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Journal of Molecular Catalysis A: Chemical 214 (2004) 213–218
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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The hydroformylation of 4-penten-1-ol and 3-buten-1-ol in water with $HRh(CO)(TPPTS)_3$ and the effects of solution ionic strength

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Received 27 October 2003; received in revised form 19 December 2003; accepted 7 January 2004

Abstract

The reaction chemistry and kinetics of the low temperature hydroformylation of the water-soluble substrates, 4-penten-1-ol and 3-buten-1-ol, in aqueous solution utilizing the catalyst $HRh(CO)(TPPTS)_3$ is reported where, TPPTS is trisulphonated triphenylphosphine. The reactions were carried out at relatively low temperature and high stirring rates (1700 rpm) to maintain similar rates of mass transfer of gases into the aqueous phase. Activation parameters and reaction selectivity for the hydroformylation of 4-penten-1-ol are found to be dependent on solution ionic strength. At $[Rh] = 5 \times 10^{-4}$ M, an activation energy for the hydroformylation of 4-penten-1-ol of 23 kcal mol^{-1} is estimated. As sodium sulfate is added to the catalytic phase the activation energy increases. The dependence of reaction selectivity on ionic strength is unexpected. The reaction can be directed to yield a product distribution of modest linearity (75%) or an exceptionally high ratio of the branched product, observed exclusively as a cyclic 2-hydroxy-3-methyltetrahydropyran (98%), by control of solution ionic strength and temperature. A wider range of selectivities can be obtained for 4-penten-1-ol in water with $HRh(CO)(TPPTS)_3$ than can be obtained in toluene with $HRh(CO)(PPh_3)_3$. The hydroformylation of 3-buten-1-ol is less sensitive to reaction conditions. An activation energy of 25 kcal mol^{-1} is estimated at $[Rh] = 2.5 \times 10^{-4}$ M. Reaction selectivity favors in this case the formation of a six-membered over a five-membered cyclic acetal and is not influenced by temperature or solution ionic strength. It appears that the hydroxy group can direct the site of CO addition to alkenols, perhaps by chelate formation, and that solution ionic strength affects its ability to do so.

Keywords: Aqueous; Catalysis; Hydroformylation; TPPTS; Kinetics

1. Introduction

The hydroformylation of propene in water over rhodium complexes of trisulfonated triphenylphosphine (TPPTS) is a process of great practical value. The technical success of the process is due to several important factors including, an efficient sulfonation method for converting triphenylphosphine to TPPTS, the solubility of propene in water, which allows for practical reaction rates, and the highly efficient manner in which TPPTS keeps rhodium in the aqueous phase [1]. The catalyst functions as an immobilized homogeneous catalyst with product removed from the catalyst by phase separation.

Although few mechanistic studies on the hydroformylation of olefins with rhodium/TPPTS systems are available, some aspects of the complex and catalyst chemistry of $HRh(CO)(TPPTS)_3$ are known. First, catalysis takes place in the aqueous phase. As a result catalytic activity decreases rapidly as the solubility of the substrate in water diminishes [2]. The activity of the water-soluble catalysts with water-insoluble substrates is increased in supported aqueous phase systems [3]. Under these circumstances the increased surface area of the adsorbed phase gives better contact between the supported aqueous phase and the non-aqueous substrate phase. Second, at high pressures of CO the complex $HRh(CO)(TPPTS)_3$ is more stable than $HRh(CO)(PPh_3)_3$ [4]. The latter compound quickly reacts with CO to yield significant quantities of $HRh(CO)_2(PPh_3)_2$ while there is no evidence for the formation of the dicarbonyl of $HRh(CO)(TPPTS)_3$ when the complex is subjected to high pressures of CO. Third, it appears that the activation barrier to exchange of coordinated and free TPPTS in aqueous solutions of $HRh(CO)(TPPTS)_3$ and TPPTS [4,5] is greater than the barrier to exchange in $HRh(CO)(PPh_3)_3$ in non-aqueous solvents [6]. In non-aqueous solvents the activation energy

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doi:10.1016/j.molcata.2004.01.003

reported for phosphine exchange in $HRh(CO)(PPh_3)_3$ is 19 kcal mol^{-1} while values in the range of 24–31 kcal mol^{-1} have been reported for exchange of TPPTS in aqueous solutions of $HRh(CO)(TPPTS)_3$ and TPPTS.

Kinetic parameters for the hydroformylation of olefins over $HRh(CO)(TPPTS)_3$ in water have not been reported. The reason for this lack of information is most likely due to experimental difficulties in measuring meaningful rates in the immobilized catalytic system. The rate of reaction is likely to be mass transfer limited; under a wide variety of conditions the rate-determining step will be dissolution of the olefinic substrate in the aqueous phase. This is less of a problem for lower olefins such as propene than it is for higher olefins, which have negligible solubility in water.

The kinetics of octene hydroformylation in aqueous ethanol has been investigated [7]. It was shown that octene solubility in 50% aqueous ethanol is approximately 10^4 times that in water alone at 25 °C. The substantially improved rates that are observed in aqueous ethanol are attributed to improved octene solubility. The empirically derived rate law is first order in both octene and catalyst concentration and has a more complex dependence on H_2 and CO concentration. The reaction shows an inverse relationship on CO at high CO partial pressures.

It has been shown that the hydroformylation of the allylic alcohols, 3-buten-2-ol and 1-octen-3-ol, can lead to exclusive formation of the cyclic acetals, 2-hydroxyl-5-methyltetrahydrofuran and 2-hydroxy-5-pentyltetrahydrofuran, respectively [8]. These are formed by carbonyl addition γ to the hydroxy group of the allylic alcohol followed by intramolecular acetal formation. Hydroformylation of 5-hexen-1-ol yields both linear and branched hydroxyl aldehydes [8].

In an effort to obtain kinetic parameters, including an activation energy for hydroformylation in water, we have investigated the kinetics of hydroformylation of two alkenols in aqueous solutions of $HRh(CO)(TPPTS)_3$. Since these substrates have significant solubility in water, mass transfer of the olefin to the aqueous phase should not be rate limiting. However, the solubility of the gases, H_2 and CO, in water may still be of concern in designing experiments for the determination of activation energies.

2. Experimental

The substrates, 4-penten-1-ol and 3-buten-1-ol, were obtained from Aldrich Chemical Company and used without further purification. Synthesis gas, 99.99% H_2:CO, 1:1, was obtained from Airco. Sodium sulfate was obtained from Aldrich and used as-received. Trisulfonated triphenylphosphine was either prepared as described previously by the direct sulfonation of triphenylphosphine [9] or received as a gift. The complex $HRh(CO)(TPPTS)_3$ was prepared as described previously [10]. Water was distilled under nitrogen in an all glass apparatus, stored in a glass container and bubbled with CO/H_2 for 25 min prior to use in the catalytic experiments.

2.1. Catalysis

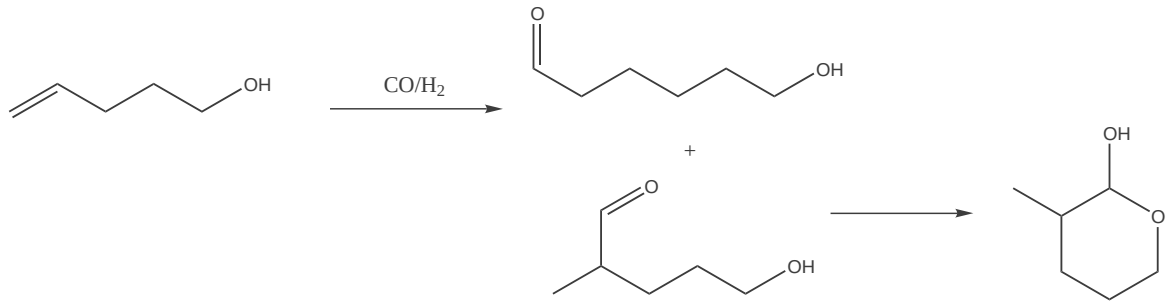
All reactions were performed in a 25 ml mechanically stirred Parr mini reactor. The rhodium complex, excess phosphine, and a minimum quantity of solvent to dissolve the solids were sealed in an ampoule. The ampoule was placed in the reactor with the substrate dissolved in the reminder of the solvent. Stirring began after the reactor was brought to the desired temperature and pressure. Initiation of stirring also broke the ampoule, released its contents, and started the reaction. A gas manifold, which consisted of a pressure regulator, ballast tank, and a digital pressure gauge, was used to monitor gas uptake at constant pressure (27 atm) within the reactor. The rhodium and phosphine concentrations for the kinetic runs were as follows: 5.0×10^{-4} M, $HRh(CO)(TPPTS)_3$ and 1.5×10^{-3} M TPPTS. Higher concentrations, 2.5×10^{-3} M, $HRh(CO)(TPPTS)_3$ and 7.5×10^{-3} M TPPTS were investigated to determine the influence of concentration of catalyst and ligand on reaction selectivity. The initial olefin concentration was held constant at 0.75 M. This gives the ratio of Rh:P:olefin = 1:6:1500 for the kinetic runs, and Rh:P:olefin = 1:6:300 for the reactions at higher rhodium concentration. The ionic strength of solution was calculated by $I = 0.5 \sum (c_i z_i^2)$, where c_i is the concentration of ionic species i and z_i that species charge. For runs at higher ionic strength the addition of sodium sulfate was added to the solvent prior the start of the reaction just before the addition of olefin.

Temperature and stirring rate (1700 rpm) were controlled with a Parr 4842 controller. Products were analyzed by gas chromatography (Varian 3300 with an HP1 column, 25 m × 0.32 mm × 0.52 μm), ^{1}H NMR spectroscopy (Bruker WP 200 or Varian RU 400), and GC mass spectroscopy.

Kinetic studies were performed by monitoring the uptake of CO and H_2 gas. The rate of hydroformylation was found to be first order with respect to the alkenol. The plots of $\ln((P_t - P_f)/(P_i - P_f))$ versus time where, $(P_t - P_f)/(P_i - P_f) = [A]_t/[A]_0$, show good linearity to 75% conversion of olefin (where P_i is the initial pressure, P_f the pressure at 100% conversion, P_t the pressure at time t, $[A]_t$ the concentration of 4-penten-1-ol at time t, $[A]_0$ the concentration of 4-penten-1-ol at time equal to 0). The reported rate constants are from the first 25% conversion; the apparent rate constants increase slightly with conversion of olefin perhaps due to increased gas solubility in water/product mixtures versus the initial solvent composition.

3. Results

The expected products from the hydroformylation of 4-penten-1-ol are the linear product, 6-hydroxy-hexan-1-al,



Scheme 1. Aldehydes expected from the hydroformylation of 4-penten-1-ol.

Table 1
Distribution of 4-penten-1-ol hydroformylation products as a function of temperature and concentration

Temperature (°C)	[Rh] = 5.0 × 10^{-4} M, I = 3.1 × 10^{-2} M (water)			[Rh] = 5.0 × 10^{-4} M, I = 6.2 × 10^{-2} M (water)			[Rh] = 2.5 × 10^{-3} M, I = 0.15 M (water)			[HRh(CO)(PPh_3)$_3$] = 5.0 × 10^{-4} M (toluene)		
	Conversion (%)	n (%)	cyc(6) (%)	Conversion (%)	n (%)	cyc(6) (%)	Conversion (%)	n (%)	cyc(6) (%)	Conversion (%)	n (%)	cyc(6) (%)
35	90	75	25	89	77	23	84	71	29	95	38	62
45	89	72	28	72	23	77	72	<2	>98	98	43	57
55	90	78	22	80	22	78	72	<2	>98	95	37	63
65	89	19	81	80	15	85	73	<2	>98	92	47	53
75	91	28	72	89	35	65						

n: normal product, 6-hydroxy-hexan-1-al; cyc(6): six-membered cyclic acetal, 2-hydroxy-3-methyltetrahydropyran.

and the branched product, 2-methyl-5-hydroxyl-pentan-1-al, as shown in Scheme 1.

Although two products are observed by gas chromatography, analysis of these by GC–MS shows that the first to elute has as its highest mass, 98 amu while the second shows a mass of 116 amu. The ^{1}H NMR spectrum of the reaction mixture clearly identifies the second product as the expected linear product by a distinctive triplet in the aldehyde region, 9.70 ppm (J_{HH} = 1.69 Hz). However, no additional aldehyde proton is detected for the second product. Rather, the spectrum is consistent with the intramolecular formation of 2-hydroxy-3-methyltetrahydropyran (Scheme 1). The apparent molecular ion observed in the mass spectrum is interpreted as the result of loss of water from the acetal.

The distribution of products in the hydroformylation of 4-penten-1-ol in water is concentration and temperature dependent. The results are summarized in Table 1 at selected temperatures. As the reaction temperature is taken from 35 to 75 °C there is a reversal in product preference from the linear product, 6-hydroxy-hexan-1-al, to the cyclic 2-hydroxy-3-methyltetrahydropyran. The temperature at which the reversal in selectivity occurs drops as

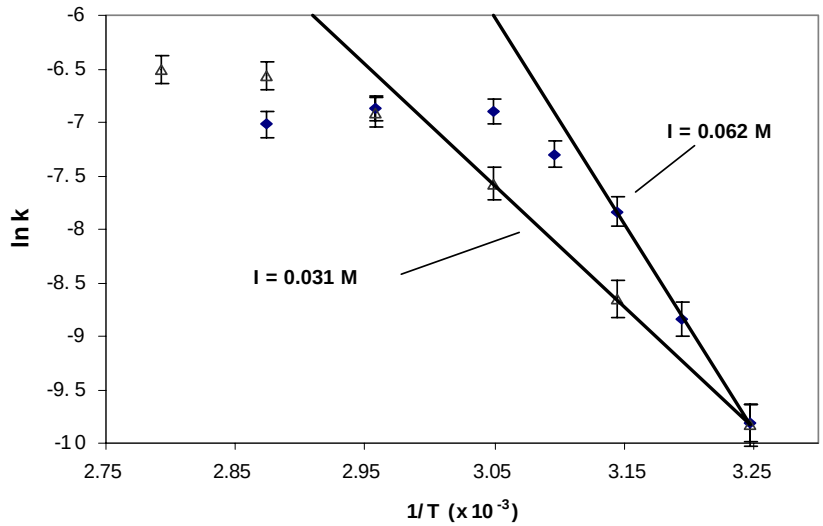
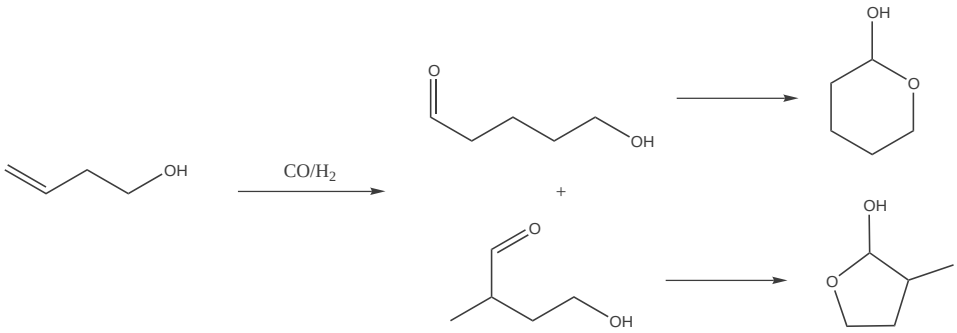


Fig. 1. Arrhenius plots for the hydroformylation of 4-penten-1-ol. The plot with the lesser slope, I = 0.031 M, gives an activation energy of 23 kcal mol^{-1}. At an ionic strength of 0.062 M the activation energy is calculated to be 34 kcal mol^{-1}.

Table 2
Distribution of 3-buten-1-ol hydroformylation products as a function of temperature and concentration

Temperature (°C)	[Rh] = 5.0 × 10^{-4} M, I = 3.1 × 10^{-2} M (water)			[Rh] = 5.0 × 10^{-4} M, I = 6.2 × 10^{-2} M (water)		
	Conversion (%)	cyc(6) (%)	cyc(5) (%)	Conversion (%)	cyc(6) (%)	cyc(5) (%)
35	100	74	26	91	77	23
45	100	72	28	98	84	16
55	80	77	23	85	75	25
65	82	73	27	89	74	26

cyc(6): six-membered cyclic acetal, 2-hydroxy-tetrahydropyran; cyc(5): five-membered cyclic acetal, 2-hydroxy-3-methyltetrahydrofuran.



Scheme 2. Products from the hydroformylation of 3-buten-1-ol.

solution ionic strength increases. Also, at the relatively high ionic strength obtained by increasing rhodium and phosphine concentration by a factor of 5, the reaction yields almost exclusively 2-hydroxy-3-methyltetrahydropyran. For comparison, the hydroformylation of 4-penten-1-ol by $HRh(CO)(PPh_3)_3$ in toluene was also investigated (Table 1). Under the reaction conditions used, [Rh] = 5.0 × 10^{-4} M, [PPh_3] = 1.5 × 10^{-3} M, and T = 35–65 °C, the reaction favors the cyclic product at all temperatures studied in all cases in toluene.

The natural log of the first-order rate constants for 4-penten-1-ol hydroformylation at [Rh] = 5.0 × 10^{-4} M and an ionic strength, I = 3.1 × 10^{-2} M, and [Rh] = 5.0 × 10^{-4} M with I = 6.2 × 10^{-2} M are plotted versus 1/T in Fig. 1. Both plots show significant curvature at higher temperature. This usually indicates that the reaction is either mass transfer limited at the higher temperatures, competing reaction mechanisms are operative, or catalyst deactivation has occurred. Although it is possible that the mass transfer of CO and H_2 gases could cause the observed curvature due to gas solubility diminishing with decreased temperature and thereby increasing the rate of the reaction, it is unlikely since the reactions were preformed at relatively high pressures. Competing mechanisms appear to be a stronger possibility for this observation since the curvature in the activation energy plot corresponds to the

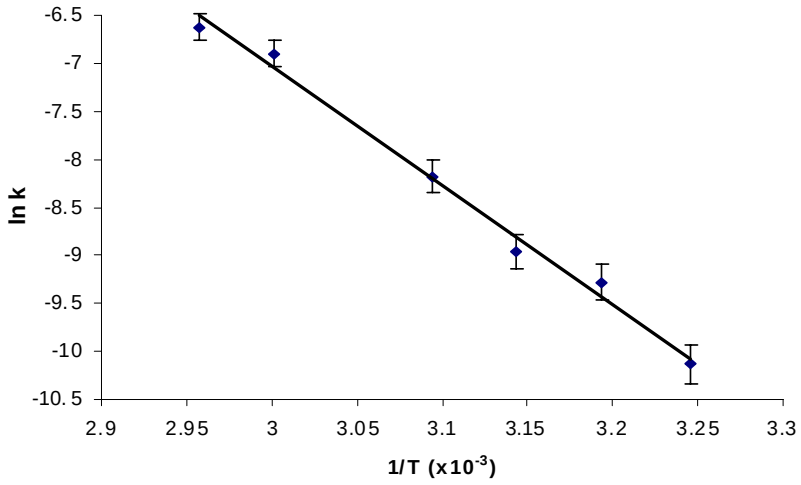


Fig. 2. Arrhenius plot for the hydroformylation of 3-buten-1-ol. The calculated activation energy is 25 kcal mol^{-1}.

shift in linear to branched ratios. The data at higher ionic strength show more curvature. An estimate can be made for the activation energy in the lower temperature range of the plots where the data is more linear. In this manner, E_a is estimated to be 23 kcal mol^{-1} at [Rh] = 5.0×10^{-4} M ($I = 3.1 \times 10^{-2}$ M) while at higher ionic strength, [Rh] = 5.0×10^{-4} M ($I = 6.2 \times 10^{-2}$ M), an E_a of 34 kcal mol^{-1} is estimated.

The kinetic data at the higher rhodium concentration, [Rh] = 2.5×10^{-3} M, shows curvature in the ln k versus $1/T$ plots at all points down to 35 °C, thus an accurate activation energy could not be determined from this data. Importantly, at 2.5×10^{-3} M Rh and the requisite concentration of TPPTS (7.5×10^{-3} M), a solution of high ionic strength is obtained; in these solutions the selectivity towards the cyclic product is >98% at temperatures of 45 °C and higher. At the same temperature and concentration of rhodium and phosphine in the non-aqueous system, $HRh(CO)(PPh_3)_3$, the selectivity is 60% branched and 40% linear.

Data for the hydroformylation of 3-buten-1-ol are shown in Table 2. Neither the linear nor the branched hydroxy aldehyde is observed directly. Rather the cyclic acetals are formed as shown in Scheme 2. Reaction selectivity is now independent of temperature. From the Arrhenius plot, Fig. 2, E_a of 25 kcal mol^{-1} is estimated for the reaction.

4. Discussion

The most interesting aspect of the hydroformylation of 4-penten-1-ol is the observed regiochemistry. The hydroformylation of simple olefins such as hexene and 1-octene in water with rhodium TPPTS catalysts yields a high percentage (>90%) of linear products [11,12]. In non-aqueous solvents and at a total phosphine to rhodium ratio of 5 to 10, typical reaction selectivity is about 75% linear with $HRh(CO)(PPh_3)_3$ as the catalyst.

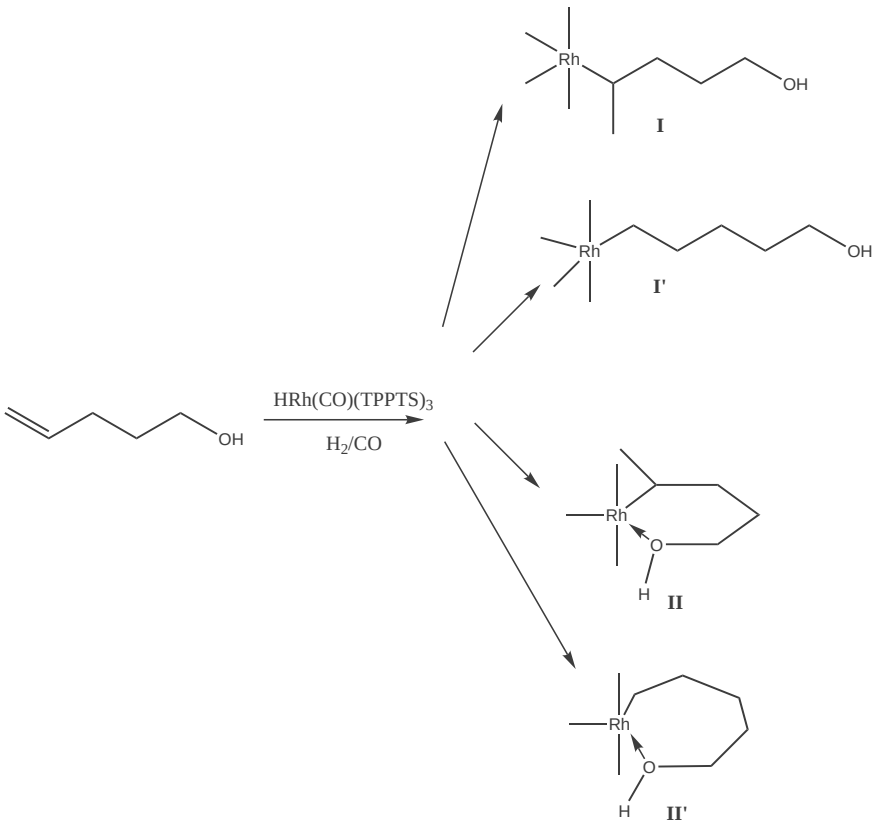
The hydroformylation of 3-buten-1-ol in toluene over rhodium phosphine catalysts also yields ∼75% linear products [13]. A similar selectivity is observed here in water for 3-buten-1-ol with yields of ∼75% six-membered cyclic acetal. In contrast, the selectivity of 4-penten-1-ol hydroformylation is solvent and temperature dependent; at low temperature (35 °C) in water the linear product is favored while in toluene the six-membered cyclic product is favored. At higher temperatures in water a reversal in selectivity is observed so that the six-membered cyclic acetal is favored. Additionally, the temperature at which the reversal is observed appears to be ionic strength dependent and at very high catalyst concentrations the selectivity to the six-membered cyclic acetal is greater than 98%.

Since the major difference between 3-buten-1-ol and 4-penten-1-ol is the substrate is the proximity of the OH group relative to the olefin functionality it is reasonable to suggest that the alcohol is able to direct the addition of CO. This could be accomplished by coordination of the OH group to the rhodium to form a chelate as a reaction intermediate.

The observed reaction selectivities can be rationalized in the context of Scheme 3. Hydride migration and β-hydride elimination are reversible and can lead to isomerization [14]. With simple olefins as the substrate, reaction selectivity is attributed to the steric demands of the modifying ligand which dictates the relative probability of forming **I** or **I′**. Bulky ligands favor intermediate **I′** which leads in turn to linear aldehydes. The alkenol substrates in principle can interact further with the metal to form the chelates, **II** and **II′**. Carbonyl insertion in either **I** or **II** leads to the cyclic acetals and insertion to **I′** or **II′** leads to the linear product. When the substrate is 3-buten-1-ol the possible intermediates are chelates that form a five- or six-membered ring structure with little energy difference between them (Scheme 2). However, when the substrate is 4-penten-1-ol the intermediate **II′** contains a seven-membered chelate ring which is less favorable than smaller chelate rings. If **I′** and **II** can interconvert rapidly by hydride migration before CO insertion, then **II** would be favored at higher temperature due to the favorable entropy term associated with chelate formation.

Other examples of directed addition of CO and H_2 to olefins include the hydroformylation of methylmethacrylate [15] and methyl-*N*-acetamidoacrylate [16]. Both substrates show excellent selectivity to the branched product, that is, CO addition to the more substituted carbon. For the latter substrate the branched product is the only product observed.

The activation energy for the hydroformylation in water of 23 kcal mol^{-1} is consistent with the values reported in the literature for the hydroformylation of a number of simple olefins with rhodium catalysts. Values include 22 kcal mol^{-1} for the hydroformylation of 1-butene with rhodium triphenylphosphine catalysts [6]; 21 kcal mol^{-1} for the hydroformylation of 1-octene with $Rh_4(CO)_{12}$ [17]; 38 kcal mol^{-1} for the hydroformylation of 1-octene starting with rhodium nitrate as the precursor to a rhodium carbonyl catalyst [18]; 17 and 18 kcal mol^{-1}, respectively, for the formation of linear and branched heptanals from 1-hexene hydroformylation over $[Rh(NBD)Cl]_2$ [19], and 22 and 19 kcal mol^{-1}, respectively, for the formation of linear and branched heptanals from 1-hexene hydroformylation with rhodium triphenylphosphine catalysts [20]. An increase in solution ionic strength leads to higher activation energy for catalysis has no precedent in the homogeneous hydroformylation literature. One can speculate from these results that the ionic strength of the solution influences the transition state involving the chelation of the hydroxyl to the metal complex. Similar to the effect observed commonly within the binding of charged substrates to enzymes [21]. This would explain why the phenomenon observed here for the hydroformylation of 4-penten-1-ol and has not been reported within aqueous media of other non-functionalized olefins.



Scheme 3. Possible reaction products from the hydroformylation of 4-penten-1-ol.

Acknowledgements

We thank NSF (CHE 9319881) for support of this work and the DuPont Education Foundation for additional support. The authors would also like to thank St. John's University for faculty support, Dr. Peter Lappe of Hoechst Werk Ruhrchemie for a gift of TPPTS and Drs. Alison Hyslop and Elise Megehee for helpful discussions.

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