



Regioselective and rapid hydroformylation of vinyl acetate catalyzed by rhodium complex modified bulky phosphite ligand

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ABSTRACT

The regioselective hydroformylation of vinyl acetate catalyzed by rhodium complex of monodentate phosphite ligand, tri-1-naphthylphosphite P(ONp)₃, was investigated. The P(ONp)₃ ligand exhibited a considerable impact on the rate and selectivity of hydroformylation of vinyl acetate, notably high turnover frequency (up to 11,520 h⁻¹) with excellent regioselectivity (99%) to the preferred branched aldehyde and high selectivity to aldehyde (93%). Significant results with the substrate having less reactive character toward hydroformylation and practically easy accessibility of the ligand (synthesized from inexpensive compound, 1-naphthol) make this system very attractive.

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1. Introduction

Hydroformylation of olefins represents efficient method to prepare aldehydes, and is one of the industrially most important C–C bond forming reactions catalyzed by Co and Rh metal complexes [1–3]. Hydroformylation has been mainly studied for terminal olefins. However, in recent year, there has been increased interest in the hydroformylation of functionalized olefins such as alkyl acrylate [4], allyl cyanide [5], allyl alcohol [6], enamide [7], and vinyl acetate [8]. The hydroformylation of such substrates offers the products having two functional groups widely used in organic syntheses. Particularly, vinyl acetate as substrate provides gate way to valuable building blocks for the preparation of bifunctional intermediate (Scheme 1), which can be further converted into synthetically useful compounds such as 1,2- and 1,3-propanediol, lactic acid and ethyl lactate.

Vinyl acetate is generally less reactive to syngas relatively to terminal alkenes [9]. The reaction suffers from a slow rate, formation of by-products and the high pressure (200 atm) is often required to achieve high turnover frequency [10]. However, there are few reports wherein hydroformylation of vinyl acetate is carried out under mild conditions [11–13] wherein good regioselectivity was achieved by sacrificing the reaction rate. Therefore, in

the past decades, efforts have been made to increase the regioselectivity with high reaction rate and decreased undesired side products [14–16]. The high reaction rates for the hydroformylation of vinyl acetate were obtained using bidentate ligands [15] or with electron-deficient ligand such as organo phosphite ligand [16] in comparison with the electron-rich analogues. We have recently reported the synthesis and application of rhodium complex of novel monodentate bulky phosphite ligand, P(ONp)₃ for the hydroformylation of olefins such as 1-hexene, styrene and cyclohexene [17]. In this context, we explore the catalytic activity of Rh/P(ONp)₃ system toward vinyl acetate hydroformylation. Herein, we report the highly regioselective and rapid hydroformylation of vinyl acetate to the branch aldehyde in the presence of Rh(CO)₂(acac) and P(ONp)₃ ligand.

2. Experimental

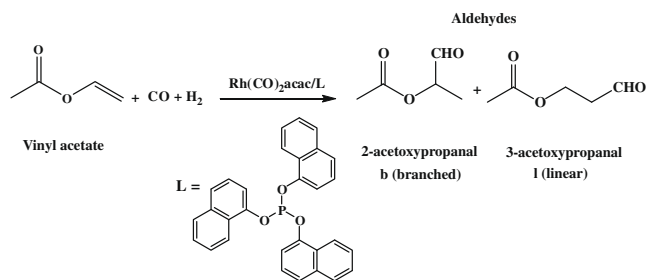
2.1. General remarks

The ligand synthesis was performed using standard Schlenk technique under nitrogen atmosphere. THF was distilled from sodium/benzophenone prior to use. Toluene was purchased from Sigma–Aldrich as anhydrous grade material and used as received. Et₃N was distilled from sodium and stored under N₂. PCl₃ and 1-naphthol were obtained from Merck, India, and used as received. Rh(CO)₂(acac), triphenyl phosphine (PPh₃), triphenyl phosphite P(OPh)₃, tricyclohexylphosphine (PCy₃), 1,3-bis(diphenylphos-

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Scheme 1. Rh/tri-1-naphthyl phosphite catalyzed hydroformylation of vinyl acetate.

phino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), tris(4-methoxyphenyl)phosphine (*p*-MeO-C₆H₄)₃P, tris(4-trifluoromethylphenyl)phosphine (*p*-CF₃-C₆H₄)₃P and vinyl acetate were purchased from M/s Sigma-Aldrich Chemicals, USA and used as received. The syngas (99.9%) used was from Hydro Gas India Pvt., Ltd., India.

The synthesis and characterization of phosphite ligand P(ONp)₃ as well as corresponding rhodium complex has been described elsewhere [17]. The hydroformylation reaction was performed in a 100 mL stainless steel autoclave (Autoclave Engineers, EZE-Seal Reactor, USA) and the reaction products were analyzed on a Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector.

3. Results and discussion

The rhodium catalyst of P(ONp)₃ was prepared in situ by mixing P(ONp)₃ with Rh(CO)₂(acac). This system catalyzed the hydroformylation of vinyl acetate. The reaction products were 2-acetoxypropanal and 3-acetoxypropanal along with acetic acid and ethyl acetate as side products. The branch aldehyde (2-acetoxypropanal) was observed as the main product with high turnover frequency.

The selectivity of products in hydroformylation process is mainly affected by variation in temperature. Temperature was varied from 70 to 100 °C at constant syngas pressure (3.0 MPa). With an increase of temperature from 70 to 100 °C, the reaction proceeds faster by a factor of ~3.7 (Table 1) along with slight decrease in the chemo selectivity toward aldehyde. However, an excellent branch aldehyde regioselectivity (98%) was obtained in the entire range of temperatures. At lower reaction temperature (70 °C), high chemo selectivity toward aldehyde was observed (94.5%), the TOF was rather low (1800 h⁻¹). At 100 °C, the TOF increased up to 6720 h⁻¹ with aldehyde selectivity decreased to 89.5%. Therefore,

Table 1
Effect of temperature and syngas pressure on Rh/tri-1-naphthyl phosphite catalyzed hydroformylation of vinyl acetate.^a

Entry	Temp. (°C)	Press. (MPa)	Conv. (%)	TOF ^b (h ⁻¹)	S _{aldehyde} (%)	b/l
1 ^c	70	3.0	15.0	1800	94.5	98/2
2	80	3.0	17.0	4080	93.0	98/2
3	90	3.0	23.5	5640	92.0	98/2
4	100	3.0	28.0	6720	89.5	98/2
5	90	2.0	12.5	3000	86.0	98/2
6	90	4.0	34.5	8280	93.0	99/1
7	90	5.0	42.0	10,000	93.0	99/1
8	90	6.0	48.0	11,520	93.5	99/1

^a Reaction conditions: sub/cat. = 4000, [Rh(CO)₂acac] = 0.23 mmol/L, P/Rh = 6.0, and solvent (toluene) = 50 mL.

^b Turnover frequency, determined based on GC, reaction time = 10 min.

^c Reaction time = 20 min.

the optimum reaction temperature was 90 °C where maximum TOF and selectivity was achieved.

The hydroformylation of vinyl acetate catalyzed by Rh/P(ONp)₃ was studied at 90 °C under different syngas pressure (2.0–6.0 MPa). Changes in the syngas pressure were found to affect the reaction rate and selectivity (Table 1). The results indicate that the hydroformylation of vinyl acetate proceeds slowly at low syngas pressure. At low syngas pressure, CO insertion may be difficult into the intermediate species as the ester carbonyl group form thermodynamically stable five and/or six member rings, resulting into considerably low TOF. TOF increased considerably with an increase in the syngas pressure (2.0–4.0 MPa) and above that there was a slight increase in the TOF. For example, when the syngas pressure was increase from 2.0 to 4.0 MPa, TOF increased by a factor of ~2.76, whereas with further increase in the syngas pressure from 4.0 to 6.0 MPa, TOF was increased only by a factor ~1.39 (see Table 1). From the above discussion one can conclude that minimum 4 MPa syngas pressure is require for achieving reasonable TOF. In all instances, regioselectivity to branch aldehyde was greater then 98%.

The effect of ligand/Rh ratio on the catalytic activity/selectivity of vinyl acetate hydroformylation was studied at 90 °C, 3.0 MPa syngas pressure by varying ligand/Rh mmol ratio 3.0–18.0 (Table 2). The results indicate that TOF was improved up to ligand/Rh of 6.0. While TOF was found to decrease as ligand/Rh increased from 6.0 to 18.0. However, chemo selectivity to aldehyde and regioselectivity to branched aldehyde were increased. This tendency is also found in enamides hydroformylation catalyzed by Rh/biphenyl based monodentate phosphite catalytic system [7].

When rhodium concentration was increased from 0.16 to 0.46 mM (ligand/Rh ratio 6) at 80 °C, 3.0 MPa syngas pressure, as expected, the rate of vinyl acetate hydroformylation reaction was found to increase with an increase in the rhodium concentration indicating linear dependency with respect to the rhodium concentration (Table 3). Similar result was also found for HRh(CO)(PPh₃)₃ catalyzed hydroformylation of vinyl acetate [18]. Aldehyde selectivity was low (90%) at low 0.16 mM rhodium concentration and improved up to 0.23 mM rhodium concentration, beyond that aldehyde selectivity remained unaffected.

For comparison, a variety of phosphine ligands were screened for rhodium catalyzed hydroformylation of vinyl acetate under

Table 2
Effect of ligand/Rh ratio on Rh/tri-1-naphthyl phosphite catalyzed hydroformylation of vinyl acetate.^a

Entry	P/Rh	Conv. (%)	TOF (h ⁻¹)	S _{aldehyde} (%)	b/l
1	3.0	20.0	4800	91.0	97/3
2	6.0	23.5	5640	92.0	98/2
3	12.0	22.0	5280	94.0	98/2
4	18.0	21.0	5040	94.0	98/2

^a Reaction conditions: sub/cat. = 4000, [Rh(CO)₂acac] = 0.23 mmol/L, temp. = 90 °C, syngas pressure (1:1) = 3.0 MPa, solvent (toluene) = 50 mL, and reaction time = 10 min.

Table 3
Effect of initial rhodium concentration on Rh/tri-1-naphthyl phosphite catalyzed hydroformylation of vinyl acetate.^a

Entry	[Rh(CO) ₂ acac] (mmol/L)	Rate × 10 ³ (m s ⁻¹)	S _{aldehyde} (%)	b/l
1	0.16	0.17	90.0	97/3
2	0.23	0.26	93.0	98/2
3	0.35	0.32	93.0	98/2
4	0.46	0.40	93.0	98/2

^a Reaction conditions: sub/cat. = 4000, P/Rh = 6.0, temp. = 80 °C, syngas pressure (1:1) = 3.0 MPa, solvent (toluene) = 50 mL, and reaction time = 10 min.

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