would eventually form a (CO + H₂) gas mixture, creating hydroformylation conditions in solution. Therefore, carbonylation of allyl alcohol results in a product distribution identical to that of hydroformylation, which we have reported in our earlier studies [8]. The water-gas shift reaction was confirmed independently by carrying out reaction using CO, water and complex 1 with no other substrates. The rate of formation of CO₂ and H₂ under carbonylation conditions of allyl alcohol studied with complex 1 is consistent with observations made [9] where 80% of CO is converted initially into H₂ and CO₂ at carbonylation conditions of 10 - 40 atm and 110 - 130 °C. The mechanism of the reaction catalysed by complex 1 is as shown in Scheme 1.

The mechanism suggested in Scheme 1 is similar to that proposed for allyl alcohol hydroformylation [8], except the hydrogen forms via an independent water-gas shift reaction.

The kinetics of the carbonylation of allyl alcohol was also investigated and it was found that the initial rates of carbonylation have a first-order dependence on catalyst, substrate and dissolved CO concentrations. The other kinetic constants remained as reported earlier [8].

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