

Contents lists available at ScienceDirect

Applied Catalysis A: General



journal homepage: www.elsevier.com/locate/apcata

One-pot synthesis of alcohols from olefins catalyzed by rhodium and ruthenium complexes

Joseph Zakzeski, Hae Ryun Lee, Yi Ling Leung, Alexis T. Bell*

Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462, United States

ARTICLE INFO

Article history: Received 2 September 2009 Received in revised form 3 December 2009 Accepted 5 December 2009

Keywords: Olefin Alcohol Aldehyde hydrogenation Hydroformylation One-pot synthesis

ABSTRACT

The one-pot synthesis of butanol and heptanol from propene and 1-hexene, respectively, was performed using Ru₃(PPh₃)Cl₂ and Rh(CO)₂(acac) in the presence of triphenylphosphene. The effects of various reaction parameters, including catalyst concentration, gas partial pressures, and temperature, were investigated. Two methods for performing the one-pot synthesis were developed and are discussed. In the first method, stoichiometric quantities of CO and propene or 1-hexene were fed to the autoclave. It was found that residual carbon monoxide necessary for the hydroformylation poisoned the Ru catalyst used for the hydrogenation. Venting the hydroformylation gases was therefore necessary for hydrogenation of the aldehyde to proceed. In the second method, sub-stoichiometric quantities of CO relative to olefin were fed to the autoclave, and CO conversion was driven to nearly 100%. In this case, the low residual CO concentration allowed the hydrogenation to proceed readily. The optimal temperatures and gas pressures for the hydroformylation were not the optimal temperatures and pressures for the hydrogenation. A strategy is described for maximizing the performance of both steps. Under optimal conditions, 100% conversion of propene to butanol could be achieved with 97% selectivity, and 99% conversion of 1-hexene to hepatanol could be achieved with 98% selectivity. The only byproduct observed in the latter case was a small amount of 2-hexene, which did not undergo hydroformylation. A possible reaction mechanism is proposed for both the hydroformylation of the olefin and the hydrogenation of aldehyde based on spectroscopic evidence.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Butanol has high energy content, low miscibility with water, and low volatility; it thus can replace or be blended into gasoline without any need to modify engine technology [1]. C₅-C₇ alcohols, as well as mixtures of alcohols, have also been proposed as additives to gasoline, diesel, and aviation fuel [2,3]. For these reasons, the production of butanol and other alcohols from agricultural and domestic wastes has attracted considerable attention [4,5]. Alternatively, alcohols could be produced by hydrogenation of aldehydes derived from the hydroformylation of alkenes obtained as products of Fischer-Tropsch synthesis. Since the hydroformylation of propene to n-butanal is already a major industrial process [6], the development of a one-pot approach for the synthesis of butanol from propene, and similarly the synthesis of C_5-C_7 alcohols from C_4-C_6 alkenes, could provide an attractive extension of existing technology to the production of transportation fuel. The challenge, therefore, is to find an appropriate catalyst,

* Corresponding author. *E-mail address:* bell@cchem.berkeley.edu (A.T. Bell). or pair of catalysts, for the hydroformylation of C_n alkenes to the C_{n+1} aldehydes and the subsequent hydrogenation of the aldehydes to C_{n+1} alcohols. Since homogenous catalysts are known to promote both steps, and attempts to combine both steps into a one-pot approach have been reported, the present investigation has focused on homogeneous catalysts.

A wide variety of homogeneous catalysts have been investigated for the hydroformylation of alkenes to aldehydes and the hydrogenation of aldehydes to alcohols. Rhodium and cobalt complexes have been demonstrated to be most effective catalysts for the hydroformylation of alkenes [7], and a thorough review of effects of metal and ligand composition on this reaction has been presented by van Leeuwen and Claver [8]. Examples of Ptcatalyzed hydroformylation reactions have also been reported [9]. Rh-based catalysts containing phosphine ligands are preferred over Co-based catalysts with or without phosphine, since Rh complexes operate at lower pressures. The hydrogenation of aldehydes to alcohols has also been investigated in great detail [10–19] and a review of this area has been presented by Kolarić and Šunjić [20]. Ru-based complexes containing phosphine ligands have been identified as the most effective ones for this reaction.

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2009.12.011

Relatively few examples of the one-pot conversion of alkenes to higher alkanols have been reported. Cobalt [21-26] and rhodium [27-30] catalysts in combination with trialkylphosphine ligands have been shown to produce alcohols; however, cobalt-based catalysts exhibit low alcohol selectivity because they promote the hydrogenation of the alkene to the corresponding alkane. Studies by Cole-Hamilton and coworkers have demonstrated the synthesis of heptanol from 1-hexene with high yields at 393 K using rhodium trialkylphosphine catalysts in alcohol solution [31–35]. The highest heptanol selectivity was achieved with PEt₃, whereas PⁱPr₃ or PⁱBu₃ produced only aldehydes and PPh₃, a well known ligand for promoting the hydroformylation of alkenes, was not effective in producing alcohols. In related work, Ichihara et al. have shown that undecanol can be prepared from 1-decene using $[Rh(CO)_2(acac)]$ in the presence of bidentate bis(alkylphosphine) ligands. Conversions of 1-decene to the linear and branched alcohols of 83% and 97% were achieved at 423 and 443 K, respectively, after 6 h [36]. Amines have also been explored as ligands for rhodium-based catalysts. For example, Mizoroki et al. have noted that tertiary amines facilitate the formation of linear and branched heptanol from 1-hexene [37]. The potential of Pdbased catalysts has been explored by Konya et al. [38], who have shown that internal C_n alkenes can be converted to C_{n+1} alcohols using a cationic palladium complex with bis-dialkylphosphine ligands in the presence of triflic acid. An attempt to use two catalysts has been reported by Haukka et al., who observed high conversions (up to 96%) of 1-hexene to C_7 alcohols using $Ru_3(CO)_{12}$ clusters in the presence of Rh or Co together with bypridine as ligands after 17 h at 423 K [39].

The aim of the present investigation was to demonstrate a process for the one-pot conversion of propene to butanol and hexene to heptanol, using Rh and Ru catalysts in combination with PPh₃. Rhodium and ruthenium were chosen because of their demonstrated effectiveness for alkene hydroformylation and aldehyde hydrogenation, respectively, whereas PPh₃ was chosen as a ligand for both metals because of its known effectiveness in combination with Rh for alkene hydroformylation and with Ru for aldehyde hydrogenation. A further motivation for considering PPh₃ is its significantly lower cost relative to PEt₃ (two orders of magnitude cheaper). Our work shows that by proper choice of reaction conditions, i.e., catalyst concentration, CO and H₂ partial pressures, and temperature, it is possible to achieve high yields of alcohol using a single reactor containing both catalysts.

2. Experimental

Reactions were conducted in stirred, 50 mL Parr autoclaves made of Hastelloy C. Between runs, the reactors were washed thoroughly with acetone and then dried in a vacuum oven for 15 min to avoid contamination. The reaction temperature was monitored using a thermocouple located inside a Hastelloy C thermowell. Reaction conditions are as follows unless indicated otherwise. During a typical propene reaction, 37.5 mmol toluene (3.46 g, Alfa-Aesar, 99.8%), 0.703 mmol decane (0.100 g, Alfa-Aesar, 99+%) as an internal standard, 15 µmol Rh(CO)₂(acac) (0.0039 g, Alfa-Aesar, 99%), 15 μmol Ru(PPh₃)₃Cl₂ (0.0144 g, 97%, Alfa-Aesar), and 76 µmol PPh₃ (0.020 g, 99%, Aldrich) were loaded into the autoclave, which was sealed and purged four times with He. The autoclave was pressurized with approximately 6.96 mmol propene (0.345 MPa, 99%, Praxair) at 293 K. The autoclave was then operated either by Method 1 or by Method 2, described below. For both cases, it was possible to estimate the conversion of propene by the drop in the autoclave pressure resulting from conversion of gaseous propene, CO, and H₂ to liquid butanal and butanol. The concentrations of n-butanal, isobutanal, n-butanol, and isobutanol were determined by gas chromatography using an Agilent Technologies 6890N gas chromatograph equipped with an HP-1 capillary column coated with crosslinked methyl siloxane and an FID detector. No other products were detected by gas chromatography.

For the conversion of 1-hexene, reactions were conducted as described below using either Method 1 or Method 2, except that 6.96 mmol 1-hexene (0.585 g, Alfa-Aesar, 98%) was loaded into the autoclave rather than propene. The concentration of n-heptanal, isoheptanal, n-heptanol, and isoheptanol were determined by gas chromatography. No other products were detected by gas chromatography.

2.1. Method 1

After pressurizing the autoclave with propene, approximately 6.96 mmol CO (0.345 MPa, 99.5%, Praxair), and 13.92 mmol H₂ (0.690 MPa, 99.999%, Praxair), were added to the autoclave at 293 K. The autoclave was then heated to reaction temperature (T_1) , typically 313 K, in about 2 min. After the designated reaction time (t_1) , typically 4 h, the gases present in the autoclave were vented and analyzed by GC/MS. Only trace quantities of normal and isobutyraldehyde were detected. The autoclave was purged 10 times with helium and allowed to equilibrate for a designated waiting time, typically 1 h. The autoclave was then purged again with helium and pressurized with approximately 69.6 mmol H₂ (3.450 MPa), and heated to reaction temperature (T_2) , typically 353 K for a designated reaction time (t_2) , typically 2 h. Stirring of the autoclave contents was done during both steps with a magnetic stir bar. Upon the completion of the reaction, the reactor was quenched in ice water to 308 K and vented. The contents of the reactor were emptied into a vial, weighed, and analyzed by gas chromatography.

2.2. Method 2

After pressurizing the autoclave with propene, approximately 5.57 mmol CO (0.276 MPa), and 57.0 mmol H₂ (2.829 MPa) were added to the autoclave at 293 K. The autoclave was then heated to reaction temperature (T_1), typically 323 K, in about 2 min. After the designated reaction time (t_1), typically 4 h, the autoclave was heated to reaction temperature (T_2), typically 373 K for a designated reaction time (t_2), typically 5 h. Stirring was done with a magnetic stir bar. Upon the completion of the reaction, the reactor was quenched and the contents analyzed as indicated in Method 1.

2.3. Spectroscopy

IR spectra were acquired using a Nicolet 6700 FT-IR equipped with a demountable liquid cell (Harrick, Inc.), which is equipped with 13 mm CaF₂ windows. Rhodium and ruthenium standards were made by dissolving Rh(CO)₂(acac) (0.0039 g) or Ru(PPh₃)Cl₂ (0.0144 g) and PPh₃ (0.02 g) in toluene (3.46 g). A portion of these samples was analyzed by transferring the liquid to the demountable liquid cell and immediately acquiring a spectrum under ambient conditions. The samples were then placed in the autoclave, which was pressured with CO (0.690 MPa) and H₂ (2.829 MPa), heated to 313 K, and stirred for 1/2 h. The autoclave was then vented, and the samples transferred to the liquid cell for further analysis. Analysis of reaction solutions was conducted by transferring a sample of the reaction solution to the cell after reaction and acquiring a spectrum under ambient conditions. Baseline correction was conducted using toluene.

¹³C NMR experiments carried out by placing the solution of interest in a Wilmad Labglass, high-pressure NMR tube, and then pressurizing the tube to 0.345 MPa with ¹³CO (Isotec, min 99%)

 13 CO). The tube was then inverted several times to enhance mixing. 13 C NMR measurements were made on a Bruker AV-600 spectrometer using D₂O in a capillary tube and a 5 mm ZBO probe with proton decoupling. 31 P NMR measurements were made on an AVQ-400 spectrometer with proton decoupling. Chemical shifts were referenced to trimethylphosphate.

3. Results and discussion

3.1. Synthesis of butanol from propene

3.1.1. Effects of hydroformylation temperature (T_1) and hydrogenation temperature (T_2)

The effect of temperature on the hydroformylation of propene to isobutanal and n-butanal is depicted in Fig. 1. The reaction proceeded under very mild conditions, and the optimal conversion was obtained at 333 K, corresponding to 83% conversion of propene to isobutanal and n-butanal. Only 0.2% of the propene was converted to aldehydes at 298 K; a decrease in propene conversion relative to that observed at 333 K was observed at higher temperatures. As discussed below, this decrease resulted from a reduction in the coordination of propene to the complex at elevated temperatures.

The effect of hydrogenation temperature (T_2) versus the conversion of butanal and isobutanal to butanol and isobutanol, respectively, is shown in Fig. 2. Although not shown, approximately 70% of the propene was converted to aldehydes during the preceding hydroformylation step. The conversion of aldehydes to the corresponding alcohols increased monotonically with temperature. At 313 K, only 0.4% of the aldehydes were hydrogenated, but increasing the temperature to 373 K resulted in nearly 97% hydrogenation of the isobutanal and n-butanal to isobutanol and n-butanol, respectively.

Taken together these results indicate that temperatures favoring aldehyde hydrogenation disfavor propene hydroformylation, and vice versa. Operation at temperatures that favor hydrogenation (~373 K) results in reduced hydroformylation activity, so longer times are required to achieve complete conversion of CO. In contrast, operation of the autoclave at temperatures that favor hydroformylation (~323 K) are insufficient for the hydrogenation of the aldehydes formed to during the hydroformylation. Increased activity is thus obtained by first operating at lower temperatures to hydroformylate propene to butanal and isobutanal and then increasing the temperature after completely consuming the CO to favor the hydrogenation of the aldehydes to the corresponding alcohols.



Fig. 1. Effect of temperature on propene conversion using Method 1.



Fig. 2. Temperature versus aldehyde conversion using Method 1.

3.1.2. Effects of H₂ and CO pressure

The effect of hydrogen pressure (P_{1,H_2}) on the rate of hydroformylation using Method 1 is depicted in Fig. 3a. In each case, after the hydroformylation, the aldehydes produced during the hydroformylation were hydrogenated to the corresponding alcohol, with a conversion of about 96%. An optimal conversion was obtained for H₂ pressures of 0.345–0.690 MPa. Reduced yields were obtained when the H₂ pressure was increased beyond this



Fig. 3. (a) Effect of H_2 pressure on conversion of propene (P_{1,H_2}) using Method 1. (b) Effect of H_2 pressure on conversion of aldehydes (P_{2,H_2}) .



Fig. 4. Effect of CO pressure on conversion of propene using Method 1.

point. In the absence of H₂, no products were obtained. Fig. 3b indicates the importance of H_2 pressure (P_{2,H_2}) for the hydrogenation of the aldehydes produced by hydroformylation. The conversion of aldehydes to alcohols increased monotonically with hydrogen pressure. Hydrogenation of the aldehydes was favored by relatively high hydrogen pressures, whereas relatively low hydrogen pressures favored the hydroformylation reaction. In direct analogy to the reaction temperature, operation of the autoclave at hydrogen pressures that favor the hydrogenation disfavors hydroformylation and vice versa. Fortunately, the optimal conditions for the hydroformylation involve lower H₂ pressures, and increasing the H₂ partial pressure at the conclusion of the hydroformylation step to facilitate hydrogenation was effected with relative ease. Moreover, hydroformylation still proceeded at hydrogen pressures that favor the hydroformylation albeit at relatively lower rates.

Fig. 4 depicts the effect of CO pressure on the formation of hydroformylation products. Again, the subsequent hydrogenation resulted in approximately 96% conversion of aldehydes to alcohols. Trace conversion was observed in the absence of added CO (the hydroformylation products resulted from the CO present on the Rh starting material), and an optimal conversion was obtained at 0.345 MPa CO. At 0.173 MPa CO, approximately 45% of the propene was converted to the aldehyde, which corresponds to nearly complete conversion of the CO. A decrease in yields was obtained at CO pressures exceeding 0.345 MPa because of inhibition of the Rh complex by CO. The reduced activity with higher gas pressures occurred because excess CO or H₂ caused coordinative saturation of the Rh complex (via the formation of stable 18-electron rhodium carbonyl complexes). Lacking open space for coordination, the complex was less able to coordinate propene, and the stability gained by the complex resulted in lower hydroformylation activity.

The hydrogenation of the aldehydes to the corresponding alcohols did not occur in the presence of CO under hydroformylation conditions, and the only products observed were isobutanal and n-butanal. The lack of hydrogenation activity resulted from poisoning of the ruthenium complex by coordinated CO. Removal of the residual CO from the autoclave after hydroformylation was therefore necessary for hydrogenation to proceed under the conditions of Method 1. Removal of CO unconsumed during hydroformylation was achieved by purging the autoclave 10 times with helium, and waiting for a period of time for the system to equilibrate before purging once again with helium. It was hypothesized that by venting and waiting the metal–carbonyl complexes in the solution equilibrated with the gas in the autoclave headspace, thereby reducing the concentration of CO



Fig. 5. Method 1 wait time after purging before beginning the hydrogenation reaction versus propene conversion.

coordinated to the metal complexes. The effect of the wait time after the initial venting of the autoclave headspace on the extent of hydroformylation and hydrogenation is depicted in Fig. 5. Without a vent of the hydroformylation gases, approximately 75% of the propene was converted to n-butanal and isobutanal, and virtually no n-butanol or isobutanol were observed (0.7% hydrogenation conversion), for a total alcohol vield of \sim 0.5% from propene. A higher yield of butanals relative to that obtained under standard conditions (70%) was obtained because of the longer time for hydroformylation (6 h versus 4 h). With a vent of the hydroformylation gas but no wait before beginning the hydrogenation, approximately 64% of the propene was converted to butryladehydes, and \sim 15% of these products were converted to n-butanol and isobutanol, for a total alcohol yield of $\sim 10\%$ from propene. As indicated in Fig. 5, the yields of aldehyde hydrogenation products increased with increasing wait time after the initial purge, culminating at approximately 70% hydrogenation conversion after a wait time of 1 h, for a total alcohol yield of \sim 50% from propene. With increased wait time, more of the CO coordinated to the Ru complex dissociated and accumulated in the autoclave headspace, from where it was then purged.

3.1.3. Effects of PPh₃ concentration

Fig. 6a depicts the effect of triphenylphosphine (PPh₃) concentration on the hydroformylation of propene to isobutanal and n-butanal and subsequent hydrogenation of isobutanal and nbutanal to isobutanol and n-butanol. In the absence of PPh₃, 18.5% of the propene was converted to aldehydes, and only 43.2% of these aldehydes underwent hydrogenation to alcohols. An optimal activity was observed upon the addition of 76 µmol PPh₃ $(\sim 20 \text{ mmol/L})$; this concentration resulted in 68% propene conversion to aldehydes, and 69% hydrogenation of the aldehydes to alcohols. Increasing the PPh₃ concentration beyond this point resulted in a decrease in the hydroformylation rate. In addition, a large decrease in the rate of aldehyde hydrogenation was observed at \sim 0.3 mmol PPh₃, and less than 10% of the aldehydes were hydrogenated to the alcohols. PPh₃ serves as a σ -donor to the metal center, which slows the rate of CO dissociation because of enhanced pi-backbonding between the metals and the carbonyl ligands [8]. The decrease in activity at high concentrations of PPh₃ results from the coordinative saturation of both the Rh and the Ru complexes with CO [8,20]. Without an open coordination site made available by CO dissociation, the metal centers are less able to bond to the olefin or the aldehyde, and a reduction in activity is



Fig. 6. (a) Effect of PPh₃ concentration on hydroformylation of propene and hydrogenation of butanal and isobutanal using Method 1. (b) Normal/iso ratio versus PPh₃ concentration.

observed. Thus, the concentration of PPh_3 has an effect similar to that of the partial pressures of CO and H_2 discussed above.

Fig. 6b depicts the ratio of the n-butanal and n-butanol to isobutanal and isobutanol. The normal/iso (n/i) ratio increases from 1.67 in the absence of PPh₃ to 3.19 with excess PPh₃. This trend is identical to that reported previously using RhH(PPh₃)₃ [40]. After the coordination of the olefin to the Rh during the hydroformylation, the hydride on the metal adds either to the one or the two position of the olefin. The presence of bulky ligands such as PPh₃ favors addition of the hydride to the less-bulky one-position. As the concentration of PPh₃ in the solution increases, more PPh₃ coordinates to the metal center, which causes the n/i isomer ratio to increase. The reactions noted above were conducted with 19 mmol/L (76 µmol) PPh₃, and an n/i ratio of about 2.5 was observed in the preceding reactions except where noted otherwise.

3.1.4. Effects of rhodium concentration

To ascertain the role of the rhodium and ruthenium in the propene hydroformylation, the concentration of Rh was varied keeping the Ru concentration constant. The results are depicted in Fig. 7. In the absence of $Rh(CO)_2(acac)$, only 0.3% of the propene was converted to n-butanal and isobutanal. The conversion of propene to n-butanal and isobutanal increased with increasing Rh



Fig. 7. Rhodium concentration versus propene and aldehyde conversion using Method 1.

concentration. These results suggest that Rh is much more active than Ru as catalyst for the hydroformylation of the propene. The subsequent hydrogenation step resulted in approximately 70% conversion of the aldehydes to alcohols regardless of the Rh(CO)₂(acac) content. These results indicate that Rh is responsible for the propene hydroformylation but is largely inactive for hydrogenation of butyraldehyde. At the conclusion of these reactions, the headspace of the autoclaves was collected and analyzed by GC/MS for propane or butane, since Rh catalysts are known in the literature to decarbonylate aldehydes [20,41–43]. Neither butane nor propane was detected, indicating that neither the decarbonylation of the aldehyde nor the hydrogenation of the olefin occurred under the conditions employed.

3.1.5. Effects of ruthenium concentration

The effect of ruthenium concentration on the hydrogenation of n-butanal and isobutanal is shown in Fig. 8. In the absence of Ru, only $\sim 2\%$ of the n-butanal and isobutanal underwent hydrogenation to the alcohols catalyzed by the rhodium complex. This observation is fully consistent with earlier reports that Rh complexes containing PPh₃ ligands are not effective for promoting the hydrogenation of aldehydes. The conversion of propene to hydroformylation products remained constant, providing further evidence that the ruthenium complex is not involved in the hydroformylation step. The yield of hydrogenation products



Fig. 8. Ru loading versus propene using Method 1.

Table 1

Hydrogenation of butyraldehyde. Reaction conditions: 37.5 mmol toluene (3.46 g), 0.703 mmol decane (0.100 g), 6.93 mmol butyraldehyde (0.50 g), 15 μ mol Ru(PPh₃)₃Cl₂ (0.0144 g), 76 μ mol PPh₃ (0.02 g), *t* = 2 h.

| | Temperature (K) | P _{H2} (MPa) | Conversion (%) |
|---|-----------------|-----------------------|----------------|
| 1 | 353 | 3.45 | 99.9 |
| 2 | 353 | 0.69 | 99.3 |
| 3 | 333 | 0.69 | 99.4 |
| 4 | 313 | 0.69 | 29.7 |

increased with increasing Ru concentration, approaching nearly 70% with 15 μ mol Ru(PPh₃)₃Cl₂ (3.8 mmol/L). Taken together, these results indicate that although the Rh complex is capable of performing some hydrogenation, the Ru complex is considerably more active for this reaction.

3.1.6. Butanal hydrogenation

A principle objective of this work was to demonstrate the onepot synthesis of butanol from propene. We, therefore, investigated the conditions necessary for the hydrogenation of nbutanal to n-butanol using $Ru(PPh_3)_3Cl_2$ in the absence of $Rh(CO)_2(acac)$ and CO. The results are presented in Table 1. As shown in entry 1, under 3.45 MPa H₂ at 353 K, nearly 100% of the butanal was hydrogenated to the n-butanol. The hydrogenation also proceeded at a lower hydrogen pressure (0.690 MPa) and temperatures as indicated by entries 2 and 3. Only when the temperature was decreased to 313 K was a relative decrease in activity observed. Thus, in the absence of CO, the hydrogenation of butyraldehyde proceeds readily under exceptionally mild conditions.

The principle reason for the higher temperature required for the hydrogenation of butyraldehyde following hydroformylation is the presence of residual CO, which poisons the Ru complex. This poisoning effectively decreases the concentration of catalyst that is effective for aldehyde hydrogenation. Increasing the temperature and H_2 pressure is therefore necessary to compensate for the lower concentration catalyst capable of carrying out the hydrogenation of butyraldehyde.

3.1.7. Method 2: propene conversion to butanol with substoichiometric CO

Based on the results presented above, we examined the feasibility of performing a one-pot synthesis of butanol from propene without the vent and purge steps. Table 2 lists the conversion of propene to butanol carried out using Method 2 (see Section 2). In this case, sub-stoichiometric quantities of CO relative to propene were fed to the autoclave, in contrast to the procedure in Method 1. Under standard conditions, the CO conversion was now driven to nearly 100%, obviating the need for a purge between the hydroformylation and hydrogenation steps. Entries 1–3 indicate the results of autoclave operation under optimal hydroformylation conditions followed by the addition of excess hydrogen and temperature increase to $T_2 = 373$ K. In all of these cases, the hydroformylation conversion measured relative

Table 3

One-pot synthesis of propene using 2-propanol as the solvent. Reaction conditions: 57.6 mmol 2-propanol (3.46 g), 0.703 mmol decane (0.100 g), 15 μ mol Rh(CO)₂(a-cac) (0.0039 g), 15 μ mol Ru(PPh₃)₃Cl₂ (0.0144 g), 76 μ mol PPh₃ (0.02 g), 6.96 mmol propene (0.345 MPa), 13.9 mmol CO (0.690 MPa), 55.7 mmol H₂ (2.76 MPa).

| | <i>T</i> ₁ (K) | <i>t</i> ₁ (h) | <i>T</i> ₂ (K) | <i>t</i> ₂ (h) | Propene conversion (%) | Aldehyde conversion (%) | n/i |
|----------------|---------------------------|---------------------------|---------------------------|---------------------------|------------------------------|-------------------------------|-----|
| 1 | 323 | 4 | 398 | 1 | 99.7 | 96.8 | 2.1 |
| 2 | 313 | 4 | 398 | 1 | 62.8 | 98.0 | 2 |
| 3 ^a | 398 | 5 | | | 47.3 | 98.1 | 1.8 |
| 4 ^a | 323 | 5 | | | 99.7 | 0.3 | 2.2 |
| | | | | | | | |

^a $T_2 = T_1$; t_1 , total run time.

to CO was nearly 100%, and the subsequent hydrogenation of butanal and isobutanal was nearly 100% after 4 h (see Entry 3). It was possible to consume more of the propene, approaching 100%, using slightly higher CO pressures as long the CO was kept substoichiometric. Entry 4 indicates the results of converting propene to butanol and isobutanol in a strictly batch manner (that is, without addition of extra hydrogen after the hydroformylation step), operating at the optimal hydroformylation temperature (T_1) followed by the optimal hydrogenation temperature (T_2) . Under these conditions, nearly 100% of the CO was converted (corresponding to \sim 80% of the propene), and nearly 79% of the resulting aldehydes were hydrogenated to butanol and isobutanol. Operation of the autoclaves continually at the optimal hydrogenation temperature (Entry 5) resulted in similar conversions as seen in Entry 4. but the overall activity was decreased since longer reaction times were required. Similarly, the use of optimal hydroformylation temperature was insufficient to facilitate the hydrogenation as discussed above, so operation of the autoclave solely at the optimal hydroformylation temperature (Entry 6) resulted in only 0.1% conversion of the aldehydes to the corresponding alcohols.

The turnover frequencies (TOF) for propene hydroformylation and butyraldehyde hydrogenation can be estimated from Table 3 for entry 1. At 323 K the TOF for propene hydroformylation is $3.22 \times 10^{-2} \, \text{s}^{-1}$, and at 398 K the TOF for butyraldehyde hydrogenation is $1.28 \times 10^{-1} \, \text{s}^{-1}$.

3.1.8. Effects of solvent composition

Cole-Hamilton and coworkers [31-32] and, more recently, Ichihara et al. have demonstrated that protic solvents, particularly ethanol, enhance the conversion of aldehydes to alcohols in contrast to aprotic solvents, such as THF, in which no aldehyde hydrogenation occurred [36]. Work by MacDougall et al. [33] has shown that the alcohol can act as hydrogen-transfer agent during the reaction of an alkene in the presence of CO and H₂, enabling the formation of alcohol directly from coordinated alkene without the formation of an aldehyde intermediate. Motivated by these observations, we explored the use of 2-propanol as a solvent to the Rh/Ru system described above. The results are shown in Table 3. Entry 1 indicates a reaction with excess CO but no vent of

Table 2

Results of one-pot synthesis using Method 2 with hydroformylation conversion relative to CO.

| | | - | | | | | |
|----------------|---------------------------|-----------|---------------------------|---------------------------|---------------------------|-------------------|-------------------------|
| | $P_{\rm H_2}~({\rm MPa})$ | T_1 (K) | <i>t</i> ₁ (h) | <i>T</i> ₂ (K) | <i>t</i> ₂ (h) | CO conversion (%) | Aldehyde conversion (%) |
| 1 ^a | 0.690 | 323 | 4 | 373 | 2 | 99.9 | 29.8 |
| 2 ^a | 0.690 | 323 | 4 | 373 | 3 | 99.9 | 76.7 |
| 3 ^a | 0.690 | 323 | 4 | 373 | 4 | 99.9 | 98.1 |
| 4 | 2.829 | 323 | 4 | 373 | 5 | 99.4 | 79.2 |
| 5 ^b | 2.829 | 373 | 20 | | | 99.7 | 79.5 |
| 6 ^b | 2.829 | 323 | 9 | | | 96.4 | 0.1 |

^a 2.691 MPa H₂ added after t_1 before ramping temperature to T_2 .

^b $T_2 = T_1$; t_1 , total run time.

the hydroformylation gases. Nearly 100% of the propene was converted to n- and isobutanol. Two general observations were noted. First, the presence of excess CO failed to poison the hydrogenation activity of the Ru complex to the extent that it did when toluene was used as the solvent. Second, there was a decrease in the n/i isomer ratio from ~2.5 in toluene to ~2.0 in 2propanol. Taken together, these results suggest that 2-propanol interacts with the coordination sphere of both the Rh and the Ru complexes. Since the steric bulk of the phosphine ligands determines the n/i isomer ratio, 2-propanol likely displaces a phosphine ligand from the Rh complex, thereby reducing the overall bulk of the complex and allowing propene to bind in the 2position more readily. Likewise, 2-propanol may aid in the displacement of CO from the Ru complex, thus allowing the hydrogenation to readily occur even in the presence of CO. Entry 2 of Table 3 shows the result of decreasing T_1 to 313 K. In accord with what was observed using toluene as the solvent, the rate of hydroformylation decreased. Similarly, increasing the temperature to the ideal hydrogenation temperature (Entry 3) resulted in a decrease in the hydroformylation rate. Maintaining the temperature continually at the optimal hydroformylation temperature resulted in high hydroformylation rates but little conversion of the aldehydes (0.3%) to the corresponding alcohols. The ability to use 2-propanol as a solvent suggests that n-butanol and isobutanol might also be used as the solvent for the conversion of propene to butanol, thereby facilitating the separation of the product from the reaction medium.

3.2. Synthesis of heptanol from hexene

3.2.1. Effects of 1-hexene hydroformylation temperature

The hydroformylation of 1-hexene to hexanal was conducted in the presence of Rh(CO)₂(acac) and PPh₃. In each experiment, the only species observed were 1-, 2-, and 3-hexene, n-heptanal, and isoheptanal. The 1-hexene selectivity, defined as moles of aldehyde formed over the sum of all products formed, and the conversion are shown in Fig. 9a. The selectivity decreased with increasing temperature with the largest decrease occurring at temperatures exceeding 333 K. The 1-hexene conversion tended to increase with increasing temperature, approaching 100% at 373 K. A slight decrease in 1-hexene conversion was observed at 333 K relative to 313 and 353 K. The origin of this decrease is discussed below. In general, higher temperatures resulted in higher 1-hexene conversion, but excessive temperatures resulted in a rapid decrease in selectivity to heptanals. Fig. 9b shows the product yields versus temperature (T_1) . At 293 K only very small quantities of heptanal are formed, and there is no evidence for 1hexene isomerization. Increasing the temperature to 313 K resulted in a large increase in hydroformylation activity, and nearly complete consumption of CO. Increasing the temperature beyond 313 K resulted in decreased yields of n-heptanal and isoheptanal. This trend was also observed during the hydroformylation of propene and is attributable to a decrease in the equilibrium concentration of olefin bound to the Rh complex. In contrast to hydroformylation, isomerization of 1-hexene to 2- and 3-hexene increased as temperature increased, and a large increase in isomerization was observed between 333 and 353 K. At temperatures below 333 K, hydroformylation dominates, and 1hexene is converted principally to aldehydes, whereas at temperatures exceeding 353 K 1-hexene isomerization dominates, and 1-hexene is converted principally to 2- and 3-hexene. Thus, the slight decrease in 1-hexene conversion observed in Fig. 9a at 333 K results because the hydroformylation, and thus overall 1-hexene conversion, becomes less favorable at elevated temperatures, but the temperature is not high enough yet to favor the 1-hexene isomerization.



Fig. 9. (a) 1-Hexene conversion and selectivity versus temperature. (b) Hydroformylation products versus temperature. Reaction conditions: 37.5 mmol toluene (3.46 g), 40.3 mmol 1-hexene (3.39 g), 0.703 mmol decane (0.100 g), 10 μ mol Rh(CO)₂(acac) (0.0025 g), 93.9 μ mol PPh₃ (0.0247 g), ~6.96 mmol CO (0.345 MPa) ~6.96 mmol H₂ (0.345 MPa), *t* = 4 h.

3.2.2. Method 1: 1-hexene conversion to heptanol with vent of excess CO

The one-pot synthesis of 1-hexene to heptanol was conducted using Method 1, in which excess CO was vented from the autoclave prior to initiating the aldehyde hydrogenation (see experimental section). Fig. 10 shows the 1-hexene conversion and selectivity versus t_1 , the hydroformylation time, at the optimal hydroformylation temperature (T_1 = 313 K). The conversion of 1-hexene to nheptanal and isoheptanal increased nearly linearly with time, reaching approximately 100% conversion of 1-hexene after 3 h. The selectivity to heptanals remained approximately constant during the course of the reaction. Subsequent reactions were conducted after 4 h to ensure nearly complete conversion of 1-hexene.

Fig. 11 shows the product yields versus hydrogenation temperature (T_2). At a hydrogenation temperature of 398 K, nearly 100% of the n-heptanal and isoheptanal formed during the initial hydroformylation was hydrogenated to n-heptanol and isoheptanol, respectively, with an overall 98% conversion of 1-hexene to n-heptanol and isoheptanol. No other aldehydes or alcohols were observed, indicating that the hydroformylation of the 2- and 3-hexene did not occur under the conditions employed. At 313 K, the optimal hydroformylation temperature, no alcohols were observed. With increasing temperature, the yield of heptanol



Fig. 10. 1-Hexene conversion and selectivity versus time for hydroformylation (t_1). Reaction conditions: 37.5 mmol toluene (3.46 g), 6.96 mmol 1-hexene (0.585 g), 0.703 mmol decane (0.100 g), 15 μ mol Rh(CO)₂(acac) (0.0039 g), 15 μ mol Ru(PPh₃)₃Cl₂ (0.0144 g), 76 μ mol PPh₃ (0.0200 g). ~13.92 mmol CO (0.690 MPa), ~57.0 mmol H₂, T_1 = 313 K.



Fig. 11. Product yield versus temperature (T_2) using Method 2. 1-Hexene conversion approximately 99.6% and n/i ratio ~3.5 in all cases.

increased, and that of heptanal decreased; however, no evidence was found for the hydrogenation of 2- and 3-hexene to the corresponding hexanes.

3.2.3. Method 2: 1-hexene conversion to heptanol with substoichiometric CO

The conversion of 1-hexene to n-heptanol and isoheptanol was conducted using Method 2, in which a sub-stoichiometric quantity reaction in order to facilitate the subsequent hydrogenation, leaving a slight excess of olefin (see Section 2). The effects of T_1, T_2 , CO partial pressure, and time on the conversion of 1-hexene and CO, the percentage of 1-hexene undergoing hydroformylation and isomerization, and the percentage of the aldehyde undergoing hydrogenation to alcohols are reported in Table 4. Entries 1 through 3 show the influence of T_1 and T_2 on conversion and selectivity. Entry 1 is for standard reaction. in which the autoclave was operated at the optimal hydroformylation temperature $(T_1 = 313 \text{ K})$ before increasing the temperature to allow the hydrogenation to occur. Under these conditions, approximately 97% of the CO was consumed in the formation of heptanal, and approximately 50% of the aldehyde was hydrogenated to heptanol. The residual 1-hexene not consumed during the initial hydroformylation isomerized to 2- and 3-hexene. Increasing T₂ to 398 K resulted in a large increase in hydrogenation rate (see Entry 2). Approximately 96% and 99% of the aldehydes formed during the hydroformylation step were hydrogenated after 1 and 2 h, respectively. Increasing T₁ from 313 to 323 K, however, resulted in a decreased hydroformylation activity and increased 1-hexene isomerization (see Entry 3), for the reasons discussed above. Since the rate of 1-hexene hydroformylation decreased and the 2- and 3hexene formed because of isomerization were not hydroformylated, relatively large amounts of CO and 1-hexene remained in the autoclave after 4 h. The residual CO inhibited aldehyde hydrogenation, and only 27% of the aldehydes were hydrogenated, whereas the residual 1-hexene isomerized to 2- and 3-hexene during the hydrogenation step.

of CO is driven to nearly 100% conversion during the first step of the

Entries 4 through 7 illustrate the influence of CO pressure. In the presence of excess of CO, near complete conversion of 1hexene to n-heptanal and isoheptanal could be achieved. Since little 1-hexene remained after the first step, little 2- and 3-hexene was formed during the subsequent hydrogenation step. The excess CO, however, inhibited the hydrogenation, so that only 19% of the aldehydes were hydrogenated at $T_2 = 373$ K. Increasing T_2 to 398 K resulted in slightly increased rates of hydrogenation (see Entry 5). Entry 6 illustrates the results of decreasing the CO pressure. Under these conditions, the large excess of 1-hexene that remained at the conclusion of the reaction isomerized to 2and 3-hexene once the hydrogenation temperature T_2 was reached. Interestingly, only a small fraction of the aldehydes formed during the reaction underwent hydrogenation. Entry 7 shows the results of a stoichiometric quantity of CO relative to 1hexene with T_2 = 398 K and t_2 = 2 h. This reaction resulted in hydroformylation and hydrogenations conversions of approximately 93 and 67%, respectively. Extending t_2 to 5 h resulted in approximately 99% conversion of the aldehydes to the corresponding alcohols (Entry 8). The slight decrease in hydrogenation rate relative to that seen in Entry 2 likely resulted because the unconsumed CO still present in the autoclave inhibited the

| 4 |
|--|
| is of one-pot synthesis using Method 2. 57.0 mmol H_2 (2.829 MPa). |
| |

| | P _{CO} (MPa) | <i>T</i> ₁ (K) | <i>t</i> ₁ (h) | T ₂ (K) | <i>t</i> ₂ (h) | 1-Hexene conversion (%) | CO conversion (%) | 1-Hexene hydroformylation (%) | Aldehyde hydrogenation (%) | 1-Hexene isomerization (%) |
|----------------|-----------------------|---------------------------|---------------------------|--------------------|---------------------------|----------------------------|----------------------|-------------------------------------|----------------------------------|----------------------------------|
| 1 | 0.331 | 313 | 4 | 373 | 5 | 100 | 97 | 88 | 50 | 11 |
| 2 | 0.331 | 313 | 4 | 398 | 2 | 99 | 100 | 90 | 99 | 10 |
| 3 | 0.331 | 323 | 4 | 373 | 5 | 99 | 87 | 69 | 27 | 30 |
| 4 | 0.690 | 313 | 4 | 373 | 5 | 100 | 49 | 98 | 19 | 2 |
| 5 | 0.690 | 313 | 4 | 398 | 2 | 100 | 48 | 97 | 31 | 3 |
| 6 | 0.193 | 323 | 4 | 373 | 5 | 99 | 98 | 55 | 15 | 44 |
| 7 | 0.345 | 313 | 4 | 398 | 2 | 99 | 94 | 93 | 67 | 6 |
| 8 | 0.345 | 313 | 4 | 398 | 5 | 99 | 97 | 96 | 98 | 3 |
| 9 ^a | 0.345 | 313 | 2 | 398 | 1 | 99 | 48 | 97 | 100 | 2 |

^a 2-Propanol (3.46 g) instead of toluene.

reaction. Taken together, these results indicate that both high hydroformylation and hydrogenation activity is possible using a stoichiometric quantity of CO and 1-hexene, but the importance of minimizing isomerization and 1-hexene conversion is critical for the hydrogenation to readily occur. Since the 2- and 3-hexene were not hydroformylated, if excessive isomerization occurs, relatively high partial pressures of unconsumed CO are present in the autoclave, and this unconsumed CO poisons the Ru catalyst and inhibits the hydrogenation.

As indicated above, 2-propanol as a solvent greatly facilitated the hydrogenation of the butanal into butanol. We therefore extended the use of 2-propanol as a solvent for the conversion of 1hexene to heptanol. The results are depicted in Entry 9 of Table 4. Both the hydroformylation and hydrogenation occurred more readily in n-propanol than in toluene. Nearly 97% of the 1-hexene was converted to n-heptanol and isoheptanol (n/i = 3.3), and the remaining 3% of the 1-hexene isomerized to 2- and 3-hexene. Considerably less time was required for similar conversion when 2-propanol was used as a solvent instead of toluene (Entry 8) (2 h versus 4 h for hydroformylation 1-hexene and 1 h versus 5 h for hydrogenation of heptanal). Moreover, an excess of CO did not inhibit the hydrogenation considerably, as observed in the case when toluene was used as the solvent as also observed for propene conversion to butanol.

Turnover frequencies for the hydroformylation of 1-hexene and the hydrogenation of heptanal occurring in toluene and 2-propanol were determined from the data presented in Entries 8 and 9 in Table 4. In toluene the TOF for 1-hexene hydroformylation at 313 K was $3.22 \times 10^{-2} \, \rm s^{-1}$ in toluene and $6.44 \times 10^{-2} \, \rm s^{-1}$ in 2-propanol, whereas the TOF for heptanal hydrogenation at 398 K was $2.58 \times 10^{-2} \, \rm s^{-1}$ in toluene and $1.29 \times 10^{-1} \, \rm s^{-1}$ in 2-propanol.

3.3. Spectroscopic analysis of Rh and Ru complexes and reaction solutions

Spectroscopic analyses using IR and ¹³C and ³¹P NMR were carried out to identify the complexes used to carry out olefin hydroformylation and aldehyde hydrogenation. Such characterization was done after dissolution of the precursor Rh and Ru complexes in toluene containing PPh₃, and following pressurization with ¹³CO. The species identified from these analyses are related to a possible mechanism for the one-pot synthesis of n-butanol and isobutanol from propene depicted in Scheme 1.

³¹P NMR analysis of Rh(CO)₂(acac) (1) (species numbers are those appearing in Scheme 1) dissolved in toluene containing an excess of PPh₃, the precursor for the hydroformylation reaction, revealed a peak associated with coordinated PPh₃ at 56.7 ppm $(J_{103Rh-31P} = 181 \text{ Hz})$, and the IR spectrum of this solution showed a single peak in the carbonyl region at 1980 cm⁻¹. This sample was sealed in an autoclave and exposed to 0.690 MPa CO and then analyzed by IR spectroscopy under ambient conditions. Two peaks were observed, one of medium intensity at 2041 and a second one of stronger intensity at 1980 cm⁻¹ (see Fig. 12, spectrum B). A sample of this solution was then placed in a high-pressure NMR tube and pressurized with 0.345 MPa¹³CO. The ¹³C NMR spectrum of this solution showed a doublet ($\delta = 189.45$ ppm, J_{103Rh-} $_{31CO}$ = 76 Hz), and the only feature observed in the ³¹P NMR was that for free PPh₃. The spectroscopic characteristics of this species strongly resemble previously reported Rh(CO)(PPh₃)(acac) (**3**) properties ($\delta_{13CO} = 189.5$ ppm, $J_{103Rh-13C} = 75$ Hz, $v_{\rm CO} = 1984 \,{\rm cm}^{-1}$) [44]. No evidence for Rh(CO)₂(acac) (1) was observed ($\delta_{13CO} = 183.7 \text{ ppm}$) [45] $v_{CO} = 2083.5$, 2014.6 cm⁻¹ [46]).

 $Ru(PPh_3)_3Cl_2$ (16) dissolved in toluene containing an excess of PPh₃ was characterized in a similar manner. The ³¹P NMR

spectrum exhibited a peak at -5.3 ppm attributed to free PPh₃ and a single broad peak at 42.1 ppm. Analysis by IR after exposure to CO under ambient conditions, two symmetric peaks were observed in the carbonyl region at 2055 and 1991 cm⁻¹ (see Fig. 12, spectrum A). The ¹³C NMR using ¹³CO showed a doublet of triplets (δ = 198.9 ppm, $J_{13C-31P}$ = 17 Hz, $J_{13C-13C}$ = 8 Hz), a triplet $(\delta = 197.0 \text{ ppm}, J_{13C-31P} = 14 \text{ Hz}, J_{13C-13C} = 17 \text{ Hz})$, and a doublet of doublets (δ = 187.6 ppm, $J_{13C-31P}$ = 14 Hz, $J_{13C-31P}$ = 131 Hz). Similar analysis by ³¹P NMR resulted in two broad singlets $(\delta = 46.6 \text{ ppm})$ and $(\delta = 46.6 \text{ ppm})$, a triplet $(\delta = 28.1 \text{ ppm})$, and a doublet of doublets (δ = 21.0 ppm, $J_{13C-31P}$ = 14 Hz, $J_{13C-31P}$ $_{31P}$ = 131 Hz). The observed features suggests that Ru(PPh₃)₃Cl₂, a 16e⁻ complex, readily binds to CO to form stable 18e⁻ complexes, and that multiple isomers exist in agreement with previous studies of the of the coordination of CO with $Ru(PPh_3)_3Cl_2$ [47]. The relative intensities of the CO stretching vibrations indicate that the two CO molecules are cis-positioned, and the positions of the two carbonyl bands agree well with those reported for Ru(CO)₂(PPh₃)₂Cl₂ (18) in KBr (2050 and 1990 cm⁻¹) [48] and in other solvents [49–52]. The presence of multiple 13 C and ³¹P NMR peaks suggests that several species and their isomers co-exist in the reaction solution. The triplet observed in both the ¹³C and ³¹P NMR is likely due to cis,trans,cis- $Ru(CO)_2(PPh_3)_2Cl_2$, in which the equivalent electronic environments of the two PPh₃ and CO ligands results in only one ¹³C and ³¹P peak. The doublet of doublets is attributed to cis, cis, trans-Ru(CO)₂(PPh₃)₂Cl₂ since, in this case, each CO ligand is both cisand trans-positioned from a PPh₃ ligand. Finally, the doublet of triplets in the ¹³C NMR spectrum is likely due to the monocarbonyl species Ru(CO)(PPh₃)₃Cl₂, which is expected to result in a doublet of triplets in the ¹³C NMR and a doublet of triplets and a doublet of doublets in the ³¹P NMR. The broad singlets observed by ³¹P NMR are therefore likely unresolved doublet of triplets and doublet of doublets rather than singlets. In the presence of H₂, the species present above readily exchange Cl for H [51], and the dissociation of CO from the Ru complex activates it for aldehyde hydrogenation.

Analysis of the reaction solution after carrying out a reaction under standard conditions containing both the Ru and Rh complexes was conducted in order to characterize the complexes present in the solution. Analysis of the carbonyl region by infrared spectroscopy resulted in peaks at 2055, 2041, 2017, 1991, and 1980 cm^{-1} (see Fig. 12, spectrum D). In addition to the features attributable to the Rh and Ru complexes, peaks associated with the heptanal C-H and C=O stretches were observed at 2816 and 1716 cm⁻¹, respectively. After the hydrogenation, the intensity of these peaks diminished considerably, and a very broad peak associated with the O-H stretch of heptanol appeared around 3361 cm⁻¹. A sample of the reaction solution was placed in a high-pressure NMR tube, which was pressurized with ¹³CO. Analysis by ¹³C NMR revealed a doublet at 199.2 ppm (I = 57 Hz), a small doublet at 194.1 ppm (I = 145 Hz), and a broad singlet at 185.7 ppm in the carbonyl region in addition to peaks associated with toluene, free PPh₃, and products. The sample was also analyzed by ³¹P NMR. The resulting spectrum exhibited a singlet at 55.87 ppm, a doublet at 40.55 ppm (J = 6 Hz), a large singlet at 39.2 ppm, a doublet at 36.7 ppm (J = 127 Hz), a singlet at 29.6 ppm, a singlet at 16.3 ppm, and a broad singlet at -5.3 ppm associated with free PPh₃ [16]. The accumulated spectroscopic evidence suggests the presence of the Rh complex [HRh(CO)₂(PPh₃)₂] (6) since the IR peaks at 2055 and 2017 cm⁻¹, the ¹³C NMR doublet at 199.2 ppm (*J* = 57.3 Hz), and the ${}^{31}P$ doublet at 36.7 ppm (J = 127 Hz) agree closely with observations for this complex reported in the literature $(v_{CO} = 2053 \text{ and } 2018 \text{ cm}^{-1} \text{ [53]}, \text{ }^{13}\text{C} = 200.3 \text{ ppm}, \text{ }_{J_{13C-}}$ $_{103Rh}$ = 63 Hz [46], ^{31}P = 37.3 ppm, $J_{31P-103Rh}$ = 138.7 Hz



Scheme 1. 1-Pot synthesis of butanol from propene.

[16,54,55]). The small doublet in the $^{31}\mathrm{P}$ NMR spectrum at 40.55 ppm may correspond to low concentrations of the monocarbonyl HRh(CO)(PPh_3)_3 [16]. The $^{31}\mathrm{P}$ singlet at 16.3 ppm, the $^{13}\mathrm{C}$ singlet at 185.7 ppm, and v_{CO} at 2055 and

1991 cm⁻¹ agree closely with the those reported for cis,cis,trans-RuCl₂(CO)₂(PPh₃)₂ (³¹P = 16.3 ppm, ν_{CO} = 2059, 1999 cm⁻¹) [50]. The remaining peaks by ³¹P NMR at 55.9 and 29.63 ppm are likely due to small amounts of Ru(PPh₃)₃H₂ (**12**).



Fig. 12. Infrared spectra of the carbonyl regions of standards and reaction solutions taken under ambient conditions. Line A: Ruthenium standard; $Ru(PPh_3)_3Cl_2$, PPh_3, toluene, CO, H₂. Line B: Rhodium standard; $Rh(CO)_2(acac)$, PPh_3, toluene, CO, H₂. Line C: Solution before reaction. Line D: Solution after reaction.

3.4. Proposed reaction mechanism

A possible mechanism for the one-pot synthesis of n-butanol and isobutanol from propene is depicted in Scheme 1. The reaction of 1-hexene likely proceeds via an analogous process except 1hexene replaces propene. The individual reactions appearing in this scheme are suggested by the experiments described above and by mechanistic work reported in the literature for both olefin hydroformylation and aldehyde hydrogenation [10–16,20,31– 35,56,57]. The number of ligands present on both the Ru and Rh species was chosen such that the complex best satisfies the 18electron rule commonly used in organometallic chemistry except for reactive species that often exhibit an open coordination site or d^8 complexes having 16 electrons.

The hydroformylation reaction is initiated by the coordination of propene to HRh(CO)(PPh₃)₂(**5**) to form HRh(CO)(PPh₃)₂(CH₂CHCH₃) (**7**). While experimental evidence for HRh(CO)(PPh₃)₂(**5**) was not observed, the dicarbonyl species, HRh(CO)₂(PPh₃)₂(**6**) was detected (see above). The hydride in (**7**) then undergoes a 1,2-insertion to form either a normal (**8**) or branched (**8**') alkyl-Rh complex. This complex then binds CO to form the 18-electron complex Rh(CO)₂(PPh₃)₂(CH₂CH₂CH₃)(**9**), which facilitates the CO migratory insertion to form Rh(CO)(PPh₃)₂(COCH₂CH₂CH₃) (**10**). The oxidative addition of H₂ forms the complex Rh(H)₂(CO)(PPh₃)₂ (**CO**CH₂CH₃) (**11**). A reductive elimination results in the formation of the aldehyde and HRh(CO)(PPh₃)₂ (**5**), closing the catalytic cycle.

Hydrogenation is initiated with the coordination of the n-butanal to the Ru(H)₂(PPh₃)₃ (**12**) to form Ru(H)₂(PPh₃)₃(HC=OC₃H₇) (**13**). As noted above, evidence was found for the presence of Ru(H)₂(PPh₃)₃ in the solution analyzed after reaction (see above). The addition of the hydride across the C=O double bond results in the formation of the alcohol and the coordinatively unsaturated Ru(PPh₃)₃ (**15**). This complex then readily bonds to H₂ to close the hydrogenation catalytic cycle. A similar process occurs for the hydrogenation of isobutanal to isobutanol. Several species in this cycle, especially Ru(PPh₃)₃, are coordinatively unsaturated 14electron complexes, which makes them particularly susceptible to coordination of other ligands, especially CO, to form complexes such as the 18-electron complexes such Ru(CO)₂(PPh₃)₃ (**19**) or Ru(CO)₂(PPh₃)₂Cl₂ (**18**), which inhibits coordination of the aldehyde and therefore hydrogenation. Removal of carbonyl groups by venting of the autoclave after the hydroformylation step restores the hydrogenation activity of the Ru complex. Likewise, the use of 2propanol as a solvent is thought to inhibit the coordination of CO to the Ru complex, thereby enhancing its activity for aldehyde hydrogenation.

4. Conclusions

Results of this study indicate the feasibility of performing a onepot synthesis of both normal and isoalcohols from alkenes with high yields under mild conditions using conventional Rh(III) and Ru(II) complexes containing PPh3 as the only ligand. Olefin hydroformylation is catalyzed principally by the rhodium complex, and hydrogenation is catalyzed by the ruthenium complex. The optimal PPh₃ to Rh or Ru ratio is approximately 10^3 :1. While the n/iratio of the products increases with increasing PPh₃ concentration. very high ligand concentrations reduce the catalytic activity of both the Rh and the Ru complexes as a consequence of excessive coordination to the metal cations. The ruthenium complex is poisoned by CO present during hydroformylation, and consequently hydrogenation does not proceed unless excess CO is purged from the reactor after the completion of the hydroformylation or a sub-stoichiometric amount of CO is used, so that the CO is completely consumed during hydroformylation. It was also found that the temperature for aldehyde hydrogenation was always higher than that for alkene hydroformylation. The use of 2propanol as the solvent greatly enhanced the rates of both the hydroformylation and hydrogenation steps.

A mechanism for the one-pot synthesis of butanol from propene is proposed based on the observations of this study (see Scheme 1) and information drawn from the literature. In this scheme, the Rh complex hydroformylates the propene to form n-butanal and isobutanal, and these products are then subsequently hydrogenated by the Ru complex to form n-butanol and isobutanol. The characteristics of the Ru catalyst indicate its susceptibility to CO poisoning. Evidence for the presence of several Rh and Ru complexes in the reaction solution was obtained. The precursor $Rh(CO)_{2}(acac)$ reacts with PPh₃ to form $Rh(CO)(PPh_{3})(acac)$, which reacts with hydrogen to form the species HRh(CO)₂(PPh₃)₂ and HRh(CO)(PPh₃) under reaction conditions. The 16e⁻ Ru(PPh₃)₃Cl₂ precursor used for the hydrogenation readily binds with CO to form 18e⁻ isomers of Ru(CO)₂(PPh₃)₂Cl₂ and Ru(CO)(PPh₃)₃Cl₂. In both the methods described above, depletion of the CO during the course of the reaction causes these latter complexes to slowly decarbonylate, thereby facilitating aldehyde hydrogenation. A similar mechanism can be envisioned for the conversion of hexene to heptanol.

Acknowledgement

This work was supported by the Methane Conversion Cooperative, funded by BP.

References

- S.-M. Lee, M.O. Cho, C.H. Park, Y.-C. Chung, J.H. Kim, B.-I. Sang, Y. Um, Energy Fuels 22 (2008) 3459.
- [2] R.M. Jimeson, M.C. Radosevich, R.R. Stevens, US Patent 6858048 (2005).
- [3] R.M. Jimeson, M.C. Radosevich, R.R. Stevens, US Patent 7559961 (2009).
- [4] T. Ezeji, N. Qureshi, H.P. Blaschek, Biotech. Bioeng. 97 (2007) 1460.
- [5] V.V. Zverlov, O. Berezina, G.A. Velikodvorskaya, W.H. Schwarz, Appl. Microbiol. Biotechnol. 71 (2006) 587.
- [6] S. Matar, L.F. Hatch, Chemistry of Petrochemical Processes, 2nd ed., Gulf Professional, Woburn, 2001.
- [7] B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallalic Compounds, 2nd ed., Wiley-VCA, Weinheim, 2002.
- [8] P.W.N.M. van Leeuwen, C. Claver (Eds.), Rhodium Catalyzed Hydroformylation, Kluwer Academic Publishers, Amsterdam, 2000.

- [9] C.-Y. Hsu, J.E. Lyons, P.E. Ellis, Jr., US Patent 4524142 (1985).
- [10] E. Fache, C. Santini, F. Senocq, J.M. Basset, J. Mol. Catal. 72 (1992) 337.
- [11] J.-Y. Kim, M.-J. Jun, W.-Y. Lee, Polyhedron 15 (1996) 3787.
- [12] R.A. Sanchez-Delgado, A. Andriollo, O.L. De Ochoa, T. Suarez, N. Valencia, J. Organomet. Chem. 209 (1981) 77.
- [13] W. Strohmeier, L. Weigelt, J. Organomet. Chem. 145 (1978) 189.
- [14] J. Tsuji, H. Suzuki, Chem. Lett. (1977) 1085.
- [15] R.A. Sanchez-Delgado, O.L. De Ochoa, J. Mol. Catal. 6 (1979) 303.
- [16] C. Bianchini, H.M. Lee, A. Meli, F. Vizza, Organometallics 19 (2000) 849.
- [17] L. Xu, G. Ou, Y. Yuan, J. Organomet. Chem. 693 (2008) 3000.
- [18] H. Fujitsu, E. Matsumura, K. Takeshita, I. Mochida, J. Org. Chem. 46 (1981) 5353.
- [19] R.A. Sanchez-Delgado, W. Lee, S.R. Choi, Y. Cho, M.-J. Jun, Transition Met. Chem. 16 (1991) 241.
- [20] S. Kolarić, V. Šunjić, J. Mol. Catal. A: Chem. 111 (1996) 239.
- [21] L.H. Slaugh, R.D. Mullineaux, US Patent 3239569 (1966).
- [22] J.L. van Winkle, R.C. Morris, R.F. Mason, US Patent 3420898 (1969).
- [23] E. Drent, J.C.L.J. Suykerbuyk, US Patent 7186868 B2 (2007).
- [24] E. Drent, J.C.L.J. Suykerbuyk, US Patent 7208606 B2 (2007).
- [25] E. Drent, J.C.L.J. Suykerbuyk, US Patent 2007/0032687 A1 (2007)
- [26] R.D. Garton, J.T. Ritchie, R.F. Caers, US Patent 7081554 B2 (2006).
- [27] M.J. Lawrenson, Fr. Dem. 1 558 222 (1969).
- [28] M.J. Lawrenson, G. Foster. Ger. Offen. 1 819 504 (1969).
- [29] J.M. Vargas, J.A. Hanin, J.C. Reisch, US Patent 5059718 (1991).
- [30] T. Mackewitz, US Patent 6559344 B2 (2003).
- [31] J.K. MacDougall, M.C. Simpson, M.J. Green, D.J. Cole-Hamilton, J. Chem. Soc. Dalton Trans (1996) 1161
- [32] J.K. MacDougall, D.J. Cole-Hamilton, J. Chem. Soc., Chem. Commun. (1990) 165.
- [33] J.K. MacDougall, M.C. Simpson, D.J. Cole-Hamilton, Polyhedron 12 (1993) 2877.
- [34] J.K. MacDougall, M.C. Simpson, D.J. Cole-Hamilton, J. Chem. Soc., Dalton Trans. (1994) 3061.
- [35] P. Cheliatsidou, D.F.S. White, D.J. Cole-Hamilton, Dalton Trans. (2004) 3425.

- [36] T. Ichihara, K. Nakano, M. Katayama, K. Nozaki, Chem. Asian J. 3 (2008) 1722.
- [37] T. Mizoroki, M. Kioka, M. Suzuki, S. Sakatani, A. Okumura, K. Maruya, Bull. Chem. Soc. Jpn. 57 (1984) 577.
- [38] D. Konya, K.Q. Almeida Leñero, E. Drent, Organometallics 25 (2006) 3166.
- [39] M. Haukka, L. Alvila, T.A. Pakkanen, J. Mol. Catal. A: Chem. 102 (1995) 79.
- [40] D. Evans, J.A. Osborn, G. Wilkinson, J. Chem Soc. A (1968) 3133.
- [41] Y. Izumi, K. Konishi, M. Tsukahara, D.M. Obaid, K. Aika, J. Phys. Chem. C 111 (2007) 10073.
- [42] M.C. Baird, C.J. Nyman, G. Wilkinson, J. Chem. Soc. A (1968) 348.
- [43] K. Ohno, J. Tsuji, J. Am. Chem. Soc. 90 (1968) 99.
- [44] L.S. Bresler, N.A. Buzina, Yu. S. Varshavsky, N.V. Kiseleva, T.G. Cherkasova, J. Organomet. Chem. 171 (1979) 229.
- [45] C. Brown, B.T. Heaton, L. Longhetti, W.T. Povey, D.O. Smith, J. Organomet. Chem. 192 (1980) 93.
- [46] T.P. Dougherty, W.T. Grubbs, E.J. Heilweil, J. Phys. Chem. 98 (1994) 9396.
- [47] F. Porta, S. Tollari, C. Bianchi, S. Recchia, Inorg. Chim. Acta 249 (1996) 79.
- [48] J.P. Collman, W.R. Roper, J. Am. Chem. Soc. 87 (1965) 4008.
- [49] T.A. Stephenson, G. Wilkinson, J. Inorg. Nucl. Chem. 28 (1966) 945.
- [50] D.W. Krassowski, J.H. Nelson, K.R. Brower, D. Hauenstein, R.A. Jacobson, Inorg. Chem. 27 (1988) 4294.
- [51] N. Ahmad, S.D. Robinson, M.F. Uttley, J. Chem. Soc. Dalton (1972) 843.
- [52] B.R. James, L.D. Markham, Inorg. Nucl. Chem. Lett. 7 (1971) 373.
- [53] M. Diéguez, C. Claver, A.M. Masdeu-Bultó, A. Ruiz, P.W.N.M. van Leeuwen, G.C.
- Schoemaker, Organometallics 18 (1999) 2107. [54] J.M. Brown, L.R. Canning, A.G. Kent, P.J. Sidebottom, J. Chem. Soc., Chem. Commun. (1982) 721.
- [55] M.S. Datt, J.J. Nair, S. Otto, Organomet. Chem. 690 (2005) 3422.
- [56] E. Mieczyńska, A.M. Trzeciak, R. Grzybek, J.J. Ziółkowski, J. Mol. Catal. A: Chem. 132 (1998) 203.
- [57] H.F. Schulz, F. Bellstedt, Ind. Eng. Chem. Prod. Res. Dev. 12 (1973) 176.