Catalysis Letters 9 (1991) 55–58

HYDROFORMYLATION OF OLEFINS WITH WATER-SOLUBLE RHODIUM CATALYSTS IN THE PRESENCE OF α-CYCLODEXTRIN

John R. ANDERSON, Eva M. CAMPI and W. Roy JACKSON *

Department of Chemistry, Monash University, Clayton Vic. 3168, Australia

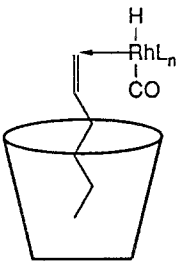
Received 7 January 1991; accepted 22 February 1991

Hydroformylation of hex-1-ene using a water soluble rhodium catalyst $HRh(CO)[PPh_2(m\text{-}C_6H_4SO_3Na)]_3$ ($HRh(CO)(TPPMS)_3$) (I), gives lower yields when α-cyclodextrin is added to the biphasic reaction system implying an interaction between the cyclodextrin and rhodium catalyst.

Keywords: Olefin hydroformylation, rhodium catalysis, water soluble phosphines, α-cyclodextrin

1. Introduction

There is much current interest in the use of water soluble catalysts in organic synthesis [1] and also of cyclodextrins as inverse phase transfer reagents [2]. In particular, the use of water-soluble rhodium catalyst systems for hydroformylation of terminal alkenes has been reported [3,4]. In this paper we report on the use of a water-soluble catalyst system with α-cyclodextrin on the biphasic hydroformylation of hex-1-ene. Under these conditions, inverse phase transfer of hex-1-ene by α-cyclodextrin should occur [5]. The water soluble rhodium catalyst bearing bulky phosphine ligands is not capable of penetrating the cyclodextrin cavity and thus it was anticipated that hydroformylation would preferentially occur on an exposed double bond leading to high selectivity for the *n*-isomer (as indicated schematically below for attack at the less hindered end of the double bond). During the progress of our work we were encouraged by the report of high



normal to iso-aldehyde ratios (n/i) from hydroformylation using water-soluble rhodium catalysts in a biphasic system [3].

2. Results and discussion

A series of hydroformylations was carried out using a 100 ml stainless steel autoclave with stirring. The product was isolated in ether, and yields were calculated from the mass of recovered material the composition of which was established by g.l.c. and confirmed by ^1H n.m.r. spectroscopy. Most reactions were carried out using hex-1-ene (5 ml, 40 mmol) with water (15 ml). With a large excess of CO/H_2 (molar ratio 1/1) in the autoclave, reaction was carried out under approximately constant pressure conditions.

3. Reactions using $HRh(CO)(TPPMS)_3$ (I)

Hydroformylation of hex-1-ene for five hours using water-soluble $HRh(CO)(TPPMS)_3$ with excess TPPMS (Ratio Rh : TPPMS : alkene = 1 : 5 : 1700) at 125 °C with 825 psi initial CO/H_2 pressure, gave a mixture of linear and branched aldehydes in ratio 7 : 3 and in an isolated yield of 55%. This result contrasts with a previous report in which a mixture of alkenes was reacted under similar conditions but using the trisulfonated phenylphosphine (TPPTS) as a rhodium ligand [3], i.e. $HRh(CO)(TPPTS)_3$ (II). Although comparable yields of aldehyde were reported, the high n/i ratio of ca 25 : 1 was not realized in our work using the monosulfonated phosphine. Other workers [6], have reported high n/i ratios (9 : 1) using the trisulfonated system but under milder reaction conditions. (80 °C, 115 psi CO using water as a hydrogen source for 15 h). Attempted reaction of hex-1-ene using (I) and TPPMS at 80 °C for twenty hours with an initial pressure of 400 psi of CO/H_2 gave only a very low yields of aldehydes (ca 5%) with a n/i ratio of 7 : 3. This low yield is in agreement with the observation of Horvath [3] that the catalytic activity is $HRh(CO)(TPPTS)_3$ in hydroformylation is low even at 100 °C with an initial CO/H_2 pressure of 725 psi.

Reactions of hex-1-ene were then carried out using $HRh(CO)(TPPMS)_3$ (II) at 125 °C, 825 psi CO/H_2, but in the presence of added α-cyclodextrin. The ratio of Rh : TPPMS : alkene : cyclodextrin was 1 : 5 : 1700 : 5. The yields of aldehyde dropped significantly to 11% with no change in the n/i ratio. It thus appears that complexation of the rhodium complex with α-cyclodextrin is occurring, leading to a less efficient catalyst system. Reports of similar adverse effects of cyclodextrins on metal catalysed reactions have appeared previously. The Rh(I) catalysed reduction (1) of arylketones was promoted by β-cyclodextrin with which they formed inclusion complexes but was inhibited by α-cyclodextrin [7]. The reduction of aldehydes using sodium formate as the hydrogen source with Ru(II), Ru(I)

and Ir(I) and TPPMS in biphasic systems was inhibited by addition of β-cyclodextrin [8].

4. Reactions using $HRh(CO)(PPh_3)$ (III) with added TPPMS

The reactions described above all involved the use of preformed $HRh(CO)(TPPMS)_3$ catalyst. Reactions were also carried out using the organic-soluble triphenylphosphine complex $HRh(CO)(PPh_3)_3$ (III) with added TPPMS. In this system mixed catalysts formed by ligand exchange, $HRh(CO)(PPh_3)_{3-n}(TPPMS)_n$ could be active. Reaction of hex-1-ene (ratio Rh : TPPMS : alkene = 1 : 5 : 1700) at 80 °C for twenty hours in the absence of water gave a mixture of aldehydes in 39% yield with *n/i* ratio 3 : 1. This isomer ratio is similar to that obtained for the hydroformylation of hex-1-ene using $HRh(CO)(PPh_3)_3$ (III) in organic solvents with added triphenylphosphine but yields are quantitative under the latter conditions. Reaction using a biphasic system under identical reaction conditions gave very similar results (33% yield, *n/i* ratio 3 : 1) suggesting that the reaction is predominantly occurring in the organic phase. Again, addition of α-cyclodextrin resulted in a lower yield (13%). These results support the conclusions reported above and by others [7] that addition of α-cyclodextrin to metal-catalysed reactions leads to lower yields presumably because of interactions between the metal complex and the cyclodextrin. The origin of this interaction that has not been defined in detail, but two previous observations appear to be relevant. First, no evidence could be found [9] for coordination between hydroxyl groups and triphenylphosphine-based rhodium catalysts ($HRh(CO)(PPh_3)_3$) during the hydroformylation of a series of unsaturated alcohols in organic solvents, suggesting that interaction of this type of catalyst with the hydroxyl groups of cyclodextrin would also be of negligible significance. Second, we note the operation of cyclodextrins as second sphere ligands for transition metal complexes [10–12] in which there is an interaction between CD-hydroxyls and appropriate ligands or ligand functional groups (e.g. interaction between α-CD-hydroxyls and NH_3-ligands in $[Rh(cod)(NH_3)_2]^+$ or (en) ligand in $[Rh(cod)(en)]^+$). On this basis, we suggest in the present case a hydrogen-bonding interaction between α-CD-hydroxyls and ligand sulphonate groups in $HRh(CO)(TPPMS)_3$. Examination of molecular models shows that $HRh(CO)(TPPMS)_3$ can easily adopt a conformation allowing hydrogen bonding between hydroxyls in a face of α-CD and three sulphonate groups, one from each of the TPPMS ligands. Thus, the effect of this complex formation is to reduce the ease of replacement of a phosphine group by reactant olefin, thus tending to inhibit hydroformylation. It has been previously suggested [13] that the relatively high stability of $HRh(CO)(TPPMS)_3$ in aqueous solution for dissociation of a phosphine group is a consequence of hydrogen bonding with the solvent.

Acknowledgements

We thank the Australian Research Council for their support and Johnson Matthey Pty. Ltd. for a loan of rhodium.

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