

REPPE REACTION CATALYZED BY SOLUBLE CARBONYLRHODIUM COMPLEXES

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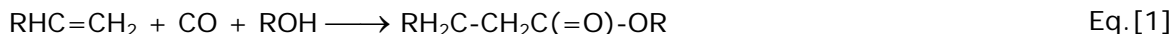
ABSTRACT

The catalysis of the hydroesterification and hydroformylation-acetalization of 1-hexene by rhodium(I), *cis*-[Rh(CO)₂(amine)₂](PF₆) complexes (amine = pyridine, 2-picoline, 3-picoline, 4-picoline, 3,5-lutidine or 2,6-lutidine) dissolved in 10 mL of ethanol or 10 mL of 80% aqueous ethanol, 0.4 mL (3 × 10⁻³ mol) of 1-hexene, [Rh] = 5 × 10⁻⁵ mol, 1-hexene/Rh = 64 under P(CO) = 0.9 atm at 100 °C for 4 h, is described in this work. The mayor products are ethyl-heptanoate, heptanal and 1,1-diethoxyheptane coming from the hydroesterification, hydroformylation reactions and the nucleophilic addition reaction of the ethanol over the formed heptanal, respectively. The reaction product distribution depends on the nature of the coordinate amine to the rhodium center.

Key Words: Catalysis, Reppe reaction, rhodium complexes; 1-hexene.

INTRODUCTION

The synthesis of oxygenated organic products by reaction of an olefinic substrate with CO and alcohols (ROH, Eq. [1]) in the presence of transition metal complexes has been know¹). This reaction has received considerable attention²⁻⁶) and it is the subject of a recent review⁷). Acetal formations under hydroformylation conditions in presence of alcohols have also been reported^{8,9}).



The products coming from the catalytic hydroesterification and hydroformylation-acetalization reactions of C₆-C₈ olefins by soluble and immobilized transition metal complexes offer access to wide range of important oxygenates compounds which could be used in a be though future industrial catalytic process for gasoline improving based on *in situ* Reppe-type reaction over olefins (ca. 43.5 %) present in typical naphtha¹⁰) Accordingly, this model of Reppe-type gasoline improving process could in principle, carry out in one step avoiding the expensive catalytic hydrogenation of the C₆-C₈

olefins step which, increase the octane content, prior to the addition of oxygenated-type compounds, like methyl-*ter*-butyleter o *ter*-ammilmethyleter used as additive in commercial gasoline.

We report in the present study the influence of nature of the coordinated amine on the catalytic hydroesterification and the hydroformylation-acetalization of 1-hexene, in ethanol or aqueous ethanol by these rhodium(I) complexes. On the other hand, 1-hexene was adopted as a model substrate because it represents ca. 33 % of the olefin fraction on typical naphtha.

EXPERIMENTAL

Materials: Pyridine (py), methyl pyridines (2-picoline (2-pic), 3-picoline (3-pic), and 4-picoline (4-pic)) and dimethyl pyridines (3,5-lutidine (3,5-lut) and 2,6-lutidine (2,6-lut)) were obtained from Aldrich and distilled over KOH. Ethanol and 1-hexene (Aldrich) were distilled prior to use. Water was doubly distilled. All gas mixtures He/H₂ (91.4%/8.6%, v/v), CO/CH₄ (95.8%/4.2%, v/v) and CO/CH₄/CO₂/H₂ (84.8%/5.1%/5.3%/4.8%, v/v) were purchased from BOC Gases and were used as received. The complexes of the type *cis*-[Rh(CO)₂(amine)₂](PF₆) (amine = 4-picoline, 3-picoline, 2-picoline, pyridine, or 2,6-lutidine) were synthesized and characterized as reported by Denise and Pannetier¹¹) and their IR spectra in chloroform demonstrated their identity and purity (two strong bands in the n(CO) region at 2095 and 2020 cm⁻¹).

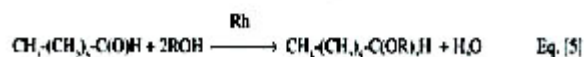
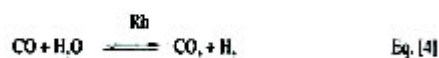
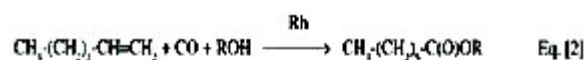
Instrumentation: Gas samples analyses from catalysis and kinetics runs were performed as described in detail previously¹²) on a Hewlett-Packard 5890 Series II programmable (ChemStation) gas chromatograph fitted with a thermal conductivity detector. The column employed was Carbosieve-B (80-100) mesh obtained from Hewlett-Packard and using the He/H₂ mixture as the carrier gas. Analyses of liquid phase were done on a Hewlett-Packard 5890 Series II programmable gas chromatograph fitted with a HP-1 (methyl silicone gum, 50 m x 0.323 mm x 0.17 mm) column and flame ionization detector, and using He as the carrier gas. A Varian Chrompack 3800 programmable gas chromatograph fitted with a CP-Sil-8-CB (phenyldimethylpolysiloxane) (30 m x 0.250 mm) column and a Varian Chrompack, Saturn 2000 mass selective detector was used to confirm the identity of the organic reaction products at the end of each run. Also the organic products were separated by column chromatography and analyzed by ¹³C and ¹H-NMR in a Jeol Eclipse 270 NMR spectrometer.

Catalyst testing: Catalytic runs were carried out in all-glass reactor vessels consisting of a 100 mL round bottom flask connected to an "O" ring sealed joint to a two-way Rotoflow Teflon stopcock attached to the vacuum line. In a typical run, a given amount of the catalyst (5 x 10⁻⁵ mol), 0.4 mL (3 x 10⁻³ mol) of 1-hexene and 10 mL of ethanol (0.17 moles) were added to the glass reactor vessel, and then the mixture was degassed by three freeze-pump-thaw cycles. The reaction vessel was charged with CO/CH₄ mixture at the desired CO partial pressure (0.7 atm at 25 °C, but 0.9 atm at 100 °C), and then suspended in a circulating thermostated glycerol oil bath set at 100 °C by 4 h. The specified temperature was maintained at ± 0.5 °C by continuously stirring the oil bath as well as the reaction mixture which was provided with a Teflon-coated magnetic stirring bar. At the end of the reaction time gas samples (1.0 mL) were taken by a gas tight syringe from the gaseous phase above the mixture and analyzed by GC. Also, liquid samples were removed and analyzed by GC and GC-MS.

The CH₄ was used as internal standard to allow calculation of absolute quantities of CO consumed and H₂ and CO₂ produced. In addition, calibration curves were prepared periodically for CO, CH₄, H₂, and CO₂, and analyzing known mixtures checked their validities. The amounts of organic products were determined by using the response factor method for gas chromatographic analyses¹³).

RESULTS AND DISCUSSION

The *cis*-[Rh(CO)₂(amine)₂](PF₆) complexes were examined as catalytic precursors for 1-hexene hydroesterification and hydroformylation-acetalization, The relative extent of the competing catalytic reactions was established by comparing the amounts of the formed products. The results are summarized in [Table I](#). Additional, control experiments show no activity toward the hydroesterification and hydroformylation-acetalization of 1-hexene under CO when a mixture of ethanol with 1-hexene was tested under similar experimental conditions in the absence of any of these carbonylrhodium catalysts.



Hydroesterification and hydroformylation-acetalization. Analyses by 1H-NMR, GC and GC-MS of the liquid phase runs reveal the presence of ethyl-heptanoate, heptanal and 1,1-diethoxy-heptane which come from coming from the 1-hexene hydroesterification in ethanol, Eq. [2], hydroformylation Eq. [3], and the addition reaction between ethanol and the formed heptanal, Eq. [5], respectively⁹).

Control experiments in the absence of any of the soluble catalysts showed formation of 1,1-diethoxy-heptane (8% of yield) when a 1.0 mL of heptanal is placed in contact with 10 mL of ethanol under P(CO) = 0.9 atm at 100 °C by 4 h. For that reason, Table I does not record the TF of acetal production due to its probably stoichiometric formation under the catalytic reaction conditions. However, the soluble *cis*-[Rh(CO)₂(4-pic)2](PF₆) complexes ([Rh] = 0.022 g (5 x 10⁻⁵ moles)) also catalyzed in 10 mL of ethanol, the acetalization of heptanal (1.0 mL) under P(CO) = 0.9 atm at 100 °C for 4 h. The heptanal conversion under the above-described conditions slightly increases from 8 to 18%.

The results in ethanol show that TF(ethyl-heptanoate)/24 h (TF(EH/24 h) values depend on the nature of the coordinated amine and decrease in the following order: 2,6-lutidine > 3,5-lutidine > 4-picoline > 3-picoline > pyridine > 2-picoline. Accordingly, the catalytic hydroesterification of 1-hexene by this Rh/(amine) system is influence principally by the basic nature of the amine being the Rh/(2,6-lut) system the most active. The observed reverse order in the case of the Rh/(2-pic)2 system is due

to the steric hindrance factor which overwhelm the electronic one. It is interesting to see on the Rh/(2,6-lut)2 system that the steric hindrance factor does not overwhelm the electronic factor even that the 2,6-lutidine amine is the most crowded among the amine using in this work.

A plot of $\ln(\text{EH})/24 \text{ h}$ values vs. pK_a of the protonated base for the sterically and nonsterically hindered pyridines used is shown in [Figure 1](#). The slope value of 0.74 suggests a modest effect in ethyl-heptanoate production on increasing basicity. The substituent effects on the hydroesterification rates suggest that addition of ethanol to Rh catalytic species prior to the ester formation is affected by the electron density at the Rh center. A detail discussion of the mechanistic implications on the catalytic hydroesterification and the hydroformylation-hydroesterification of 1-hexene in methanol by these Rh/amine systems was reported¹⁵).

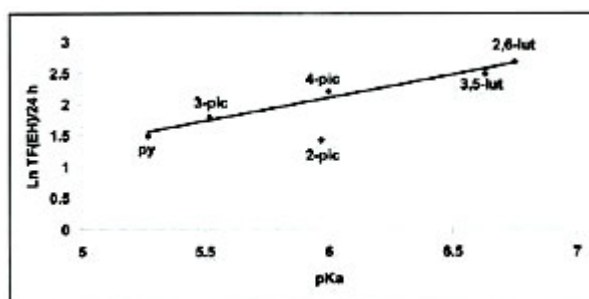


Fig. 1

On the other hand, the results related to the catalytic hydroformylation-acetalization of 1-hexene by these Rh/(amine) systems does not show a comprehensible tendency about the influence of the electronic and steric factors.

Based on the amounts of methyl-heptanoate, heptanal and 1,1-dimethoxy-heptane formed ([Table 1](#)) it can be observed that the hydroesterification of 1-hexene is more favored than hydroformylation-acetalization reactions by a factor ranging from 1.6 to 2.5 time for the more basic amine, namely: 4-picoline (61% yield of ester), 3,5-lutidine (61% yield of ester), and 2,6-lutidine (77% yield of ester). However, the opposite tendency is observed when the amines are the less basic, pyridine (35% yield of ester) and 3-picoline (38% yield of ester) and 2-picoline (44% yield of ester). The yields of ester, aldehyde and acetal were calculated base on CG data and by considering the total yields of the above three oxygenated products equal to 100%. These results suggested that the electronic factor induced by the methyl groups of the coordinate amine influences the rate of these two competing reactions, hydroesterification vs hydroformylation-acetalization.

Table I. WGSR, hydroesterification and hydroformylation-acetalization of 1-hexene in ethanol, catalyzed by the *cis*-[Rh(CO)₂(amine)₂](PF₆) complexes^a

Amine (pKa) ^b	[CO ₂] (Total) mol x 10 ⁻⁵	TF(CO ₂) ^c Total	[H ₂] mol x 10 ⁻⁵	TF(H ₂) ^c	[EH] ^d mol x 10 ⁻⁵	TF(EH) ^{d,e}	[Heptanal] mol x 10 ⁻⁵	[DEH] ^d mol x 10 ⁻⁵
Pyridine (5.27)	12.5	17	5.2	7	3.7	4.4	2.0	4.9
3-Picoline (5.52)	14.9	31	6.5	3	5.0	6.0	3.1	5.0
2-Picoline (5.97)	10.8	14	6.1	8	3.4	4.1	2.0	2.3
4-Picoline (6.00)	10.9	45	5.8	7	7.5	9.0	2.5	2.2
3,5-Lutidine (6.63)	11.4	18	4.4	7	10.0	12.0	2.7	3.8
2,6-Lutidine (6.75)	9.9	12	5.7	7	12.1	14.5	0.9	2.7

^a[Rh] = (5 x 10⁻⁵ mol), [1-hexene] = 0.4 mL (3 x 10⁻³ mol), 1-hexene/Rh = 64, 10 mL (0.17 mol) of ethanol, P(CO) = 0.9 atm at 100 °C for 4 h.

^bFrom Ref. 14.

^cTF(product) = [(mol of product)/(mol of Rh) x (rt)] x 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%.

^dEH = Ethyl-heptanoate; DEH = 1,1-Diethoxy-heptane.

WGSR catalysis. The WGSR is a well known side reaction under Reppe reaction conditions¹). All of these soluble Rh complexes are also active for the catalysis of the WGSR under the conditions required for the catalytic hydroesterification/hydroformylation-acetalization of 1-hexene. Even that reagents and solvents used were pre-dried, formation of water occurred via acetal formation, Eq. [5]. GC analyses of the gas phase of the catalytic runs allowed the identification of H₂ and CO₂ as sole gaseous products. The H₂ and certain amount of CO₂ come from the WGSR. The other amount of CO₂ produced comes from catalytic hydroformylation of 1-hexene under CO/H₂O, Eq. (3) and the total CO₂ mass balance matches both, Eq. [3] and Eq. [4].

Further, a control experiment shows no WGSR activity in the absence of any of soluble *cis*-[Rh(CO)₂(amine)₂]⁺ catalysts under similar reaction conditions. The results in ethanol show that TF(H₂) are low and almost similar, suggesting that the nature of the amine does not control the WGSR rates in these systems. Different trend was observed in the catalysis of the WGSR by *cis*-[Rh(CO)₂(amine)₂](PF₆) dissolved in 80% aqueous pyridine or substituted pyridines. For example the TF(H₂) decreased from 4-picoline (80) to 2,6-lutidine (1) under the following catalysts conditions: [Rh] = 10 mM, 10 mL of 80% aqueous amine under P(CO) = 0.9 atm at 100 °C. In those Rh(amine)₂/aqueous amine system the steric factor control the rate of H₂ and CO₂ formation¹²).

Hydroesterification, hydroformylation-acetalization and WGSR catalysis in 80% aqueous ethanol. The catalytic hydroesterification and hydroformylation-acetalization of 1-hexene by the *cis*-[Rh(CO)₂(amine)₂](PF₆) complexes was also carried out in 80% aqueous ethanol (Table II). Under the following reaction conditions: (5 x 10⁻⁵ mol), [1-hexene] = 0.4 mL (3 x 10⁻³ mol), 1-hexene/Rh = 64; 10 mL of 80% aqueous ethanol under P(CO) = 0.9 atm at 100 °C for 4 h, the GC and GC-mass analyses of the liquid phase runs allowed the identification and quantification of ethyl-heptanoate, heptanal and 1,1-diethoxy-heptane. Also these Rh(amine)₂ systems in aqueous ethanol catalyzed the WGSR. These results show that in presence of water the hydroformylation-acetalization reactions (Eqs. [3] and [5]) are more favored than the observed for the Rh(amine)₂/ethanol systems described above under similar reaction conditions.

Table II. WGS, hydroesterification and hydroformylation-acetalization of 1-hexene in aqueous ethanol, catalyzed by the *cis*-[Rh(CO)₂(amine)₂](PF₆) complexes^a

Amine (pKa) ^b	[CO ₂] (Total) mol x 10 ⁻³	TF[CO ₂] Total	[H ₂] mol x 10 ⁻⁵	TF(H ₂) ^c	[EH] ^d mol x 10 ⁻⁵	TF(EH) ^d	[Heptanal] mol x 10 ⁻²	[DEH] ^e mol x 10 ⁻⁵
Pyridine (5.27)	13.2	17	5.9	7	3.5	4	1.9	4.9
3-Picoline (5.52)	11.0	31	3.1	3	3.8	5	4.9	2.6
2-Picoline (5.97)	12.9	14	6.6	8	3.6	4	2.0	4.0
4-Picoline (6.00)	25.6	45	5.8	7	6.1	7	7.9	11.5
3,5-Lutidine (6.63)	11.9	18	5.7	7	4.7	6	8.9	4.5
2,6-Lutidine (6.75)	11.0	13	6.1	7	2.3	3	2.3	2.2

^a[Rh] = (5 x 10⁻³ mol), [1-hexene] = 0.4 mL (3 x 10⁻³ mol), 1-hexene/Rh = 64, 10 mL of 80% aqueous ethanol, P(CO) = 0.9 atm at 100 °C for 4 h.

^bFrom Ref. 14.

^cTF(product) = [(mol of product)/(mol of Rh) x (rt)] x 24 h, where (rt) = reaction time in hours. Experimental uncertainty < 10%.

^dEH = Ethyl-heptanoate. DEH = 1,1-Diethoxy-heptane.

CONCLUSIONS

In this work we carried out the catalytic transformation of 1-hexene, which is present in about 33% among the olefins in the LSR, in oxygenated compounds (esters and aldehyde-acetals) under CO atmosphere and this approximation constitutes a promissory work for a future industrial catalytic process for gasoline improving based on Reppe type reaction. Ethyl-heptanoate, heptanal and 1,1-diethoxy-heptane were synthesized by the hydroesterification and hydroformylation-acetalization of 1-hexene. The above reactions were catalyzed by soluble *cis*-[Rh(CO)₂(amine)₂](PF₆) complexes in ethanol or aqueous ethanol under carbon monoxide atmosphere. Formation of 1,1-dimethoxy-heptane comes principally from the nucleophilic addition reaction between ethanol and catalytic formed heptanal. Further, these Rh(amine)₂ catalytic systems are active for the WGS under the hydroesterification and hydroformylation-acetalization reaction conditions. The electronic factor of the coordinate amine influences the rate. Namely, the Rh(2,6-lut)₂ system shows to be the most active among the amine-catalysts tested toward the hydroesterification in comparison to the hydroformylation-acetalization reactions. The opposite is observed for the less basic pyridine.

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