# CATALYTIC REACTIONS OF CARBON MONOXIDE

# Influence of Ethylene on the Hydrogenation of CO over Ruthenium

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The interactions of  $C_2H_4$  with  $H_2$  and CO were investigated over a SiO<sub>2</sub>-supported Ru catalyst. To differentiate carbon sources, <sup>13</sup>C-labeled CO and unlabeled  $C_2H_4$  were used. Product analysis was carried out by isotope-ratio gas chromatography/mass spectrometry. In the absence of CO,  $C_2H_4$  undergoes extensive hydrogenation. Small amounts of CH<sub>4</sub> and  $C_{3+}$  olefins and paraffins are also observed, indicative of  $C_2H_4$  hydrogenolysis and homologation. The presence of CO strongly suppresses  $C_2H_4$  hydrogenolysis, but enhances  $C_2H_4$  homologation. The hydrogenation of CO to hydrocarbons is strongly influenced by the presence of  $C_2H_4$ . With increasing  $C_2H_4$  partial pressure, the hydrogenation of CO to hydrocarbons is progressively suppressed, but the hydroformylation of  $C_2H_4$  to form propanal (and some 1-propanol) is enhanced. The product distributions observed for the reactions of  $C_2H_4$  and  $H_2$ , and  $C_2H_4$ , CO, and  $H_2$ , can be described in terms of a chain growth mechanism involving  $C_1$  and  $C_2$  monomer units.

## Introduction

The influence of low molecular weight olefins on Fischer-Tropsch synthesis over group VIII (groups  $8-10)^{41}$  metals has been examined by a large number of investigators<sup>1-28</sup> with the aim of

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either understanding the mechanism of chain growth or influencing the distribution of products formed. Most of this work has been conducted by using Co catalysts. In an early study by Smith et al.,<sup>1</sup> it was observed that yields of olefins and alcohols could be increased significantly when ethylene was added to the synthesis gas. The interactions of low molecular weight olefins (i.e., ethylene, propylene, and butylene) with H<sub>2</sub> and CO were investigated extensively by Eidus and co-workers.<sup>2-15</sup> They observed that addition of olefins to  $H_2/CO$  mixtures led to an increase in the formation of  $C_{3+}$  hydrocarbons. Studies conducted with <sup>14</sup>C-labeled olefins revealed that the majority of the hydrocarbons derived from the olefin when the olefin-to-hydrogen ratio exceeded unity. When this ratio fell below unity, the hydrocarbons contained carbon from both CO and the added olefin. Similar observations were made by Gibson and Clarke<sup>16</sup> on the basis of experiments conducted with <sup>14</sup>CO. From an analysis of the distribution of radioactivity in the products, it was concluded that the added olefin undergoes decomposition to produce one-carbon fragments which can then serve as monomer for chain growth. Subsequent studies by Pichler et al.<sup>17</sup> using <sup>14</sup>C-labeled  $\alpha$ -olefins established that, over both Co and Fe, olefin readsorption led to the initiation of hydrocarbon chains, the effectiveness of this process decreasing rapidly with increasing chain length. Pichler and Schulz<sup>18</sup> also observed that the <sup>14</sup>C-labeled  $\alpha$ -carbon atom of 1-hexadecene underwent exchange with an adsorbed  ${}^{12}C_1$ species, and the released  ${}^{14}C_1$  species participated in chain propagation. More recently, Kibby et al.<sup>19</sup> have reported that ethylene and propylene addition gave large increases in the yield of liquid hydrocarbons and greatly lowered the yield of methane.

The influence of olefin addition on the distribution of products formed over Fe catalysts has not been investigated as thoroughly as that for Co catalysts. Hall et al.<sup>20</sup> concluded from studies involving <sup>14</sup>C<sub>2</sub>H<sub>4</sub> addition that ethylene can act as a chain initiator, although not to the same extent as primary alcohols. Molina et al.<sup>21</sup> noted that ethylene addition caused on enhancement of C<sub>3</sub> products and a reduction in the methane content. Barrault et al.,<sup>22</sup>

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Figure 1. Schematic diagram of analytical system.

on the other hand, found that additions of ethylene significantly enhanced the formation of methane and  $C_3-C_4$  hydrocarbons. An enhancement in the formation of higher molecular weight products has also been reported by Dwyer and Somorjai.<sup>23</sup> When ethylene or propylene was added to synthesis gas passed over an Fe(III) single crystal, significantly higher yields of higher hydrocarbons resulted. By contrast, though, Satterfield et al.<sup>24</sup> found no change in the  $C_{3+}$  product yield with ethylene addition during Fischer-Tropsch synthesis over a fused iron catalyst.

In the case of Ru catalysis, it has been postulated<sup>25</sup> that the low yields of  $C_2$  and  $C_3$  olefins over these catalysts may be due to the reincorporation of these products into growing chains. Ekerdt and Bell<sup>26</sup> observed that the addition of 2% ethylene to an  $H_2/CO$  mixture resulted in an enhanced yield of propylene. Subsequent studies by Kellner and Bell<sup>25</sup> demonstrated that at concentrations above 1% ethylene addition enhanced the rates of  $C_3$  and  $C_4$  formation but suppressed the synthesis of  $C_{6+}$  hydrocarbons. Kobori et al.<sup>27</sup> have examined the effects of ethylene, propylene, and 4-octene addition. When <sup>12</sup>C-labeled olefins were added to a  ${}^{13}CO/H_2$  mixture, the isotopic distribution of products showed that the carbon from the additives was incorporated randomly into the products. Very recently Morris et al.28 investigated the effects of ethylene and propylene addition on the hydrogenation of CO over Ru supported on silica, 13x zeolite, titania, and magnesia. For Ru/SiO<sub>2</sub> and Ru/13x zeolite, ethylene addition markedly increased the rates of higher hydrocarbon formation without greatly influencing the methanation rate, whereas for Ru/TiO<sub>2</sub> and Ru/MgO ethylene addition enhanced the rate of higher hydrocarbon formation by a factor of less than 2 and reduced the methanation rate. With increasing proportion of ethylene in the feed, the yield of methane decreased and the yield of  $C_{3+}$  products increased. Propylene addition to CO hydrogenation over  $Ru/SiO_2$  increased the rates of  $C_2$  and  $C_{4+}$ hydrocarbon formation without markedly affecting the methanation rate.

The objectives of this study were to investigate the influence of ethylene addition on the hydrogenation of CO over  $Ru/SiO_2$ and to compare the product distribution obtained with those for CO hydrogenation in the absence of ethylene and ethylene homologation in the absence of CO. To enable identification of the source of carbon in the products, <sup>13</sup>C-labeled CO and unlabeled  $C_2H_4$  were used. Products were analyzed by isotope-ratio gas chromatography/mass spectrometry. Among the issues investigated were the influence of ethylene addition on the reactions of CO and the participation of ethylene in processes of hydrocarbon chain initiation and growth. The influence of ethylene addition on methane formation was also examined.

#### **Experimental Section**

A 4.3% Ru/SiO<sub>2</sub> catalyst is used in this investigation. Details concerning its preparation and initial reduction are presented elsewhere.<sup>29</sup> The dispersion of the catalyst is 0.27 as determined by H<sub>2</sub> chemisorption at 373 K.

Hydrogen is purified by passage through a Deoxo unit (Engelhard Industries) and 5-Å molecular sieve. Helium (99.999%) and ethylene (99.95%) are used without further purification. Isotopically labeled carbon monoxide (Isotec, Inc.) consisting of 89.3% <sup>13</sup>CO, 9.86% <sup>13</sup>C<sup>18</sup>O, and 0.36% <sup>12</sup>CO is used as received.

Reactants are supplied from a gas flow manifold at a pressure of 1 atm to a stainless steel microreactor heated by a fluidized sand bath. The catalyst (0.51 g) is reduced in flowing H<sub>2</sub> for 12 h at 573 K prior to each series of experiments. Reduction is continued at the reaction temperature of 493 K for 2 h before an experiment is initiated. The reactant stream is then introduced and the reaction allowed to continue for 15 min before product samples are taken for analysis. Reduction is resumed and maintained for at least 2 h between experiments. The activity of the catalyst was checked periodically by returning to base case conditions. The activity remained constant to within 5% of its standard activity.

The reactor effluent is analyzed by a combination of gas chromatography and mass spectrometry to determine the product distribution and the <sup>13</sup>C content of each of the products. The products are first separated by gas chromatography and then each eluted product is combusted to  $CO_2$ . The <sup>13</sup>C content of the  $CO_2$  is determined by mass spectrometry. This analytical approach has been described by Sano et al.<sup>30</sup> and Matthews and Hayes<sup>31</sup> and is termed isotope-ratio gas chromatography/mass spectrometry.

A schematic of the analytical system is presented in Figure 1. The product is injected simultaneously into two gas chromatographs using a 10-port gas sampling valve. CO, CO<sub>2</sub>, and C<sub>1</sub>-C<sub>4</sub> hydrocarbons are separated on a 0.32-cm-o.d.  $\times$  1.8-m stainless steel column packed with Chromosorb 106. A thermal conductivity detector quantifies the concentrations of these components.

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TABLE I: Conversion of  $C_2H_4$  to Products in the Reaction of  $H_2$  and  $C_2H_4^{a}$ 

feed		convn of $C_2H_4$ to				
$H_2/C_2H_4$	C <sub>2</sub> H <sub>6</sub>	CH4	C <sub>3+</sub>	total	convn to $CH_4$	
1.00	$8.3 \times 10^{-1}$	$9.3 \times 10^{-3}$	$2.7 \times 10^{-2}$	$8.7 \times 10^{-1}$	2.9	
0.50	$4.3 \times 10^{-1}$	$3.3 \times 10^{-3}$	$1.1 \times 10^{-2}$	$4.4 \times 10^{-1}$	3.3	
0.25	$1.2 \times 10^{-1}$	$8.0 \times 10^{-4}$	$4.6 \times 10^{-3}$	$1.3 \times 10^{-1}$	5.8	
0.125	$4.4 \times 10^{-2}$	$2.5 \times 10^{-4}$	$1.7 \times 10^{-3}$	$4.6 \times 10^{-2}$	6.0	

<sup>*a*</sup> Reaction conditions: feed  $P_{C_2H_4} = 0.40$  atm; T = 493 K.

 $C_3$  and heavier hydrocarbons are separated on a 0.25-mm-i.d. × 50-m fused silica column coated with SE-54 (1.0  $\mu$ m film thickness). The effluent of the capillary column is split inside the GC oven by using a glass-lined capillary union (Scientific Glass Engineering) connected to two fused silica transfer lines. One line (0.11 mm i.d.) feeds into the GC flame ionization detector. The complete product distribution is determined by normalizing the C<sub>3</sub> analyses from the packed and capillary columns.

The second transfer line (0.20 mm i.d.) carries the effluent from the gas chromatograph to a capillary combustion unit. The combuster consists of a 0.13-mm  $\times$  2-m Pt wire inside a 0.20-mm  $\times$  2-m fused silica line. The combustion unit is operated at an average temperature of 850 K. Because the fused silica becomes brittle at high temperatures, it is contained in a 0.64-cm-o.d. stainless steel tube for protection. Oxygen is introduced upstream of the combuster through a capillary transfer line (0.06 mm i.d.). The pressure of the O<sub>2</sub> line is set to give an average composition of 20% O<sub>2</sub> in He entering the combuster.

The combuster effluent is leaked into a vacuum chamber containing the probe of a quadrupole mass spectrometer. The leak is accomplished by coupling the combuster directly to the inlet restrictor of the mass spectrometer, with the combuster outlet at atmospheric pressure. It was found that the flow rate through the combuster sufficiently exceeds the effective throughput of the vacuum chamber so that no scavenger gas is needed at the capillary coupling to exclude air from the mass spectrometer inlet. Chromatograms obtained by monitoring the ion currents for masses 45 ( ${}^{13}CO_2$ ) and 44 ( ${}^{12}CO_2$ ) showed no significant peak dispersion relative to that observed by using the FID.

The operating temperature of the combuster and the  $O_2$  partial pressure were chosen to achieve complete combustion of the hydrocarbon peaks. The extent of combustion was determined by injecting  $C_{3+}$  hydrocarbon mixtures into the GC and monitoring masses corresponding to hydrocarbon fragments. Complete combustion was achieved when the most abundant hydrocarbon fragments were no longer detected over a range of initial hydrocarbon concentrations.

The isotopic composition of the methane product is determined by direct GC MS analysis of the packed column effluent. A second capillary inlet restrictor from the mass spectrometer is coupled with the packed GC column. The parent ion peaks for labeled and unlabeled methane are measured. Following the elution of methane, the mass spectrometer is switched to monitor the  $CO_2$  peaks of the capillary combuster effluent.

Data acquisition and mass spectrometer control are achieved through interfacing to an IBM PC microcomputer. During an experiment, data of two mass intensities and three amplified GC channels are taken at the rate of five scans per second per GC or MS channel. The data are stored on floppy disks, and the chromatograms are subsequently analyzed and the peaks integrated by the computer.

#### Results

Reactions of  $H_2$  and  $C_2H_4$ . Ethylene and hydrogen react to form ethane, methane, and higher hydrocarbons which are primarily linear olefins and branched olefins and paraffins. Hydrogenation to ethane accounts for more than 90% of the ethylene converted to products. The distribution of methane and  $C_{3+}$ hydrocarbon products is shown in Figure 2 for an equimolar feed of  $H_2$  and  $C_2H_4$  at 493 K and a total pressure of 0.80 atm. The rates of formation of hydrocarbons are shown as a function of n, the number of carbon atoms in each molecule. Under these



Figure 2. Distribution of  $C_1-C_8$  hydrocarbons produced by reaction of  $H_2$  and  $C_2H_4$  at 493 K.  $P_{H_2} = P_{C_2H_4} = 0.40$  atm.



Figure 3. Proportions of linear olefin, linear paraffin, and branched products observed in the reaction of  $H_2$  and  $C_2H_4$ .

conditions, the conversions of ethylene are 0.83 to ethane, 0.009 to methane, and 0.027 to  $C_{3+}$  hydrocarbons. It is interesting to observe that the carbon number distribution of  $C_{3+}$  products does not decrease monotonically, but rather oscillates so that products containing an even number of carbon atoms predominate.

The relative amounts of linear olefins and paraffins and branched products in the  $C_{3+}$  fractions are shown in Figure 3. Branched isomers dominate the  $C_5$  and heavier products. For a given carbon number,  $\alpha$ - and  $\beta$ -olefin contents decrease and the branched product fraction increases with increasing  $H_2:C_2H_4$  feed ratio. The fractional conversions of ethylene to ethane, methane, and  $C_{3+}$  products are given in Table I. Although ethane is the



Figure 4. Distribution of  $C_1$ - $C_8$  hydrocarbons produced by reaction of  $H_2$  and CO at 493 K.  $P_{H_2} = 0.40$  atm;  $P_{CO} = 0.20$  atm.



Figure 5. Proportions of linear olefin, linear paraffin, and branched products observed in the reaction of  $H_2$  and CO.

most abundant product under all conditions, the production of  $C_{3+}$  hydrocarbons relative to  $CH_4$  increases with decreasing  $H_2:C_2H_4$  feed ratio.

Reaction of  $H_2$  and CO. Figure 4 shows the hydrocarbon product distribution for the reaction of a 2:1 H<sub>2</sub>:CO feedstream under the same conditions as those used for the H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> reaction in Figure 2. The rates of formation of C<sub>3+</sub> products follow a linear decrease on a plot of log ( $N_{C_n}$ ) vs. *n*, while the point for C<sub>2</sub> lies below the line and the point for C<sub>1</sub> lies above the line. Under these conditions, the conversion of CO is 0.078 and the chain growth probability,  $\alpha$ , for C<sub>3+</sub> products is 0.53. The relative amounts of  $\alpha$ -olefins, *n*-paraffins, and branched products are shown in Figure 5. The  $\alpha$ -olefins content is low and generally decreases with increasing carbon number for C<sub>3+</sub> products. The *n*-paraffin content is high for all carbon numbers, but branched products constitute the largest fraction of the C<sub>4+</sub> product. The other significant product of the reaction is H<sub>2</sub>O; however, quantitative measurement is not possible.

Reactions of  $H_2$ ,  $\dot{C}_2H_4$ , and CO. A feed consisting of a 2:2:1 mixture of  $C_2H_4$ : $H_2$ :<sup>13</sup>CO was used as a base case for this series of reactions. Figure 6 shows the distribution of hydrocarbon products, exclusive of oxygenates. The combustion analysis shows



Figure 6. Distribution of  $C_1$ - $C_{10}$  hydrocarbons produced by reaction of  $H_2$ ,  $C_2H_4$ , and CO at 493 K.  $P_{H_2} = P_{C_2H_4} = 0.40$  atm;  $P_{CO} = 0.20$  atm.

that the carbon atoms which make up these hydrocarbons are derived only from ethylene. The labeled (CO-derived) carbon does not appear in either methane or higher hydrocarbons in amounts greater than the natural abundance level. Accounting for the experimental error associated with determining such low <sup>13</sup>C abundances gives a maximum CO-derived carbon content of about 2%. The conversions of ethylene are 0.055 to ethane and 0.090 to methane and C<sub>3+</sub> hydrocarbons.

The CO-derived carbon appears in propanal and 1-propanol. Each of these products contains 33% CO-derived carbon. Both products are produced at rates comparable to hydrocarbon synthesis rates during the reaction of  $H_2$ ,  $C_2H_4$ , and CO, but neither is produced in measurable quantities from CO and  $H_2$  alone. The fractional conversion of CO to propanal and 1-propanol is 0.025, while the conversion of CO to hydrocarbon products is only 0.005.

Another interesting feature of Figure 6 is the change in the product distribution which is caused by CO. A comparison of the reaction product from  $C_2H_4$  and  $H_2$  in the absence of CO with that in the presence of CO (Figures 2 and 6) reveals that CO suppresses methane formation relative to chain growth and causes the  $C_{4+}$  hydrocarbon production rates to fall on a line on a semilogarithmic plot. The latter result is similar to an Anderson-Schulz-Flory distribution, neglecting  $C_1$ - $C_3$  products, with an apparent chain growth probability of 0.55. These changes occur despite the fact that CO itself does not participate in the chain growth process. The addition of CO also suppresses the hydrogenation of ethylene to ethane. Under the reaction conditions described in Figure 6, the conversion of ethylene to ethane is 0.055, but when no CO is present, the conversion to ethane is 0.83.

The structural composition of the hydrocarbon products is described in Figure 7. The effect of CO on the olefin content of the  $C_2H_4/H_2$  reaction products is seen by comparing Figures 3 and 7. The presence of CO increases the  $\alpha$ - and  $\beta$ -olefin fractions significantly while it decreases the *n*-paraffin fraction. Branched products are less abundant when CO is present, particularly in the lighter products. For example, the C<sub>4</sub> product contains only 8% branched product when CO is present, compared with 35% branched product in the absence of CO. Decreasing  $P_{\rm H_2}$  in the H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>/CO reaction produces changes in the products distribution that are similar to those observed when CO is added to the H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> reaction mixture: the linear olefin fraction increases, and the proportion of branched product decreases.

The rates of CH<sub>4</sub> and C<sub>3</sub>-C<sub>6</sub> hydrocarbon production are shown as functions of  $P_{CO}$  in Figure 8, and the corresponding conversions of C<sub>2</sub>H<sub>4</sub> and CO are given in Table II. The methane rate decreases by a factor of 3 when 0.007-atm CO is present in the H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed. Similarly, the conversion of ethane decreases by

TABLE II: Effects of P<sub>CO</sub> on the Conversions of C<sub>2</sub>H<sub>4</sub> and CO to Products in the Reaction of H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CO<sup>a</sup>

feed		convn of C <sub>2</sub> H <sub>4</sub> to		convn o	f CO to
$P_{\rm CO}$ , atm	C <sub>2</sub> H <sub>6</sub>	$C_1 + C_{3+}$	0	НС	O¢
0	0.83	$3.6 \times 10^{-2}$	0		
0.02	0.11	$8.1 \times 10^{-2}$	$8.0 \times 10^{-4}$		$1.5 \times 10^{-2}$
0.05	$8.9 \times 10^{-2}$	$9.0 \times 10^{-2}$	$3.1 \times 10^{-3}$		$2.5 \times 10^{-2}$
0.10	$7.3 \times 10^{-2}$	$6.9 \times 10^{-2}$	$5.3 \times 10^{-3}$	$1.0 \times 10^{-3b}$	$2.1 \times 10^{-2}$
0.20	$5.5 \times 10^{-2}$	$9.0 \times 10^{-2}$	$1.2 \times 10^{-2}$	$5.0 \times 10^{-3 b}$	$2.5 \times 10^{-2}$

<sup>a</sup> Reaction conditions: feed  $P_{C_2H_4} = 0.40$  atm; feed  $P_{H_2} = 0.40$  atm; T = 493 K. <sup>b</sup> These values have an uncertainty of  $\pm 50\%$  due to the uncertainty in the <sup>13</sup>C content of the products near the natural abundance level. <sup>c</sup>C<sub>2</sub> oxygenated products.

	TABLE III: Eff	ects of PCH	on the Conversion	s of C <sub>2</sub> H <sub>4</sub> and CO	to Products in the React	ion of H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> , and CO <sup>a</sup>
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feed		<u> </u>	convn of C <sub>2</sub> H <sub>4</sub> to		convn ol	f CO to	
	$P_{C_2H_4}$ , atm	C <sub>2</sub> H <sub>6</sub>	$C_1 + C_{3+}$	0	НС	O <sup>c</sup>	
	0				$7.8 \times 10^{-2}$		
	0.034	$7.2 \times 10^{-1}$	$2.8 \times 10^{-1}$		$2.4 \times 10^{-2}$		
	0.067	$3.2 \times 10^{-1}$	$5.2 \times 10^{-1}$	$2.8 \times 10^{-2}$	$1.0 \times 10^{-2}$	$9.4 \times 10^{-3}$	
	0.10	$4.0 \times 10^{-1}$	$4.7 \times 10^{-1}$	$2.4 \times 10^{-2}$	$9.0 \times 10^{-3 b}$	$1.2 \times 10^{-2}$	
	0.20	$1.0 \times 10^{-1}$	$2.4 \times 10^{-1}$	$2.4 \times 10^{-2}$	$6.0 \times 10^{-3 b}$	$2.4 \times 10^{-2}$	
	0.40	$5.5 \times 10^{-2}$	$9.0 \times 10^{-2}$	$1.2 \times 10^{-2}$	$5.0 \times 10^{-3b}$	$2.5 \times 10^{-2}$	

<sup>a</sup> Reaction conditions: feed  $P_{H_2} = 0.40$  atm; feed  $P_{CO} = 0.20$  atm; T = 493 K. <sup>b</sup> These values have an uncertainty of  $\pm 50\%$  due to the uncertainty in the <sup>13</sup>C content of the products near the natural abundance level. <sup>c</sup>C<sub>2</sub> oxygenated compounds.



Figure 7. Proportions of linear olefin, linear paraffin, and branched products observed in the reaction of H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CO.

a factor of 7. The rates of production of the higher hydrocarbons increase by factors ranging from less than 2 (for  $C_3$ ) to 10 (for  $C_5$ ) when 0.02-atm CO is added to the feed, although CO-derived carbon is not present in the products. As  $P_{CO}$  is increased further, methane and ethane formation both exhibit weak negative dependences on  $P_{CO}$ , while  $C_{3+}$  rates exhibit weak positive dependences.

Figure 9 shows the rates of propanal and 1-propanol synthesis as functions of the partal pressure of CO in the  $H_2/C_2H_4$  feed. Other aldehydes and alcohols are not produced at measurable rates. The conversion of CO to oxygenates under these conditions ranges from 0.015 to 0.025, as shown in Table II.

The effects of adding  $C_2H_4$  to a 2:1  $H_2$ :<sup>13</sup>CO feed are shown in Figure 10 and Table III. Methane formation is inhibited by the presence of  $C_2H_4$  in the feed. At a  $CO/C_2H_4$  ratio of 2.0, 90% of the methane formed is derived from ethylene. At higher  $P_{C_2H_4}$ , all of the methane is derived from ethylene. The rates of production of all  $C_{3+}$  hydrocarbons increase as the partial pressure of ethylene fed increases from 0.015 to 0.10 atm. The ethylene conversion in these cases is greater than 90%. The rates all exhibit maxima as the partial pressure of ethylene is increased above 0.10 atm.

The rates of formation of propanal and 1-propanol as functions of  $P_{C,H_4}$  are shown in Figure 11. The oxygenates exhibit strong positive dependences on ethylene pressure at low  $P_{C_2H_4}$ , but the



Figure 8. Influence of  $P_{CO}$  on the rates of production of  $C_1-C_6$  hydrocarbons.  $P_{H_2} = P_{C_2H_4} = 0.40$  atm.



Figure 9. Influence of  $P_{CO}$  on the rates of production of C<sub>3</sub> oxygenates.  $P_{\rm H_2} = P_{\rm C_2H_4} = 0.40$  atm.

rates level off as  $P_{C_2H_4}$  approaches  $P_{CO}$ . The distributions of <sup>12</sup>C and <sup>13</sup>C hydrocarbon products are shown in Figure 12 for the reaction between 0.60-atm syngas and

TABLE IV: Effects of  $P_{H_2}$  on the Conversions of  $C_2H_4$  and CO to Products in the Reaction of  $H_2$ ,  $C_2H_4$ , and  $CO^a$ 

feed		convn of $C_2H_4$ to convn of CO to			f CO to	)	
$P_{\rm H_2}$ , atm	C <sub>2</sub> H <sub>6</sub>	$C_1 + C_{3+}$	0	НС	$O^b$		
0.15	$2.2 \times 10^{-2}$	$1.2 \times 10^{-2}$	$1.6 \times 10^{-3}$		$1.6 \times 10^{-3}$		
0.25	$6.6 \times 10^{-2}$	$4.4 \times 10^{-2}$	$5.6 \times 10^{-3}$	$1.0 \times 10^{-3}$	$5.6 \times 10^{-3}$		
0.40	$1.8 \times 10^{-1}$	$1.7 \times 10^{-1}$	$1.9 \times 10^{-2}$	$5.0 \times 10^{-3}$	$1.9 \times 10^{-2}$		

<sup>a</sup> Reaction conditions: feed  $P_{C_2H_4} = 0.20$  atm; feed  $P_{CO} = 0.20$  atm; T = 493 K. <sup>b</sup>C<sub>2</sub> oxygenated compounds.

TABLE V: Effect of Temperature on the Conversions of C<sub>2</sub>H<sub>4</sub> and CO to Products in the Reaction of H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CO<sup>a</sup>

 		convn of C <sub>2</sub> H <sub>4</sub> to	convn c	of CO to		
<i>Т</i> , К	C <sub>2</sub> H <sub>6</sub>	$\frac{C_1 + C_2}{C_1 + C_{3+}}$	0	HC	O <sup>b</sup>	
 493	$5.7 \times 10^{-2}$	$4.3 \times 10^{-2}$	$6.0 \times 10^{-3}$	$3.0 \times 10^{-3}$	$1.2 \times 10^{-2}$	
473	$4.3 \times 10^{-2}$	$3.7 \times 10^{-2}$	$8.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	$1.6 \times 10^{-2}$	
453	$2.4 \times 10^{-2}$	$2.2 \times 10^{-2}$	$6.5 \times 10^{-3}$	$1.0 \times 10^{-3}$	$1.3 \times 10^{-2}$	
433	$1.1 \times 10^{-2}$	$6.2 \times 10^{-3}$	$4.4 \times 10^{-3}$		$8.7 \times 10^{-3}$	

<sup>a</sup> Reaction conditions: feed  $P_{H_2} = 0.30$  atm; feed  $P_{C_2H_4} = 0.40$  atm; feed  $P_{CO} = 0.20$  atm. <sup>b</sup>C<sub>2</sub> oxygenated compounds.



Figure 10. Influence of  $P_{C_2H_4}$  on rates of production of  $C_1$ - $C_6$  hydrocarbons.  $P_{H_2} = 0.40$  atm;  $P_{CO} = 0.20$  atm.



Figure 11. Influence of  $P_{C_2H_4}$  on rates of production of C<sub>3</sub> oxygenates.  $P_{H_2} = 0.40$  atm;  $P_{CO} = 0.20$  atm.

0.034-atm ethylene. Of the methane produced, 37% derives from CO. In each  $C_{3+}$  product, 30  $\pm$  2% of the carbon atoms derive from CO. It is interesting to note that this fraction does not vary with carbon number for the higher hydrocarbons. Under these conditions, the conversion of ethylene to ethane is 0.72 and to CH<sub>4</sub> and C<sub>3+</sub> hydrocarbons is 0.28, while the conversion of CO to all products is less than 0.024. Oxygenates are not produced at measurable rates.



Figure 12. Distribution of C<sub>2</sub>H<sub>4</sub>-derived and <sup>13</sup>CO-derived hydrocarbons.  $P_{H_2} = 0.40$  atm;  $P_{CO} = 0.20$  atm;  $P_{C_2H_4} = 0.034$  atm.



**Figure 13.** Effects of H<sub>2</sub> partial pressure on the distribution of C<sub>1</sub>-C<sub>8</sub> hydrocarbon products.  $P_{C_2H_4} = P_{CO} = 0.20$  atm; T = 493 K.

The rates of hydrocarbon production are strong functions of  $H_2$  pressure, as can be seen in Figure 13. The rate of methane formation increases with  $P_{H_2}$  but the rates of formation of  $C_{3+}$  hydrocarbons increase more rapidly. The effects of  $P_{H_2}$  on the



**Figure 14.** Effects of temperature on the distribution of  $C_1-C_8$  hydrocarbon products.  $P_{H_2} = 0.30$  atm;  $P_{C_2H_4} = 0.40$  atm;  $P_{CO} = 0.20$  atm.

conversion of  $C_2H_4$  and CO to products are given in Table IV. It is notable that a 2.7-fold increase in  $P_{H_2}$  causes a roughly 10-fold increase in the conversion of products derived from  $C_2H_4$ .

The effect of temperature on the product distribution is shown in Figure 14, and Table V lists the conversions of  $C_2H_4$  and CO. As with increasing H<sub>2</sub> pressure, decreasing temperature shifts the products to a higher average molecular weight. It is noted that in all cases the dominant products contain four carbon atoms.

#### Discussion

Comparison with Previous Studies. The reactions between  $H_2$ , CO, and  $C_2H_4$  over supported CO were investigated extensively by Eidus and co-workers.<sup>2-15</sup> By the use of a 1:1  $H_2:C_2H_4$  mixture, it was observed that in the absence of CO very little homologation of ethylene occurred. When CO was added to the feed gas, the hydrogenation of ethylene to ethane decreased and the homologation of ethylene to  $C_{4+}$  products increased with increasing CO concentrations in the range 0.3–6.0%. Analysis of the products revealed that in a 1:1  $H_2:C_2H_4$  mixture containing 5% CO more than 90% of the carbon in  $C_{4+}$  products derived from ethylene. Studies with <sup>14</sup>C-labeled CO confirmed this observation. The presence of carbon from CO was observed only when the  $C_2H_4/H_2$  ratio in the feed gas mixture was reduced significantly below 1.2.

Most of the observations reported here are in qualitative agreement with those of Eidus and co-workers.<sup>2-15</sup> The principal exception is the need for the presence of CO to initiate the homologation of  $C_2H_4$ . As seen in Figure 2 and Table I, homologation can proceed at a substantial rate in the absence of CO, provided that  $H_2$  is present in the feed. The failure of Eidus to observe ethylene homologation over supported Co may have been a consequence of the reaction conditions chosen, since the homologation of propylene, 1-butene, and 1-hexene did occur in the absence of CO. Kibby et al.<sup>19</sup> also reported recently the homologation of  $C_2H_4$  and  $H_2$  alone over supported Co catalysts, and Molina et al.<sup>21</sup> and Hugues et al.<sup>32,33</sup> observed  $C_2H_4$  homologation over Fe catalysts.

The present study has shown that the addition of ethylene to a synthesis gas mixture of fixed composition results in an increase in the rate of formation of  $C_{3+}$  hydrocarbons and a decrease in the rate of CH<sub>4</sub> formation. The first of these observations is consistent with those of Morris et al.<sup>28</sup> for Ru supported on SiO<sub>2</sub>, 13x zeolite, TiO<sub>2</sub>, and MgO. However, in contrast to the present The Journal of Physical Chemistry, Vol. 90, No. 20, 1986 4803



Figure 15. Proposed scheme of chain growth for the reaction of  $H_2$  and  $C_2H_4. \label{eq:hamiltonian}$ 

SCHEME I

$$C_{2}H_{4g} = C_{2}H_{4s} \xrightarrow{H_{8}} C_{2}H_{5s} \xrightarrow{H_{8}} C_{2}H_{6g}$$

$$xH_{8} \downarrow_{1}^{\dagger}$$

$$C_{2}H_{(5-x)} + xH_{2}$$

$$\downarrow_{1}$$

$$CH_{y}, CH_{z} \xrightarrow{H_{8}} CH_{4g}$$

work, the authors noted a modest increase in the rate of  $CH_4$  formation for  $Ru/SiO_2$  upon addition of ethylene. Since the reaction conditions used in this study and that of Morris et al.<sup>28</sup> are very similar, no explanation for the discrepancy can be offered. It is noted, however, that Morris et al.<sup>28</sup> did observe a decrease in the rate of  $CH_4$  formation for  $Ru/TiO_2$  and Ru/MgO.

Reactions of  $H_2$  and  $C_2H_4$ . Ethylene in the presence of  $H_2$  over Ru can undergo hydrogenation, hydrogenolysis, and homologation. Of these processes, hydrogenation predominates, accounting for over 90% of the  $C_2H_4$  converted to products. The participation of  $H_2$  in all three processes is evident from the data presented in Table I. Not only the conversion to  $C_2H_6$  but also the conversions to  $CH_4$  and  $C_{3+}$  hydrocarbons increase with the  $H_2/C_2H_4$  ratio in the feed, for fixed inlet partial pressure of  $C_2H_4$ . The data also indicate that hydrogenolysis is more sensitive to the  $H_2/C_2H_4$  ratio than either hydrogenation or homologation; as the  $H_2/C_2H_4$  ratio increases from 0.125 to 1.0, the conversion of  $C_2H_4$  to  $CH_4$  increases by a factor of 37 while the conversions to  $C_2H_6$  and  $C_{3+}$ hydrocarbons increase by factors of 19 and 16, respectively.

The hydrogenation and hydrogenolysis of  $C_2H_4$  can be interpreted by using a reaction scheme similar to that proposed by Sinfelt<sup>34</sup> to explain the kinetics of ethane hydrogenolysis. The elementary steps envisioned are shown in Scheme I. The reaction of  $C_2H_4$  begins by its associatve adsorption into a di- $\sigma$ - or  $\pi$ -bonded state.<sup>35</sup> Addition of atomic hydrogen produces an ethyl group which can then undergo either hydrogen addition or hydrogen abstraction. The former process produces  $C_2H_6$ , whereas the latter leads to CH<sub>3</sub> via the species  $C_2H_{(5-x)_6}$ . This scheme is consistent with the observation that the rates of  $C_2H_4$  hydrogenation and hydrogenolysis is found experimentally to increase more rapidly than the rate of hydrogenation (see Table I), it is inferred that the dehydrogenation of  $C_2H_5$ , is not at equilibrium and occurs preferentially in the forward direction.

The chain growth process for  $C_2H_4$  homologation can be described in terms of the scheme presented in Figure 15. It is assumed that  $C_2H_4$  forms two monomer units: a two-carbon unit designated  $C_{2_4}^{m}$  and a single-carbon unit designated  $C_{1_4}^{m}$ . The first of these species might be envisioned as  $C_2H_{4_4}$ , and the second as  $CH_{2_4}$ . Chain growth is postulated to begin from both one- and two-carbon surface species, which are designated  $C_{1_4}$  and  $C_{2_4}$ .

<sup>(32)</sup> Hugues, F.; Besson, B.; Bussiere, P.; Dalmon, J. A.; Basset, J. M. Nouv. J. Chim. 1981, 5, 207.

<sup>(33)</sup> Hugues, F.; Besson, B.; Basset, J. M. J. Chem. Soc., Chem. Comm. 1980, 719.

<sup>(34)</sup> Sinfelt, J. H. Catal. Rev. 1969, 3, 175.

<sup>(35)</sup> Hills, M. M.; Parmeter, J. E.; Mullins, C. B.; Weinberg, W. H. J. Am. Chem. Soc. 1986, 108, 3554.



Figure 16. Proposed scheme of chain branching.

respectively. The first of these species might be CH<sub>3</sub>, while the second might be  $C_2H_{5_1}$ . The addition of  $C_{1_1}^{m}$  or  $C_{2_1}^{m}$  to the chain initiators then leads to the formation of a homologous series of surface intermediates, designated as  $C_{n_s}$ . Precedence for chain growth via the addition of  $CH_2$  or  $C_2H_4$  to alkyl species has been established by studies with organometallic complexes.<sup>36-38</sup> Termination of the growing chains is taken to occur via either  $\beta$ -hydride transfer or reductive elimination, the first of these processes leading to an  $\alpha$ -olefin and the second to a paraffin. Both termination steps are well-known in organometallic chemistry.<sup>36,37</sup> The formation of internal olefins and branched products can occur by a 1-2 shift in the point of attachment of the growing alkyl chain, as is illustrated in Figure 16.

The carbon number distribution of products formed by  $C_2H_4$ homologation can be described by the scheme given in Figure 15. In the application of this scheme, the surface coverages by  $C_1^{m}$ and C2,<sup>m</sup> are taken to be constant and independent, and no account is made for chain branching. The rate of formation of a hydrocarbon containing n carbon atoms is given by

$$N_{\rm C_s} = k_{\rm t} \theta_n \tag{1}$$

where  $\theta_n$  is the surface coverage by a chain containing *n* carbon atoms and  $k_t$  is the rate coefficient for chain termination (assumed to be independent of n). The magnitude of  $\theta_n$  can be related to the coverages of  $C_{1_i}^m$  and  $C_{2_i}^m$ ,  $\theta_{1_i}^m$  and  $\theta_{2_i}^m$ , by imposing a steady-state balance on the rates of formation and consumption of  $C_{n_s}$ . Thus

$$0 = k_{p_1}\theta_1^{m}\theta_{n-1} + k_{p_2}\theta_2^{m}\theta_{n-2} - k_{p_1}\theta_1^{m}\theta_n - k_{p_2}\theta_2^{m}\theta_n - k_t\theta_n$$
(2)

where  $k_{p_1}$  and  $k_{p_2}$  are the rate coefficients for chain propagation via  $C_{1_s}^{m}$  and  $C_{2_s}^{m}$ , respectively. Equation 2 can be rewritten as

$$0 = \theta_n - \alpha_1 \theta_{n-1} - \alpha_2 \theta_{n-2} \tag{3}$$

where  $\alpha_1$  and and  $\alpha_2$  are defined as

$$\alpha_{1} = k_{p_{1}}\theta_{1}^{m} / (k_{p_{1}}\theta_{1}^{m} + k_{p_{2}}\theta_{2}^{m} + k_{t})$$
(4)

and

$$\alpha_2 = k_{p_2} \theta_2^{m} / (k_{p_1} \theta_1^{m} + k_{p_2} \theta_2^{m} + k_t)$$
(5)

The parameters  $\alpha_1$  and  $\alpha_2$  represent the probability of chain growth by  $C_{1}^{m}$  and  $C_{2}^{m}$ , respectively. The form of eq 3 is identical with that derived by Novak et al.<sup>39</sup> to account for chain growth by independent one- and two-carbon monomer units during CO hydrogenation. The solution to this equation is given by

$$\theta_n = \left[ \frac{\theta_2 - \theta_1 x_2}{x_1 - x_2} \right] x_1^{n-1} + \left[ \frac{\theta_1 x_1 - \theta_2}{x_1 - x_2} \right] x_2^{n-1}$$
(6)

where

$$x_{1,2} = 0.5(\alpha_1 \pm (\alpha_1^2 + 4\alpha_2)^{1/2})$$
(7)

Since  $x_2$  has a negative value, the product distribution predicted



Figure 17. Comparison of calculated and experimental product distributions for the reaction of  $H_2$  and  $C_2H_4$ .



Figure 18. Proposed scheme of chain growth for the reaction of  $H_2$ , C<sub>2</sub>H<sub>4</sub>, and CO.

TABLE VI: Calculated Chain Growth Parameters<sup>a</sup>

	feed				
$P_{\rm H_2},$ atm	$P_{C_2H_4},$ atm	P <sub>CO</sub> , atm	$\theta_2/\theta_1$	$\alpha_1$	α2
0.40	0.40	0.0	7,1	$1.1 \times 10^{-2}$	$7.1 \times 10^{-2}$
0.40	0.40	0.0	1.0	$1.5 \times 10^{-2}$	$7.5 \times 10^{-2}$
0.40	0.40	0.20	1.0	$2.7 \times 10^{-1}$	$1.2 \times 10^{-1}$

<sup>*a*</sup> Reaction temperature = 493 K.

by eq 6 oscillates as a function of n, with the magnitude of the oscillations decreasing as n increases. The oscillatory character of the distribution is controlled for the most part by the ratio  $\alpha_2/\alpha_1$ : as  $\alpha_2/\alpha_1$  increases, the magnitude of the oscillations increases.

A fit of eq 6 to the data presented in Figure 2 is illustrated in Figure 17. It is apparent that a good representation of the data can be achieved with the indicated parameter values. The high value of  $\theta_2/\theta_1$  suggests that chain initiation occurs primarily from two-carbon centers, and the high ratio of  $\alpha_2/\alpha_1$  suggests that chain growth via addition of  $C_{2*}^{m}$  occurs more rapidly than via addition of  $C_{1_s}^{m}$ .

Reactions of  $H_2$ ,  $C_2H_4$ , and CO. The distribution of products formed when  $C_2H_4$  homologation proceeds in the presence of CO can be described by the scheme presented in Figure 18. This reaction mechanism is a modification of that presented in Figure 15. Since CO inhibits chain termination by reductive elimination of alkyl groups, the value of the termination rate coefficient for forming methane,  $k'_t$ , is expected to be smaller than that for other products.

<sup>(36)</sup> Hermann, W. A. Angew. Chem., Int. Ed. Engl. 1982, 21, 117.
(37) Muetterties, E. L.; Stein, J. Chem. Rev. 1980, 80, 479.

<sup>(38)</sup> Bell, A. T. Catal. Rev.-Sci. Eng. 1981, 23, 203.

<sup>(39)</sup> Novak, S.; Madon, R. J.; Suhl, H. J. Chem. Phys. 1981, 74, 6083.



Figure 19. Comparison of calculated and experimental product distributions for the reaction of  $H_2$ ,  $C_2H_4$ , and CO.

A fit of eq 6 to the data given in Figure 6 is shown in Figure 19, and values of the parameters  $\theta_2/\theta_1$ ,  $\alpha_1$ , and  $\alpha_2$  are given in Table VI. The theoretical distribution of  $C_{3+}$  products was obtained by forcing eq 6 to match the experimentally observed ratio of  $N_{C_4}/N_{C_1}$  and then adjusting  $\alpha_1$  and  $\alpha_2$  to obtain a best fit for  $N_{C_4}/N_{C_4}$  for  $n \ge 5$ . The value of  $\theta_2/\theta_1$  given in Table VI was then back-calculated. The experimentally observed value of  $N_{C_4}/N_{C_1}$  could not be matched, though, without further parameter adjustment. To achieve a fit between experiment and theory it was necessary to assume that  $\alpha_2' = 7\alpha_2$ , where  $\alpha_2'$  is the probability of chain growth associated with the formation of  $C_4$ . The implication of this adjustment is that the addition of  $C_2$ ,<sup>m</sup> to  $C_2$ , proceeds more rapidly than the addition of  $\alpha_2' = 7\alpha_2$  and  $\theta_2/\theta_1 = 1.0$  in the modeling of  $C_2H_4$  homologation has only a small effect on the best-fit values of  $\alpha_1$  and  $\alpha_2$  and does not significantly perturb the quality of the agreement between theory and experiment, as may be seen in Figure 17.

Table VI shows that in the presence of CO the values of  $\alpha_1$  and  $\alpha_2$  increase relative to the corresponding values observed in the absence of CO. These changes can be attributed in large measure to a reduction in the rate of chain termination via paraffin formation. The decrease in the ratio  $\alpha_2/\alpha_1$  upon CO addition to the feed gas indicates that the rate of propagation via  $C_{2_i}^m$  falls relative to the rate of propagation via  $C_{1_i}^m$ . This change is difficult to interpret since it may be caused by various combinations of changes in  $k_{p_2}$ ,  $k_{p_1}$ ,  $\theta_2^m$ , and  $\theta_1^m$ . Assignment of a dominant cause for the reduction in  $\alpha_2/\alpha_1$  is not possible.

The results presented in Figures 17 and 19 and in Table VI demonstrate clearly the strong influence of  $C_2H_4$  on the hydrogenation of CO. With increasing  $C_2H_4$  partial pressure in the feed gas, the conversion of CO to hydrocarbons decreases, but the proportion of carbon derived from <sup>13</sup>CO in the  $C_{4+}$  hydrocarbons remains independent of carbon number (see Figure 12). These results indicate that the syntheses of  $C_{4+}$  hydrocarbons from CO and  $C_2H_4$  proceed via similar intermediates and reaction pathways. The increase in the absolute rates of formation of  $C_{3+}$  hydrocarbons with increasing  $C_2H_4$  partial pressures observed for  $P_{C_2H_4} < 0.20$  atm indicates that  $C_2H_4$  is a more efficient source

of intermediates for chain initiation and chain growth than CO is. The suppression in the contribution of CO to chain growth as  $P_{C_2H_4}$  increases is very likely due to the fact that the reaction of  $C_2H_4$  with adsorbed CO to form propanal is more rapid than the dissociation of CO to form carbon and from there CH<sub>2</sub> and CH<sub>3</sub> groups. Consistent with this interpretation, it is observed (see Figure 11) that the conversion of CO to propanal increases monotonically with increasing  $P_{C_2H_4}$ . The decrease in  $C_{3+}$  hydrocarbon formation for  $P_{C_2H_4} > 0.20$  atm is probably due to the lowering in the  $H_2/C_2H_4$  ratio. As can be seen from Table I, this ratio influences the homologation of  $C_2H_4$ . Quite possibly, at high  $C_2H_4$  partial pressures, the surface coverage of adsorbed H<sub>2</sub> is sufficiently suppressed to inhibit  $C_2H_4$  homologation. This interpretation is supported by the results presented in Figure 13.

The results of the present study clearly indicate that ethylene formed via the hydrogenation of CO can undergo extensive secondary reaction. The presence of CO inhibits the hydrogenation of ethylene to ethane and hence the formation of a stable  $C_2$ hydrocarbon product. A major portion of the readsorbed ethylene will participate in the initiation and propagation of chain growth. A significant fraction will react with adsorbed CO and hydrogen to form propanal (or 1-propanol). Ethylene readsorption will also result in a suppression of CH<sub>4</sub> formation. This would explain why the yield of CH<sub>4</sub> produced over Ru catalyst is observed to decrease as the conversion of CO to products increases.<sup>40</sup>

### Conclusions

The reaction of  $C_2H_4$  and  $H_2$  over Ru produces, in addition to  $C_2H_6$ ,  $CH_4$  and  $C_{3+}$  olefins and paraffins. A large fraction of the  $C_{4+}$  hydrocarbons are branched. The carbon number distribution of the  $C_{3+}$  products does not decrease monotonically, but rather oscillates so that products with an even number of carbon atoms predominate. The formation of  $CH_4$  is ascribed to the hydrogenolysis of  $C_2H_4$  and the formation of  $C_{3+}$  hydrocarbons to homologation of  $C_2H_4$  via chain growth, involving  $C_1$ and  $C_2$  monomer units. An accurate description of the product distribution is achieved by using the proposed mechanism.

The addition of  $C_2H_4$  to synthesis gas has a strong influence on the hydrogenation of CO. Above a  $C_2H_4/CO$  ratio of 1.0, the formation of hydrocarbons from CO is completely suppressed and only the hydroformylation of  $C_2H_4$  to form propanal (and some 1-propanol) is observed. The presence of CO suppresses the hydrogenation of  $C_2H_4$  to  $C_2H_6$  but has relatively little effect on  $C_2H_4$  hydrogenolysis and homologation. The selectivities of CH<sub>4</sub> and  $C_{3+}$  products are influenced by the partial pressures of  $C_2H_4$ , CO, and H<sub>2</sub>. High selectivity to  $C_{3+}$  products and low selectivity to CH<sub>4</sub> are observed for high  $C_2H_4$ , CO, and H<sub>2</sub> partial pressures and low reaction temperatures. The observed distribution of products can be described theoretically by using a modified version of the mechanism for  $C_2H_4$  homologation.

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Registry No. C<sub>2</sub>H<sub>4</sub>, 74-85-1; CO, 630-08-0; Ru, 7440-18-8.

<sup>(40)</sup> Kim, C. J. Exxon Research and Engineering Co., Clinton Township, Annandale, NJ, personal communication.

<sup>(41)</sup> In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III  $\rightarrow$  3 and 13.)