

# Applications of the Water-Gas Shift Reaction. Hydroformylation and Hydrohydroxymethylation with CO and H<sub>2</sub>O

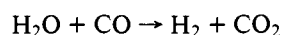
Richard M. Laine

Contribution from the Physical Organic Chemistry Group, The Chemistry Laboratory, SRI International, Menlo Park, California 94025. Received September 14, 1977

**Abstract:** Basic aqueous alcoholic solutions prepared from Ru<sub>3</sub>(CO)<sub>12</sub> or Rh<sub>6</sub>(CO)<sub>16</sub> are active catalysts for the water-gas shift reaction (H<sub>2</sub>O + CO → H<sub>2</sub> + CO<sub>2</sub>). Conditions are described wherein these same solutions are employed to catalyze the hydroformylation of 1-pentene to hexanal and 2-methylpentanal. The ruthenium-catalyzed hydroformylation exhibits one of the highest selectivities for straight-chain aldehydes (97 ± 1% hexanal:3 ± 1% 2-methylpentanal) of any known hydroformylation catalyst. The rhodium-catalyzed reaction, which is much less selective, catalytically reduces the aldehydes formed to alcohols. Evidence suggests that metal carbonyl cluster compounds may serve as components of the active catalyst solution.

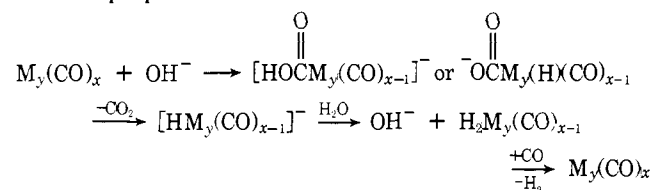
## Introduction

The homogeneous catalysis of the water-gas shift reaction (WGSR)



by basic aqueous alcoholic solutions of Ru<sub>3</sub>(CO)<sub>12</sub>, H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>, and Ru<sub>6</sub>C(CO)<sub>17</sub> has recently been demonstrated.<sup>1,2</sup> This work has been expanded to include a number of group 8 and group 6 metal carbonyls—e.g., Os<sub>3</sub>(CO)<sub>12</sub>, Rh<sub>6</sub>(CO)<sub>16</sub>, Ir<sub>4</sub>(CO)<sub>12</sub>, H<sub>2</sub>FeRu<sub>3</sub>(CO)<sub>12</sub>, and Mo(CO)<sub>6</sub>—as active homogeneous WGSR catalyst precursors.<sup>3-5</sup>

A general reaction sequence to account for the observations has been proposed:<sup>1,3,6</sup>



The presence of intermediate anionic metal hydrides in the proposed sequence is supported by the detection and isolation of [H<sub>3</sub>Ru<sub>4</sub>(CO)<sub>12</sub>]<sup>-</sup> as the major component in the active WGSR catalyst solutions deriving from either Ru<sub>3</sub>(CO)<sub>12</sub> or H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>.<sup>1,3</sup>

It is well known that metal hydrides can act as homogeneous catalysts for the hydrogenation of organic substrates. Thus, the detection and isolation of catalytically generated hydrides from active WGSR catalyst solutions prompted us to investigate the interaction of alkenes with active WGSR catalyst solutions; it was anticipated that CO and H<sub>2</sub>O used in conjunction with a WGSR catalyst solution would effect reactions normally requiring an independent source of H<sub>2</sub>.<sup>7</sup>

This paper reports studies on the interaction of 1-pentene under selected conditions with active WGSR catalyst solutions obtained using Ru<sub>3</sub>(CO)<sub>12</sub>, H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>, or Rh<sub>6</sub>(CO)<sub>16</sub> as the catalyst precursors.

## Experimental Section

**General Methods.** Methanol used in the kinetic runs was distilled from sodium methoxide in a nitrogen atmosphere immediately prior to use. Tetrahydrofuran (THF) was distilled from sodium benzo-phenone ketyl under N<sub>2</sub> immediately prior to use. Triruthenium dodecacarbonyl and hexarhodium hexadecacarbonyl were purchased from Strem Chemical Co. The rhodium complex was used as received; the ruthenium complex was purified by careful sublimation or by recrystallization from dichloromethane/hexane. Tetrahydridotetraruthenium dodecacarbonyl and tetraphenylarsonium trihydridotetraruthenium dodecacarbonyl were prepared by the methods of

Kaeszi.<sup>8,9</sup> Pure 1-pentene (99%) was purchased from MCB and used as received.

**Analytical Methods.** Gas analysis was performed with a Hewlett-Packard Model 5750 gas chromatograph using a 3.3 m × 0.328 cm molecular sieve column and 8.5% hydrogen in helium effluent gas. Product analysis was performed using a Hewlett-Packard Model 5711 gas chromatograph equipped with FID using a 4.0 m × 0.328 cm column packed with 5% Carbowax on acid-washed Chromosorb G. Infrared spectra were obtained using either a Perkin-Elmer Model 247 or 281 infrared spectrometer. Product identification was performed by comparison with authentic samples purchased from Aldrich.

**Catalytic Runs Using CO/H<sub>2</sub>O.** In a Teflon-lined Parr general purpose bomb reactor of 34-mL volume containing a magnetic stir bar are mixed 4.72 g (6.0 mL) of methanol, 1.15 g (1.0 mL) of 3.05 N KOH solution, 0.260 g (2.00 mmol) of *n*-butyl ether as internal standard for chromatographic analysis, 2.53 g (4.0 mL, 36.0 mmol) of 1-pentene or 2-pentene, and 0.10 mmol of Rh<sub>6</sub>(CO)<sub>16</sub> (106 mg), Ru<sub>3</sub>(CO)<sub>12</sub> (63 mg), or 0.075 mmol of H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> (58 mg). The reactor is sealed and degassed by three 800 psi pressurization/depressurization cycles with CO. The reactor is then charged to 800 psi CO and heated with magnetic stirring to 135 ± 1 or 150 ± 1 °C for the reaction period. The reactor is then cooled to 0 °C and both the gases above the reaction mixture<sup>10</sup> and the reaction mixture itself are analyzed by gas chromatography. The analysis of the reaction mixture necessitates opening the reactor to take samples; this must be done quickly to avoid loss of 1-pentene. The catalyst solutions do not appear to be particularly air sensitive; however, prolonged exposure was avoided.

The water-gas shift reaction catalysis was run in an identical manner without added 1-pentene.

**Catalytic Runs Using CO/H<sub>2</sub>.** In the same bomb reactor described above are mixed 7.0 mL of THF, 4.0 mL of 1-pentene, 0.260 g of *n*-butyl ether, and one of the following: 0.1 mmol of Ru<sub>3</sub>(CO)<sub>12</sub>, 0.075 mmol of H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>, or 0.075 mmol of (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As<sup>+</sup>[H<sub>3</sub>Ru<sub>4</sub>(CO)<sub>12</sub>]<sup>-</sup>. The reactor is sealed and degassed as above with 150 psi of hydrogen. The reactor is then charged to 150 psi with hydrogen and then to 1050 psi with CO. The reaction mixture is then heated to 150 ± 1 °C for 0.25 h and cooled to 0 °C; the pressure is released, and the reaction solution is analyzed. The Ru<sub>3</sub>(CO)<sub>12</sub>-catalyzed reaction gives 3.2 mmol of C<sub>6</sub> aldehydes, 83 ± 2% hexanal, and 17 ± 2% methylpentanal. The H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>-catalyzed reaction gives 1.7 mmol of C<sub>6</sub> aldehydes with identical product ratios. The (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>As<sup>+</sup>[H<sub>3</sub>Ru<sub>4</sub>(CO)<sub>12</sub>]<sup>-</sup>-catalyzed reaction gives 1.4 mmol of C<sub>6</sub> aldehydes with a ratio of 94 ± 2% hexanal:6 ± 2% 2-methylpentanal.

**Catalytic Reduction of C<sub>6</sub> Aldehydes.** A mixture of C<sub>6</sub> aldehydes (1.22 × 10<sup>-2</sup> mol) consisting of 31 ± 1% hexanal and 69 ± 1% 2-methylpentanal was added to an active rhodium WGSR catalysis solution that had previously been used to catalyze the WGSR at 135 °C for 24 h. The mixture was degassed as above and charged to 800 psi CO and heated at 135 °C for three consecutive 0.5-h periods. Analysis of the product mixtures gave at 0.5 h 5.68 mmol of C<sub>6</sub>H<sub>12</sub>O, 17% hexanal, 83% 2-methylpentanal; and 6.50 mmol of C<sub>6</sub>H<sub>14</sub>O, 42% 1-hexanol, 58% 2-methyl-1-pentanol; at 1.0 h 2.04 mmol of C<sub>6</sub>H<sub>12</sub>O,

**Table I.** Kinetic Data for Ruthenium- and Rhodium-Catalyzed Hydroformylation and Hydrohydroxymethylation

	Ru <sub>3</sub> (CO) <sub>12</sub> , 135 °C	Ru <sub>3</sub> (CO) <sub>12</sub> , 150 °C <sup>d</sup>	H <sub>4</sub> Ru <sub>4</sub> (CO) <sub>12</sub> , 150 °C	Rh <sub>6</sub> (CO) <sub>16</sub> , 135 °C	Rh <sub>6</sub> (CO) <sub>16</sub> , 150 °C	Rh <sub>6</sub> (CO) <sub>16</sub> , 135 °C <sup>b</sup>
	Initial Product Ratios <sup>a</sup>					
C <sub>6</sub> H <sub>12</sub> O	32.3 (3.68 ± 0.20)	32.3 (6.63 ± 0.30)	32.3 (7.66 ± 0.20)	4.3 (7.10 ± 0.25)	2.1 (7.02 ± 0.25)	0.31 (6.60 ± 0.40)
C <sub>6</sub> H <sub>14</sub> O		32.3 (0.11 ± 0.02)	32.3 (0.16 ± 0.04)	9.0 (1.42 ± 0.25)	6.3 (3.32 ± 0.25)	0.36 (4.60 ± 0.40)
time, h	0.5	0.5	0.5	0.5	0.5	0.5
	25% Conversion <sup>c</sup> Ratios					
C <sub>6</sub> H <sub>12</sub> O	24.0 (4.12 ± 0.20)	24.0 (7.10 ± 0.30)	24.0 (7.80 ± 0.30)			
C <sub>6</sub> H <sub>14</sub> O	32.3 (0.07 ± 0.03)	32.3 (0.21 ± 0.02)	32.3 (0.26 ± 0.04)			
time, h	1.0	1.0	~1.0			
	50% Conversion Ratios					
C <sub>6</sub> H <sub>12</sub> O	19.0 (3.72 ± 0.25)	19.0 (5.70 ± 0.30)	19.0 (5.95 ± 0.30)	4.3 (7.10 ± 0.25)	2.1 (7.02 ± 0.25)	0.31 (6.60 ± 0.40)
C <sub>6</sub> H <sub>14</sub> O	24.0 (0.08 ± 0.02)	32.3 (0.32 ± 0.04)	32.3 (0.35 ± 0.04)	9.0 (1.42 ± 0.25)	6.3 (3.32 ± 0.25)	0.36 (4.60 ± 0.40)
time, h	1.75	2.0	1.75	~0.5	0.5	~0.5
	75% Conversion Ratios					
C <sub>6</sub> H <sub>12</sub> O	13.3 (2.85 ± 0.20)	11.5 (3.23 ± 0.35)	13.3 (3.67 ± 0.20)	0.60 (3.35 ± 0.20)	0.60 (4.29 ± 0.20)	0.19 (3.71 ± 0.35)
C <sub>6</sub> H <sub>14</sub> O	15.7 (0.11 ± 0.02)	19.0 (0.48 ± 0.04)	19.0 (0.43 ± 0.05)	3.5 (7.80 ± 0.30)	2.60 (9.75 ± 0.20)	0.41 (6.35 ± 0.40)
time, h	3.5	~4.0	3.0	1.75	1.5	~1.5
	95% Conversion Ratios					
C <sub>6</sub> H <sub>12</sub> O	4.6 (2.17 ± 0.10)	4.0 (1.97 ± 0.15)	4.6 (1.95 ± 0.10)			
C <sub>6</sub> H <sub>14</sub> O	10.1 (0.29 ± 0.02)	8.1 (0.94 ± 0.06)	11.5 (0.84 ± 0.08)	1.20 (20.0 ± 1.55) <sup>e</sup>	1.3 (22.82 ± 1.05) <sup>e</sup>	0.65 (21.30 ± 1.30)
time, h	8.0 ± 0.5	9.5 ± 0.5 <sup>f</sup>	8.5 ± 0.5 <sup>f</sup>	6.0 ± 0.25	4.5 ± 0.25	6.0 ± 0.25
WGSR <sup>g,h</sup>						
mol H <sub>2</sub> /mol catalyst, 24 h	55 ± 3			115 ± 10		

<sup>a</sup> All product ratios are hexanal/2-methylpentanal or 1-hexanol/2-methyl-1-pentanol. The numbers in parentheses are quantities present in mmol. <sup>b</sup> Reaction with *trans*-2-pentene. <sup>c</sup> Conversion of alkene to product. <sup>d</sup> The rate of reaction decreases slightly on doubling the base concentration. <sup>e</sup> Olefin conversion is >99%. <sup>f</sup> The longer reaction times are the result of slight increases in isomerization of 1-pentene to 2-pentenes. <sup>g</sup> WGSR catalyst system without 1-pentene. <sup>h</sup> Reference 3.

5% hexanal, 95% 2-methylpentanal; and 10.10 mmol of C<sub>6</sub>H<sub>14</sub>O, 35% 1-hexanol, 65% 2-methyl-1-pentanol; at 1.5 h 12.15 mmol of C<sub>6</sub>H<sub>14</sub>O, 30% 1-hexanol, and 70% 2-methyl-1-pentanol.

## Results and Discussion

In the presence of 1-pentene, the Ru<sub>3</sub>(CO)<sub>12</sub> and H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> WGSR catalyst systems catalyze hydroformylation of the alkene, producing a mixture of C<sub>6</sub> aldehydes. The Rh<sub>6</sub>(CO)<sub>16</sub> WGSR catalyst system catalyzes hydroformylation of the alkene to a mixture of C<sub>6</sub> aldehydes, which are subsequently reduced to the corresponding C<sub>6</sub> alcohols (hydrohydroxymethylation).<sup>11</sup> Table I summarizes the data for both the ruthenium- and rhodium-catalyzed WGSR hydroformylation and hydrohydroxymethylation reactions.

**Hydroformylation and Hydrohydroxymethylation.** The ruthenium-catalyzed hydroformylation reaction produces C<sub>6</sub> aldehydes with one of the highest selectivities for straight-chain aldehydes (97 ± 1% hexanal to 3 ± 1% 2-methylpentanal, 32:1 ratio) found for any hydroformylation catalyst.<sup>12</sup> Unfortunately, beyond periods of 1 h, the base in solution catalyzes aldol condensation, which removes aldehyde somewhat faster than it is formed. Thus, at higher conversions, preferential condensation of hexanal together with some isomerization of 1-pentene to 2-pentenes results in a drop in the hexanal/2-methylpentanal ratios.<sup>13</sup>

The rhodium-catalyzed reaction partially avoids the condensation side reaction through rapid reduction of the aldehyde products to alcohols. The rhodium-catalyst solution shows very little selectivity for straight-chain products; thus, the product ratios (at 95–100% conversion) are essentially 1:1 1-hexanol to 2-methyl-1-pentanol. Yields are normally 60 ± 5% based on starting alkene.

The low selectivity found for the rhodium-catalyzed reaction is probably the result of extensive catalytic isomerization of the alkene prior to hydroformylation. This is demonstrated by substitution of *trans*-2-pentene for 1-pentene that results in

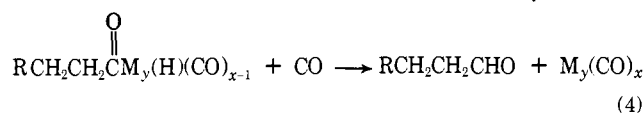
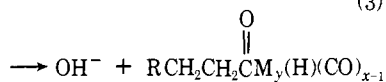
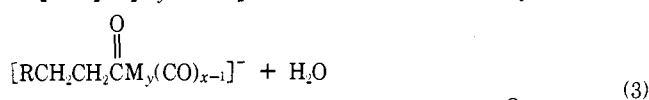
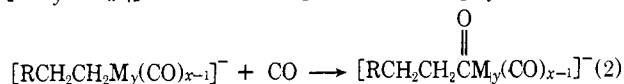
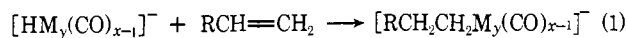
C<sub>6</sub> alcohols wherein 1-hexanol accounts for up to 40% of the product (see Table I).

Both the ruthenium- and rhodium-catalyzed reactions convert 1–5% of the 1-pentene to the by-products methyl hexanoate and methyl 2-methylpentanoate. Other products of both catalytic reactions are 2-ethylbutanal or 2-ethyl-1-butanol, but yields of these products are never greater than 1%. Hydrogenation of the 1-pentene to pentane does not occur with the catalyst systems described here, although it does occur with most of the standard hydroformylation reactions that use CO and H<sub>2</sub>.<sup>12</sup>

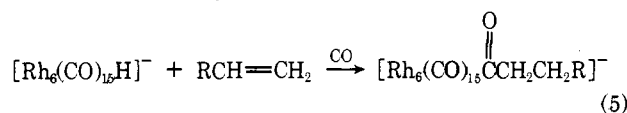
**Catalyst Solutions.** The clear red ruthenium hydroformylation catalyst solution has metal carbonyl stretching vibrations that are similar to those described for the low-pressure ruthenium-catalyzed WGSR.<sup>1</sup> These include ν<sub>CO</sub> 2088 (w), 2036 (sh), 2010 (vs), 1993 (s), 1974 (sh), and 1964 cm<sup>-1</sup> (mbr). Acidification of the reaction solution results in quantities of Ru<sub>3</sub>(CO)<sub>12</sub>, H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>, and small amounts of an as yet unidentifiable ruthenium carbonyl species.<sup>14</sup>

The rhodium-catalyzed reaction solution has a clear, deep-red to violet color, with methyl carbonyl stretching vibrations of ν<sub>CO</sub> 2088 (w), 2060 (sh), 2036 (s), 1875 (m), 1844 (ms), and 1787 cm<sup>-1</sup> (m). The color and the pattern and intensities of the metal carbonyl stretching modes are nearly identical with those reported by Chini<sup>15</sup> for Rh<sub>12</sub>(CO)<sub>34</sub><sup>2-</sup>.<sup>16</sup>

**Catalytic Intermediates.** The WGSR catalyst solutions derived from Ru<sub>3</sub>(CO)<sub>12</sub> and Rh<sub>6</sub>(CO)<sub>16</sub> have the same metal carbonyl stretching absorptions in the presence and absence of alkene. Therefore, it is possible that the catalytic intermediates which catalyze the WGSR participate in the hydroformylation reactions. For example, an anionic metal carbonyl hydride formed during the normal course of CO conversion could be intercepted by alkene and react by hydride addition, CO insertion, and reductive elimination of aldehyde before returning to the WGSR catalytic pathway.<sup>17</sup>



Support for steps 1 and 2 is found in the work of Chini, who reported that  $[\text{Rh}_6(\text{CO})_{15}\text{H}]^-$  reacts with alkene under CO to form an anionic acyl:<sup>18</sup>



Unfortunately, it is not obvious from the experimental work that catalytic intermediates that are necessary for the catalysis of the WGSR are in fact also involved in the catalysis of hydroformylation and hydrohydroxymethylation. If these intermediates are involved, then the hydroformylation and hydrohydroxymethylation reactions offer the opportunity to probe the catalysis of the WGSR, because the initial insertion reaction, eq 1, traps the intermediate anionic metal carbonyl hydrides. This "trapping reaction", if properly done, could allow the indirect evaluation of the reactivity and the extent of participation of the metal hydrides in catalysis of the WGSR.

Support for our contention that common intermediates are involved in WGSR catalysis and hydroformylation catalysis is found in the following observations.

As mentioned above, the catalysis solutions deriving from  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ , and  $\text{Rh}_6(\text{CO})_{16}$  have the same metal carbonyl stretching absorptions in the presence and absence of alkene, and thus similar intermediates could be expected for both types of reactions.

As stated in the Introduction, the anionic carbonyl hydride  $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$  has been isolated as the major component of the low-pressure ruthenium-catalyzed WGSR. If  $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$  is also important to the hydroformylation reaction, then we can test this by changing the ruthenium catalyst precursor to  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ . Since  $\text{Ru}_3(\text{CO})_{12}$  is not the true catalyst for the WGSR or the hydroformylation reaction, an induction period must precede the onset of catalysis. Therefore, introduction of a catalyst precursor closer in structure to the active catalyst should result in a shorter induction period and a shorter reaction time.

$\text{H}_4\text{Ru}_4(\text{CO})_{12}$  readily forms the anionic metal carbonyl hydride  $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$  on reaction with base. Consequently, if  $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$  is more akin to the true hydroformylation catalyst than  $\text{Ru}_3(\text{CO})_{12}$ , a shorter induction period and shorter reaction times should result. As found in Table I, the use of  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  (0.075 mmol under standard conditions, 150 °C)<sup>19</sup> not only reduces the induction period and reaction time, but also boosts the initial yield of aldehyde with identical product ratios (32.5). Similar results were very recently reported by Petit on the hydroformylation of propene with CO and H<sub>2</sub>O.<sup>4</sup> Substitution of equivalent amounts of  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  for  $\text{Ru}_3(\text{CO})_{12}$  resulted in an increase in C<sub>4</sub> aldehydes of 68% under the same conditions; this reaction also obtains high selectivity for straight-chain aldehydes.

**Hydroformylation with CO/H<sub>2</sub>.** In another series of reactions,  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ , and  $(\text{C}_6\text{H}_5)_4\text{As}^+[\text{H}_3-$

$\text{Ru}_4(\text{CO})_{12}]^-$  were each tested for their ability to catalyze hydroformylation with CO and H<sub>2</sub>. Both the  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  and the  $\text{Ru}_3(\text{CO})_{12}$  catalyst precursors gave C<sub>6</sub> aldehydes with product ratios of 83 ± 2% hexanal:17 ± 2% 2-methylpentanal. These results correlate well with literature values.<sup>12</sup> The  $(\text{C}_6\text{H}_5)_4\text{As}^+[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ -catalyzed reaction gave C<sub>6</sub> aldehydes with a product ratio of 94 ± 2% hexanal:6 ± 2% 2-methylpentanal.

These findings strongly support the necessity of an anionic metal carbonyl hydride, possibly  $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$  or a simple derivative in the ruthenium-catalyzed hydroformylation. Moreover, they strongly suggest that WGSR catalyst intermediates participate directly in the WGSR ruthenium-catalyzed hydroformylation. If this is so then the following conclusion can be drawn about the mechanism of the ruthenium-catalyzed WGSR. Given that the ruthenium catalyst "fixes" ~4.0 mmol of CO as aldehyde in 1 h at 135 °C, it must also convert a similar number of moles of CO and H<sub>2</sub>O to CO<sub>2</sub> and hydrogen (as metal hydride) so that the hydrogen may be used to effect hydroformylation. From this point of view, it can be seen that during 1 h of hydroformylation ~40 mol of hydrogen are produced per mol of catalyst. The same ruthenium catalyst system produces ~55 mol of H<sub>2</sub>/mol of catalyst in 24 h in the absence of alkene. The conclusion then is that the rate-limiting step in the ruthenium-catalyzed WGSR is loss of hydrogen from metal hydride.<sup>20</sup>

**Catalytic Reduction of Aldehydes.** One important question about the rhodium-catalyzed hydroformylation and hydrohydroxymethylation regards the mode of production of C<sub>6</sub> alcohols from 1-pentene. Again, it is not obvious from the data whether C<sub>6</sub> alcohols are formed stepwise via hydroformylation and then reduction, or by way of an intermediate that partitions between aldehyde and alcohol products. Support for a two-step process comes from the demonstration that the rhodium-catalyzed WGSR solution actively reduces aldehydes. Thus, addition of 12.20 mmol of a mixture of 1-hexanal (31 ± 1%) and 2-methyl-1-pentanal (69 ± 1%) to a solution that had previously been used to catalyze the WGSR at 135 °C for 24 h, when heated (135 °C) under 800 psi CO for 0.5 h, results in the reduction of 53 ± 1% of the C<sub>6</sub> aldehydes to alcohols with a composition of 42 ± 1% 1-hexanol and 58 ± 1% 2-methyl-1-pentanol. The unreacted aldehyde contained 17 ± 1% hexanal and 83 ± 1% 2-methylpentanal. An additional 1 h of heating converted all the remaining aldehyde to alcohol.

These results show that the rates of reduction of both C<sub>6</sub> aldehydes to alcohols are significantly faster than hydroformylation, and reduction of the straight-chain aldehyde is preferred by roughly a factor of 2.

Recent work by Chini on the chemistry of  $\text{Ru}_6(\text{CO})_{16}$  and derivatives in base<sup>18,21</sup> points to  $\text{Rh}_6(\text{CO})_{15}\text{H}^-$  as an active intermediate in the rhodium-catalyzed reactions. We are investigating this possibility.

As mentioned above, a communication by Petit was published that describes work similar to that reported here. Comparison of Petit's work to our own shows several distinct differences. For example, we have determined that catalysis of the WGSR by  $\text{Rh}_6(\text{CO})_{16}$  is roughly twice as fast as when  $\text{Ru}_3(\text{CO})_{12}$  is used under identical conditions (see Table I). Petit reports that his  $\text{Ru}_3(\text{CO})_{12}$  WGSR catalysis system is one to two orders of magnitude faster than our system and can be run 35 °C cooler; moreover, his  $\text{Ru}_3(\text{CO})_{12}$  system is twice as fast as the  $\text{Rh}_6(\text{CO})_{16}$  system, which is run 50 °C higher. Another important difference is the fact that our rhodium-catalyzed reaction actively reduces the resulting aldehydes to alcohols, which does not occur in Petit's study.

These apparent differences may result from different reaction conditions, especially where pH is concerned.<sup>22</sup> Our preliminary studies over a pH range of 9–13 under standard conditions (150 °C) show little change in product selectivity

(for either catalyst system). Complications arise from catalyst decomposition in the rhodium system below pH 10 and  $\text{Ru}_3(\text{CO})_{12}$  sublimes out of the reaction solution below pH 10. At lower pH values, the rates are also slower; both reactions produce considerably more  $\text{C}_6$  methyl esters; and an induction period occurs in the rhodium catalyst system, resulting in brown solutions that appear (IR spectra) to be  $\text{Rh}_6(\text{CO})_{15}\text{X}^-$  species that slowly convert to  $\text{Rh}_{12}(\text{CO})_{30}^{2-}$ . The aldehyde reduction reaction still occurs, through the rate at pH 10 is  $\sim 20\%$  of that at pH 13.

We have found an unexpected but more reasonable explanation for the differences between our work and that of Petit's. Apparently most of the group 8 second- and third-row carbonyl clusters interact strongly with small tertiary amines (see, for example, ref 23). We will discuss this as well as the effects of pH changes at further length elsewhere.<sup>24</sup>

**Acknowledgments.** We would like to thank the referees for several helpful suggestions and comments. This work was supported in part by National Science Foundation Chemical Engineering Grant 77-21246.

## References and Notes

- R. M. Laine, R. G. Rinker, and P. C. Ford, *J. Am. Chem. Soc.*, **99**, 252 (1977); paper presented at the 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977, Abstracts, No. INOR-99.
- (a) Eisenberg has also recently reported the homogeneous catalysis of the water-gas shift reaction employing what apparently is a mononuclear rhodium complex in acidic solution. C.-H. Cheng, D. E. Hendriksen, and R. Eisenberg, *J. Am. Chem. Soc.*, **99**, 2791 (1977). (b) Patents by D. M. Fenton (U.S. Patents 3 539 298 and 3 490 872) describe the use of group 8 metal salts and base to homogeneously catalyze the water-gas shift reaction, but do not describe the use of group 8 metal carbonyls.
- P. C. Ford, R. G. Rinker, R. M. Laine, C. Ungerman, V. Landis, and S. A. Moya, *Adv. Chem. Ser.*, in press; *J. Am. Chem. Soc.*, in press.
- H. C. Kang, C. H. Mauldin, T. Cole, W. Slegier, K. Cann, and R. Petit, *J. Am. Chem. Soc.*, **99**, 8323 (1977).
- R. B. King, A. D. King, R. M. Hanes, and C. C. Frazier, *Adv. Chem. Ser.*, in press; paper presented at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978, Abstracts, No. INOR-119.
- D. J. Darensbourg and J. A. Froelich, paper presented at the 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977, Abstracts, No. INOR-124. See also J. A. Froelich and D. J. Darensbourg, *Inorg. Chem.*, **16**, 960 (1977).
- Presented in part at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978, Abstracts, No. INOR-120.
- S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3942 (1975).
- J. W. Koepke, J. R. Johnson, S. A. R. Knox, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97**, 3942 (1975).
- (a) Hydrogen analyses were quite reproducible, whereas analyses for  $\text{CO}_2$  repeatedly gave lower values than expected based on product yields. This result is probably due to a complex set of high-pressure equilibria involving  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{KOH} \rightleftharpoons \text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}$ . At high olefin conversion (high  $\text{CO}_2$  production), the KOH concentration is considerably depleted so that in the rhodium-catalyzed reactions,  $\text{KHCO}_3$  (identified by comparison with an authentic sample) can be isolated in up to 70% yield based on initial KOH concentration. The ruthenium reactions contain  $\text{KHCO}_3$  and large quantities of  $\text{KHCO}_2$ . P. C. Ford, private communication. (b) In both the ruthenium- and rhodium-catalyzed reactions with 1-pentene, analysis of the gas phase gave no indication of free  $\text{H}_2$  until conversion of olefin approached 90%, although  $\text{CO}_2$  production was evident. Additionally no  $\text{H}_2$  production was noted during the rhodium-catalyzed reduction of aldehydes to alcohols.
- (a) Catalytic hydrohydroxymethylation employing  $\text{Fe}(\text{CO})_5$  and base as reported by Reppe is extremely inefficient in terms of catalyst consumption, reaction rates, and substrate reactivity. The present work represents considerable improvement in these areas. W. Reppe and H. Vetter, *Justus Liebigs Ann. Chem.*, **582**, 133 (1953). (b) Preliminary work in the area using a similar system ( $\text{Rh}_2\text{O}_3$ /tertiary amine) has been performed by Iqbal and described by Olivé and Olivé. G. H. Olivé and S. Olivé, *Transition Met. Chem.*, **1**, 77 (1976).
- I. Wender and P. Pino, Ed., "Organic Synthesis via Metal Carbonyls", Wiley, New York, N.Y., 1977, pp 43-231, and references cited therein.
- Reaction of *trans*-2-pentene with the  $\text{Ru}_3(\text{CO})_{12}$  WGSR catalysis system under the established conditions produces mainly hexanal and 2-methyl-pentanal via isomerization, with a rate of reaction approximately 20 times slower than with 1-pentene. R. M. Laine, unpublished work.
- Up to 50% of the original amount of  $\text{Ru}_3(\text{CO})_{12}$  can be converted from the untreated catalyst solutions on standing under  $\text{N}_2$  for 1-2 days.
- (a) S. Martinengo and P. Chini, *Gazz. Chim. Ital.*, **102**, 344 (1972); (b) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 299 (1969).
- (a)  $\text{Rh}_{12}(\text{CO})_{34}^{2-}$  has been identified as the major species in the Union Carbide process, which produces ethylene glycol from CO and  $\text{H}_2$ : A. K. Smith and J. M. Basset, *J. Mol. Catal.*, **2**, 229 (1977). (b) It was recently reported that the  $\text{Rh}_{12}(\text{CO})_{34}^{2-}$  is stable to 270 °C under 20 000 psi of 1:1  $\text{H}_2$ -CO; thus we expect  $\text{Rh}_{12}(\text{CO})_{34}$  to remain stable under our conditions. J. L. Vlda, L. A. Cosby, R. A. Flato, W. E. Walker, and R. L. Pruett, Abstracts, 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978, No. INOR-5.
- R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).
- P. Chini, S. Martinengo, and G. Garlaschelli, *J. Chem. Soc., Chem. Commun.*, 709 (1972).
- $1 \times 10^{-4}$  mol of  $\text{Ru}_3(\text{CO})_{12}$  contains sufficient ruthenium to produce  $0.75 \times 10^{-4}$  mol of  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ .
- Ford et al. have also suggested that loss of hydrogen from the metal hydrides is the rate-limiting step in the ruthenium and ruthenium/iron catalysis of the WGSR. P. C. Ford, R. G. Rinker, C. Ungermann, R. M. Laine, V. Landis, and S. A. Moya, *J. Am. Chem. Soc.*, in press.
- More recent work by Chini is described in a review: P. Chini, G. Longoni, and V. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976).
- In the present study KOH is used as base and pH is  $\sim 13$ . In the work described by Petit, 25%  $(\text{CH}_3)_3\text{N}$  in  $\text{H}_2\text{O}$  is used as base dissolved in THF. We have determined experimentally that 25%  $(\text{CH}_3)_3\text{N}$  in  $\text{H}_2\text{O}$  has a pH of  $\sim 12$  and proper dilution with THF results in a pH of  $\sim 10$ .
- C. Choo Yin and A. J. Deeming, *J. Organomet. Chem.*, **133**, 123 (1977).
- Paper submitted for publication.