

The Influence of Propylene on CO Hydrogenation over Silica-Supported Ruthenium

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Reactions of C_3H_6 , H_2 , and CO were studied over Ru/SiO₂. Processes of hydrocarbon chain growth were investigated by comparing product distributions observed in the reactions of C_3H_6 and H_2 , and of C_3H_6 , H_2 , and CO. In the latter experiments, the source of carbon in the products was identified by using ¹³C-labeled CO and unlabeled C_3H_6 and analyzing the products by isotope-ratio gas chromatography–mass spectrometry. Hydrogenation to C_3H_8 is the dominant reaction in the absence of CO. Small conversions of C_3H_6 to CH_4 , C_2H_6 , and C_4+ products are also observed. Schemes for C_3H_6 hydrogenolysis and hydrogenation are discussed and a chain growth mechanism for C_3H_6 homologation is proposed. The latter involves C_1 , C_2 , and C_3 monomer units and is shown to describe the observed product distribution. The presence of CO enhances homologation relative to hydrogenolysis and suppresses hydrogenation. The addition of C_3H_6 to a CO/ H_2 feedstream reduces the rate of CO hydrogenation to form hydrocarbons. However, the overall rates of production of C_4+ hydrocarbons increase with increasing C_3H_6 partial pressure as a result of C_3H_6 homologation. The formation of butanal and butanol via hydroformylation is also observed. Comparisons between the reactions of C_2H_4 and C_3H_6 are made and implications of their similarities and differences are discussed. © 1987 Academic Press, Inc.

INTRODUCTION

Reactions of low-molecular-weight olefins with H_2 and CO have been investigated in order to examine chain growth processes that occur during Fischer–Tropsch synthesis over Group VIII metals (1–12). Such studies are conducted by observing changes in the product distribution effected by the addition of olefin to synthesis gas and/or by labeling the olefin isotopically and observing its incorporation into the products. This body of work was reviewed in a previous paper (12). In general, it has been found that low-molecular-weight olefins (i.e., ethylene, propylene, and butylene) added to H_2 and CO over Co catalysts participate in hydrocarbon chain initiation and growth, often by forming single-carbon species that act as monomer units (1–6), and that the olefins enhance the selectivity to liquid hydrocarbons (1–4, 7). Over Ru catalysts, added ethylene or propylene has

been observed to increase the rates of higher hydrocarbon formation (8–12) and in some cases to reduce the rate of methane formation (11, 12). In our previous work (12), we found that, for C_2H_4 /CO ratios greater than one, the hydrocarbon products derived entirely from C_2H_4 and the reaction of CO and H_2 to produce hydrocarbons was suppressed. Homologation of C_2H_4 in the absence of CO was also observed in our investigation (12) as well as in other studies (7, 13). A chain growth scheme involving one- and two-carbon monomer units was shown to be consistent with the product distribution observed in the reaction of C_2H_4 and H_2 alone (12).

Comparisons between the influences of propylene and ethylene addition on the CO/ H_2 reaction have been made by a number of investigators (1–4, 6, 7, 11). Golovina *et al.* (2) observed that the conversion of C_3H_6 to higher hydrocarbons was lower than that of C_2H_4 by a factor of 4, using an

olefin concentration of 1.5% over a Co catalyst. More recently, studies conducted by Morris *et al.* (11) over Ru/SiO₂ also showed a fourfold lower conversion of C₃H₆ than C₂H₄ to C₄₊ products, using 5% added olefin. No suppression of methane production was observed upon addition of either C₂H₄ or C₃H₆ (11). Kibby *et al.* (7) examined olefin addition to synthesis gas as well as olefin homologation in the absence of CO over Co catalysts. Propylene and ethylene both reduced the rate of methane production, ethylene being more effective than propylene, and both greatly increased the yield of liquid hydrocarbons. In the absence of CO, homologation was observed for both olefins, giving similar product distributions but higher rates for C₂H₄ than for C₃H₆.

The objectives of the present study were to examine the influence of propylene addition on CO hydrogenation over Ru/SiO₂ and to compare the results with those obtained previously for ethylene (12). The distributions of C₃H₆- and CO-derived products were determined by using ¹³C-labeled CO and unlabeled C₃H₆ and employing isotope-ratio gas chromatography-mass spectrometry for analysis. To investigate reactions of C₃H₆ with H₂ and CO, two courses of study were taken. In the first, effects of C₃H₆ on the reactions of CO to produce methane and higher hydrocarbons were examined. Reactions of propylene occurring during the CO/H₂ reaction were also studied. In the other part of the work, propylene homologation in the absence of CO was examined in order to understand more clearly the participation of propylene in hydrocarbon chain growth processes.

EXPERIMENTAL

The catalyst consists of 4.3% Ru/SiO₂ and has a dispersion of 0.27 as determined by H₂ chemisorption at 373 K. Its preparation is discussed elsewhere (14). Propylene (99.6%), helium (99.999%), and carbon monoxide (88.3% ¹³CO, 11.2% ¹³C¹⁸O, and

0.5% ¹²CO, Isotec) are used as received. Hydrogen is purified by passage through a Deoxo unit (Engelhard) and 5-Å molecular sieve.

The catalyst (0.51 g) is contained in a stainless-steel microreactor which is heated by a fluidized sand bath. Experiments are carried out by first reducing the catalyst in flowing H₂ at the reaction temperature of 493 K for 2 h, and then introducing the reactant stream at a pressure of 1 atm. The reaction is allowed to continue for 15 min before product samples are analyzed. Reduction at the reaction temperature is maintained between experiments. Further details concerning the experimental procedure have been presented previously (12).

The reactor effluent is analyzed to determine both its composition and the isotopic abundance in each of the products. The analytical system consists of a combination of gas chromatography and mass spectrometry and is discussed in detail elsewhere (12). Briefly, the composition is determined using two gas chromatographs. The light gases are separated on a column packed with Chromosorb 106 and are quantified using a thermal conductivity detector. C₄ and heavier hydrocarbons are separated on a capillary column coated with SE-54 and are quantified by feeding part of the column effluent to a flame ionization detector. The complete product composition is determined by normalizing the C₄ analyses from the packed and capillary columns. The isotopic abundance is determined by feeding the other part of the capillary column effluent to a capillary combustor in which each product is converted to CO₂. The ¹³C content of the CO₂ is determined by mass spectrometry. The result is a pair of mass chromatograms for masses 45 (¹³CO₂) and 44 (¹²CO₂) which yield the distributions of ¹³CO- and C₃H₆-derived products. The mass spectrometer and gas chromatographs are interfaced to an IBM PC microcomputer for data acquisition and mass spectrometer control.

RESULTS

Reactions of H₂ and C₃H₆

Propylene reacts with hydrogen to produce propane, methane, ethane, and heavier hydrocarbons which are primarily linear paraffins. Figure 1 shows the distribution of hydrocarbons, excluding propane, produced from an equimolar H₂/C₃H₆ feedstream at 493 K and 0.80 atm. The rates of production of hydrocarbons are shown as a function of the number of carbon atoms in the product. The fractional conversion of propylene to propane is 0.97, while the conversion to methane and ethane (C₁₊₂) is 0.024 and to heavier hydrocarbons (C₄₊) is 0.010. It is noted that, while the rate generally decreases by a factor of 3 or more with an increase of one carbon atom in the product, anomalous behavior is observed for the rates of production of C₆ and C₉ hydrocarbons.

The structural composition of the products is illustrated in Fig. 2. The relative

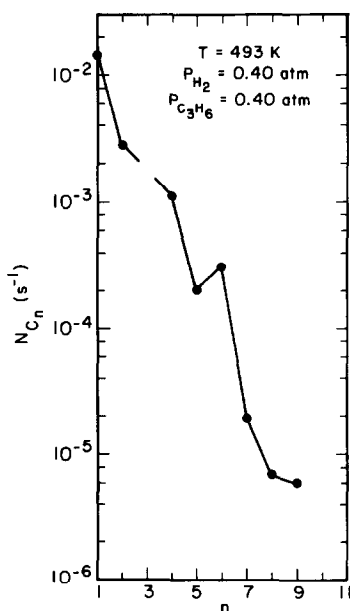


FIG. 1. Distribution of C₁ through C₉ hydrocarbons produced by reaction of H₂ and C₃H₆ at 493 K. $P_{H_2} = P_{C_3H_6} = 0.40 \text{ atm}$.

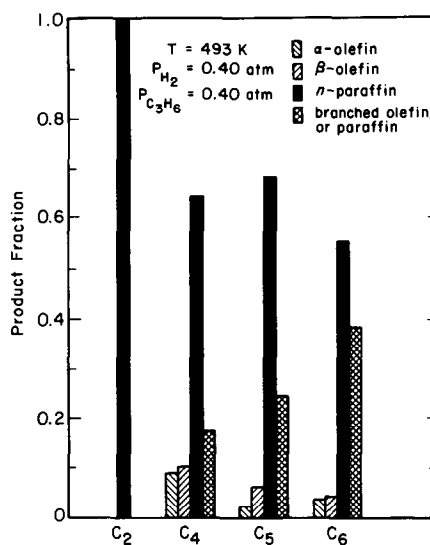


FIG. 2. Proportions of linear olefin, linear paraffin, and branched products observed in the reaction of H₂ and C₃H₆.

amounts of linear α - and β -olefins, n -paraffin, and branched olefins and paraffins are shown as a function of carbon number. The product consists primarily of n -paraffins, with branched isomers becoming significant for the heavier hydrocarbons. As the H₂/C₃H₆ feed ratio decreases, the linear olefin fraction increases at the expense of n -paraffins, and branched products become more predominant. For example, at H₂/C₃H₆ = 0.25, the C₄ product consists of 0.56 linear olefin, 0.30 branched species, and only 0.14 n -paraffin, and the C₆ product contains 0.75 branched olefins and paraffins, 0.19 linear olefins, and 0.06 n -paraffins.

The conversions of C₃H₆ to products are given in Table 1 for various H₂/C₃H₆ feed ratios. Hydrogenation to propane decreases from 0.97 of the propylene converted to 0.25, as the H₂/C₃H₆ ratio decreases from 1.0 to 0.25. Conversion to hydrocarbons other than propane decreases from 0.034 to 0.0048 as the feed H₂/C₃H₆ ratio decreases from 1.0 to 0.25. At the same time, the production of C₄₊ relative to C₁₊₂ hydrocarbons doubles.

TABLE 1
Conversion of C_3H_6 to Products in the Reaction of H_2 and C_3H_6

Feed H_2/C_3H_6	Conversion of C_3H_6 to:			Total	Conv. to C_{4+} / Conv. to C_{1+2}
	C_3H_8	C_{1+2}	C_{4+}		
1.00	9.7×10^{-1}	2.4×10^{-2}	1.0×10^{-2}	1.00	0.42
0.75	7.3×10^{-1}	1.1×10^{-2}	4.7×10^{-3}	7.5×10^{-1}	0.43
0.50	4.9×10^{-1}	7.2×10^{-3}	3.9×10^{-3}	5.0×10^{-1}	0.53
0.25	2.5×10^{-1}	2.5×10^{-3}	2.3×10^{-3}	2.5×10^{-1}	0.91

Note. Reaction conditions: feed $P_{C_3H_6} = 0.040$ atm, $T = 493$ K.

Reaction of H_2 and CO

The product distribution for the reaction of a 2:1 H_2 :CO feedstream is shown in Fig. 3. The rates of formation of C_{3+} hydrocarbons decrease linearly with carbon number on a lognormal scale, exhibiting a chain growth probability, α , of 0.53. The conversion of CO under these conditions is 0.078. The relative amounts of linear olefins and paraffins and branched products are shown in Fig. 4. In the light gases, the *n*-paraffin

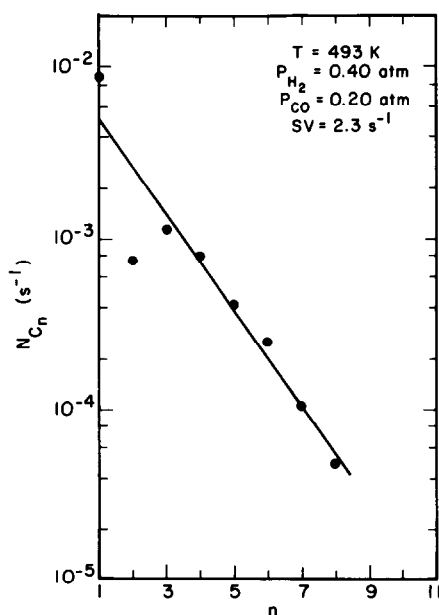


FIG. 3. Distribution of C_1 through C_8 hydrocarbons produced by reaction of H_2 and CO at 493 K. $P_{H_2} = 0.40$ atm, $P_{CO} = 0.20$ atm.

content is high, while branched products dominate the heavier products. Linear olefins constitute a small fraction of all products.

Reactions of H_2 , C_3H_6 , and CO

Propylene, CO, and H_2 react to produce, in addition to propane, C_{4+} and C_{1+2} hydrocarbons and C_4 oxygenates. The distribution of hydrocarbon products of a 2:2:1 H_2 : C_3H_6 : ^{13}CO feedstream are shown in the top curve of Fig. 5. The lower curves indicate the source of carbon atoms in the products, as determined from the combus-

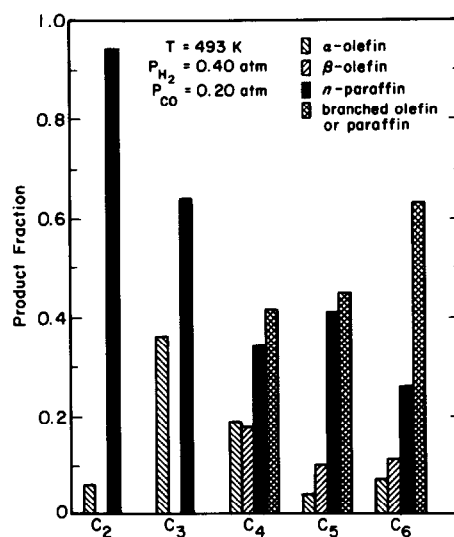


FIG. 4. Proportions of linear olefin, linear paraffin, and branched products observed in the reaction of H_2 and CO.

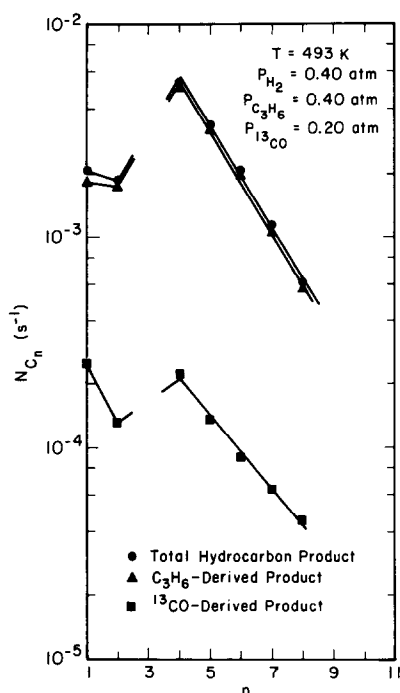


FIG. 5. Distribution of C_3H_6 -derived and ^{13}CO -derived hydrocarbons produced by reaction of H_2 , C_3H_6 , and ^{13}CO at 493 K. $P_{H_2} = P_{C_3H_6} = 0.40$ atm, $P_{CO} = 0.20$ atm.

tion analysis. CO-derived carbon constitutes only 12% of the carbon in methane and between 4.0 and 7.5% of the carbon atoms in C_{2+} hydrocarbons except propane. In the oxygenated products butanal and butanol-1, 25% of the carbon atoms derive from CO.

Although CO participates only minimally in hydrocarbon chain growth, the presence of CO affects the formation of hydrocarbons from C_3H_6 . By comparing Figs. 1 and 5, it is observed that CO suppresses the formation of methane and, to a lesser extent, ethane, and it enhances the formation of C_{4+} products. The presence of CO also results in a lognormal relationship between rate and carbon number for C_{4+} hydrocarbons, which is similar to an Anderson-Schulz-Flory distribution. The apparent α value of 0.57 which may be calculated for the C_{4+} portion of the product distribution is virtually the same as that observed dur-

ing CO hydrogenation. The conversion of C_3H_6 to C_3H_8 decreases from 0.97 to 0.08 when 0.20 atm CO is added to the H_2/C_3H_6 feed, while the conversion of C_3H_6 to other hydrocarbons increases from 0.034 to 0.040. It is interesting to note that the production from C_3H_6 of C_{4+} hydrocarbons relative to C_{1+2} hydrocarbons increases from 0.42 to 12.0 when CO is added to the H_2/C_3H_6 feed. The conversion of CO to hydrocarbons under the reaction conditions described in Fig. 5 is 0.013.

The relative amounts of linear olefins, n -paraffins, and branched isomers are shown in Fig. 6. Linear olefins constitute the largest fraction of the C_2 and C_{4+} products. Branched olefins and paraffins are present in significant quantities in the heavier hydrocarbons. The influence of CO on the composition of hydrocarbons derived from C_3H_6 may be seen by comparing Figs. 2 and 6. The presence of CO in the feed-stream shifts the products from primarily paraffinic to olefinic, with the proportion of branched isomers remaining roughly the same. Decreasing P_{H_2} in the reaction of H_2 , C_3H_6 , and CO increases the ratio of linear

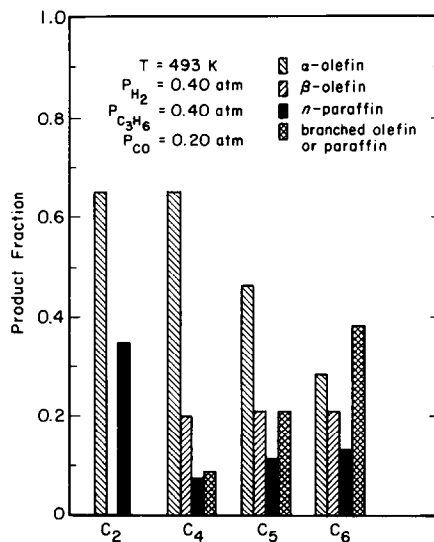


FIG. 6. Proportions of linear olefin, linear paraffin, and branched products observed in the reaction of H_2 , C_3H_6 , and CO.

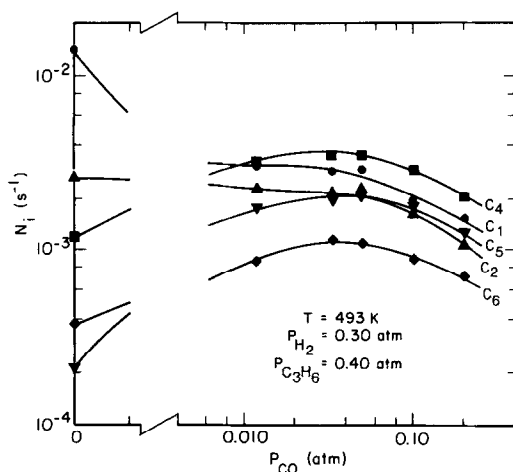


FIG. 7. Influence of P_{CO} on the rates of production of C_1 through C_6 hydrocarbons. $P_{H_2} = 0.30$ atm, $P_{C_3H_6} = 0.40$ atm.

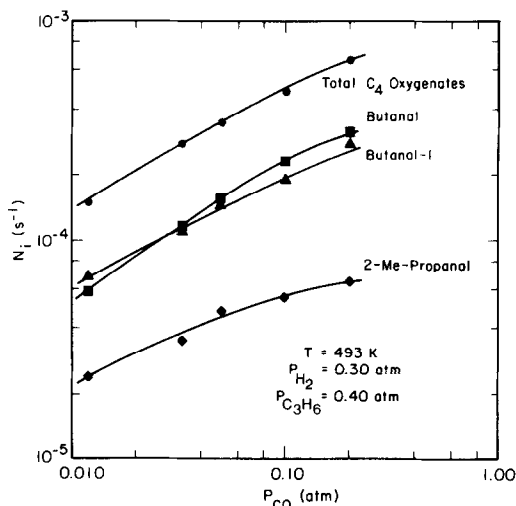


FIG. 8. Influence of P_{CO} on the rates of production of C_4 oxygenates. $P_{H_2} = 0.30$ atm, $P_{C_3H_6} = 0.40$ atm.

olefins to n -paraffins and, to a lesser extent, decreases the proportion of branched products. It is interesting to note that adding CO to the H_2/C_3H_6 feed and decreasing P_{H_2} in the H_2/C_3H_6 reaction have similar effects on the ratio of linear olefins to n -paraffins.

The effect of P_{CO} on the rates of production of C_1 , C_2 , and C_{4+} hydrocarbons is shown in Fig. 7. The corresponding conversions of C_3H_6 to C_3H_8 are given in Table 2. The addition of 0.012 atm CO to the H_2/C_3H_6 feed reduces the rate of methane formation by a factor of 5 and the conversion of C_3H_6 to C_3H_8 by a factor of 3. At the same time, the rates of production of C_{4+}

hydrocarbons increase by factors of 2 or more. The rates of formation of C_1 and C_2 hydrocarbons decrease and the rates of formation of C_{4+} products exhibit maxima as P_{CO} is increased above 0.05 atm.

The rates of production of C_4 oxygenates are shown as functions of P_{CO} in Fig. 8. The combustion analysis indicates that these products contain 25% CO-derived carbon. At the highest CO partial pressure, the conversion of CO to oxygenates is 0.0023 and to hydrocarbons is 0.0046, while the conversion of C_3H_6 to oxygenates is 0.0012 and to hydrocarbons other than propane is 0.015.

TABLE 2

Effects of P_{CO} on the Conversions of C_3H_6 and CO to Products in the Reaction of H_2 , C_3H_6 , and CO

P_{CO} (atm)	Conversion of C_3H_6 to:			Conversion of CO to:	
	C_3H_8	$C_{1+2} + C_{4+}$	Oxy.	H_6	Oxy.
0	7.3×10^{-1}	1.6×10^{-2}	0	—	—
0.01	2.5×10^{-1}	2.2×10^{-2}	2.6×10^{-4}	2.5×10^{-2}	8.7×10^{-3}
0.5	2.1×10^{-1}	2.5×10^{-2}	6.1×10^{-4}	1.9×10^{-2}	4.9×10^{-3}
0.10	1.8×10^{-1}	2.1×10^{-2}	8.3×10^{-4}	2.6×10^{-3}	3.3×10^{-3}
0.20	1.7×10^{-1}	1.5×10^{-2}	1.2×10^{-3}	4.6×10^{-3}	2.3×10^{-3}

Note. Reaction conditions: feed $P_{C_3H_6} = 0.40$ atm, feed $P_{H_2} = 0.30$ atm, $T = 493$ K.

TABLE 3

Effects of $P_{C_3H_6}$ on the Conversions of C_3H_6 and CO to Products in the Reaction of H_2 , C_3H_6 , and CO

$P_{C_3H_6}$ (atm)	Conversion of C_3H_6 to:			Conversion of CO to:	
	C_3H_8	$C_{1+2} + C_{4+}$	Oxy.	HC	Oxy.
0	—	—	—	7.8×10^{-2}	—
0.031	3.4×10^{-1}	2.7×10^{-1}	4.3×10^{-3}	2.8×10^{-2}	6.7×10^{-4}
0.071	1.9×10^{-1}	1.4×10^{-1}	4.3×10^{-3}	2.9×10^{-2}	1.5×10^{-3}
0.20	1.7×10^{-1}	8.5×10^{-2}	4.1×10^{-3}	1.9×10^{-2}	4.1×10^{-3}
0.40	0.3×10^{-2}	4.0×10^{-2}	2.8×10^{-3}	1.3×10^{-2}	5.6×10^{-3}

Note. Reaction conditions: feed $P_{H_2} = 0.40$ atm, feed $P_{CO} = 0.20$ atm, $T = 493$ K.

The effect of $P_{C_3H_6}$ on the rates of hydrocarbon production is shown in Fig. 9 and the corresponding conversions are given in Table 3. The addition of 0.035 atm C_3H_6 to the H_2/CO feed inhibits methane formation and enhances the production of C_{2+} hydrocarbons. As $P_{C_3H_6}$ is increased further, the methane rate displays a negative dependence and C_{2+} hydrocarbon rates show weak positive dependences on $P_{C_3H_6}$. Both CO- and C_3H_6 -derived hydrocarbons are included in the rates shown in Fig. 9. For the same experiments, the rates of formation of hydrocarbons from CO are given in

Fig. 10. These rates were determined by multiplying each rate in Fig. 9 by the fraction of that product which is derived from CO. The addition of 0.035 atm C_3H_6 to the H_2/CO feed reduces the rate of formation of methane from CO by a factor of 6 and the rate of formation of ethylene and ethane from CO by a factor of 3. The reaction of CO to form C_{4+} hydrocarbons is not affected by the presence of C_3H_6 in the feed at low $P_{C_3H_6}$ but is inhibited for $P_{C_3H_6} > 0.10$ atm.

The rates of production of C_4 oxygenates are shown as functions of $P_{C_3H_6}$ in Fig. 11.

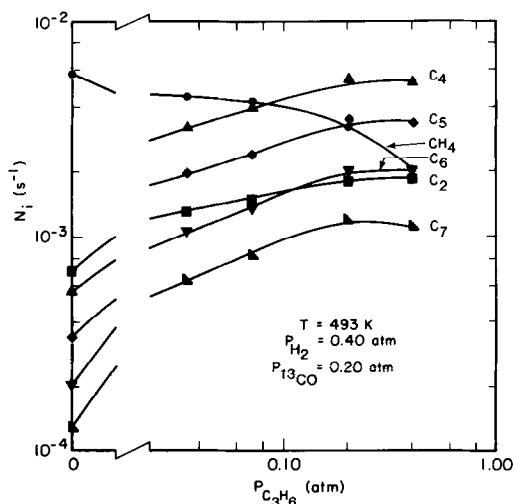


FIG. 9. Influence of $P_{C_3H_6}$ on the rates of production of C_1 through C_7 hydrocarbons. $P_{H_2} = 0.40$ atm, $P_{CO} = 0.20$ atm.

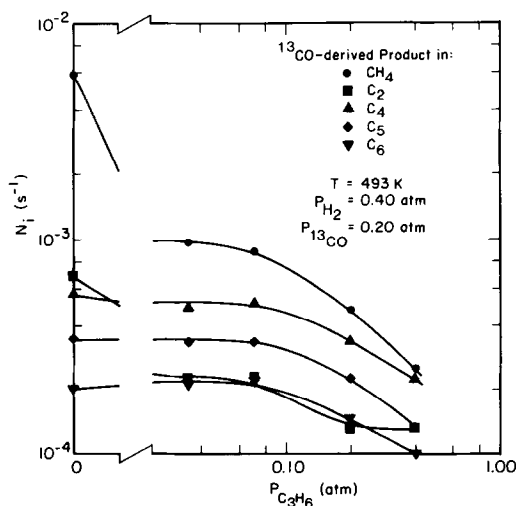


FIG. 10. Influence of $P_{C_3H_6}$ on the rates of production of ^{13}CO -derived hydrocarbons. $P_{H_2} = 0.40$ atm, $P_{CO} = 0.20$ atm.

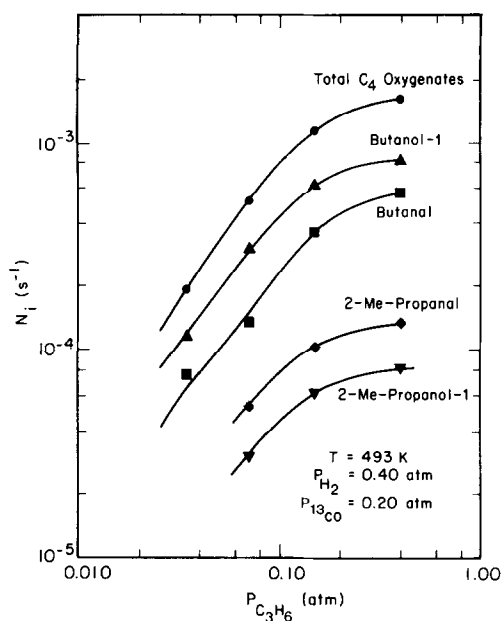


FIG. 11. Influence of $P_{C_3H_6}$ on the rates of production of C_4 oxygenates. $P_{H_2} = 0.40$ atm, $P_{CO} = 0.20$ atm.

The rates exhibit strong positive dependences at low $P_{C_3H_6}$ and level off at high $P_{C_3H_6}$.

The effect of P_{H_2} on the hydrocarbon product distribution is shown in Fig. 12 and conversions of C_3H_6 and CO are given in Table 4. The methane rate increases rapidly with increasing P_{H_2} . The dependence of the rate on P_{H_2} increases with increasing carbon number, resulting in a higher average molecular weight of the product at higher P_{H_2} .

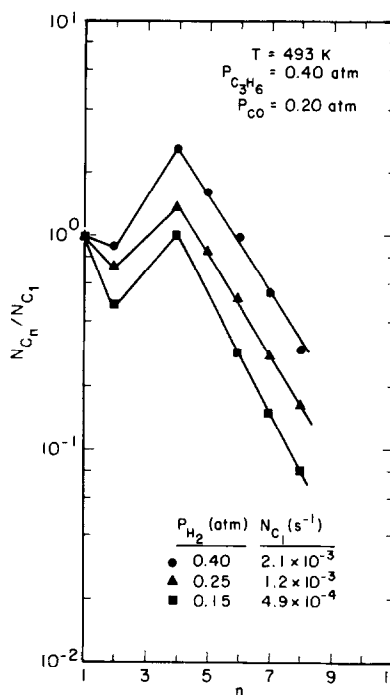


FIG. 12. Effects of H_2 partial pressure on the distribution of C_1 through C_8 hydrocarbon products. $P_{C_3H_6} = 0.40$ atm, $P_{CO} = 0.20$ atm, $T = 493$ K.

DISCUSSION

Comparison with Previous Work

Reactions of C_2H_4 and H_2 over Ru were examined in our previous study (12). It was found that, in the absence of CO, C_2H_4 undergoes homologueation, hydrogenation, and hydrogenolysis, and that the conversions of C_2H_4 to C_2H_6 , CH_4 , and C_{3+} hydrocarbons increase with an increasing $H_2/$

TABLE 4

Effects of P_{H_2} on the Conversions of C_3H_6 and CO to Products in the Reaction of H_2 , C_3H_6 , and CO

P_{H_2} (atm)	Conversion of C_3H_6 to:			Conversion of CO to:	
	C_3H_8	$C_{1+2} + C_{4+}$	Oxy.	H_6	Oxy.
0.15	4.0×10^{-2}	3.4×10^{-3}	2.8×10^{-4}	1.2×10^{-3}	5.6×10^{-4}
0.25	5.9×10^{-2}	1.3×10^{-2}	8.7×10^{-4}	4.3×10^{-3}	1.7×10^{-3}
0.40	8.3×10^{-2}	4.0×10^{-2}	2.8×10^{-3}	1.3×10^{-2}	5.6×10^{-3}

Note. Reaction conditions: feed $P_{C_3H_6} = 0.40$ atm, feed $P_{CO} = 0.20$ atm, $T = 493$ K.

C_2H_4 feed ratio. An oscillatory product distribution was observed, with even-numbered hydrocarbons favored. The product distribution was shown to be consistent with a chain growth scheme involving one- and two-carbon monomer units.

Many of the results of C_3H_6/H_2 reactions reported here are similar to those observed for C_2H_4 and H_2 . Hydrogenation accounts for more than 90% of the olefin converted to products, and conversions to hydrocarbons other than the corresponding paraffin are similar for the two olefins. The chief difference is that propylene is less selective than ethylene for homologation relative to hydrogenolysis. For H_2 /olefin feed ratios of one, ratios of the conversions to homologation products (C_{n+}) relative to hydrogenolysis products (C_{n-}) are 2.9 for C_2H_4 and 0.42 for C_3H_6 . The two olefins exhibit similar decreases in conversions to C_{n-} and C_{n+} products with a decreasing H_2 /olefin feed ratio. Observations of C_3H_6 homologation in the absence of CO have been reported by Kibby *et al.* (7) over supported Co catalysts and by Leconte *et al.* (13) over silica-supported Ru. The product distribution for the C_3H_6/H_2 reaction reported by Kibby *et al.* (7) is very similar to that observed for the $C_3H_6/H_2/CO$ reaction in the present study: high rates of formation of C_{4+} products relative to the CH_4 rate, and a lognormal relationship between rates and carbon number for C_{5+} products. Leconte *et al.* (13) report the distribution of only C_1 – C_4 products for the C_3H_6/H_2 reaction. The relative concentrations are similar to those reported here for the C_3H_6/H_2 reaction. According to the authors, the mechanism of C–C bond formation is similar in CO hydrogenation and in olefin homologation (13).

As in the absence of CO, propylene is less reactive than ethylene for homologation in the presence of CO. For a 2 : 2 : 1 olefine : H_2 : CO reaction mixture, the conversion of C_2H_4 to hydrocarbons other than C_2H_6 is 0.090 (12) but the conversion of C_3H_6 to hydrocarbons other than C_3H_8 is only 0.040. Ratios of olefin conversions to

C_{n+} relative to C_{n-} are 70 for C_2H_4 and 12 for C_3H_6 . Adding CO to the olefin/ H_2 feed inhibits hydrogenation for both olefins, but CO is less effective in inhibiting the hydrogenation of C_3H_6 than that of C_2H_4 . Production of oxygenates occurs analogously in the reactions of the two olefins with H_2 and CO: the olefin C_nH_{2n} reacts with $^{13}CO_s$ to produce the aldehyde $C_nH_{2n+1}^{13}CHO$ and the alcohol $C_nH_{2n+3}^{13}CH_2OH$. The rates of production of oxygenates are three to four times lower in the C_3H_6 reaction than in the C_2H_4 reaction.

The addition of propylene to a CO/ H_2 feedstream was shown in the present study to decrease the rate of methane formation and to increase the rates of production of C_2 and C_{4+} hydrocarbons. The first result is consistent with observations made by Kibby *et al.* (7) using Co catalysts and by Kobori *et al.* (10) using Ru. It differs, however, from the results of Morris *et al.* (11) who observed no change in the methane rate when C_3H_6 was added to CO/ H_2 over Ru/ SiO_2 . Increases in C_2 and C_{4+} rates are qualitatively consistent with the observations of Morris *et al.* (11), Kibby *et al.* (7), and Kobori *et al.* (10). Compared with ethylene (12), propylene is less effective in reducing methane formation. For example, a threefold reduction in the methane rate compared with the CO/ H_2 reaction requires an olefin/CO feed ratio of 2.0 for C_3H_6 but of only 0.5 for C_2H_4 (12). In general, it is found that propylene added to synthesis gas incorporates into higher hydrocarbons less than ethylene does (Ref. (1, 3, 11)). The results reported here and in our previous study (12) agree with this observation. At an olefin/CO feed ratio of 0.5, the olefin conversions to C_{n+} hydrocarbons are 0.46 for C_2H_4 and 0.10 for C_3H_6 . At sufficiently high olefin/CO ratios, both olefins inhibit the reaction of CO and H_2 to produce C_{n+} hydrocarbons. This effect is observed with ethylene at olefin/CO ratios greater than 0.2, but in the case of propylene olefin/CO ratios greater than 0.5 are required. At an olefin/CO ratio of 2, the conversion of CO

cess. One- and two-carbon monomer units, designated C_1^m and C_2^m are formed from adsorbed propylene. The three monomer species may be viewed as CH_2 , C_2H_4 , and C_3H_6 . Initiation of chain growth occurs by the addition of a monomer unit to one of the surface species C_1 , C_2 , or C_3 . These chain initiators may consist of the alkyl groups CH_3 , C_2H_5 , and C_3H_7 , respectively. Propagation of chain growth occurs when one of the monomer units adds to a hydrocarbon chain, C_n . Chain termination occurs by either β -hydride abstraction to form the α -olefin or reductive elimination to form a paraffin.

Relative rates of formation of hydrocarbons can be formulated using the scheme described above. The development which follows is analogous to that describing ethylene homologation in our previous work (12) and to that describing the participation of one- and two-carbon monomer units in CO hydrogenation presented by Novak *et al.* (17). It is assumed that surface coverages by the monomer units, which are denoted θ_1^m , θ_2^m , and θ_3^m , are constant and independent. It is also assumed that specific rates of chain growth and chain termination are independent of chain length.

The rate of formation of a hydrocarbon containing n carbon atoms is given by

$$N_{C_n} = k_t \theta_n, \quad [1]$$

where k_t is a rate coefficient for chain termination and θ_n is the coverage by a hydrocarbon chain containing n carbon atoms. It is recognized that k_t describes termination to both olefins and paraffins. To relate the coverage of C_n to those of the monomers, C_1^m , C_2^m , and C_3^m , the following steady-state balance is imposed on the rates of formation and consumption of C_n :

$$0 = k_{p_1} \theta_1^m \theta_{n-1} + k_{p_2} \theta_2^m \theta_{n-2} + k_{p_3} \theta_3^m \theta_{n-3} - k_{p_1} \theta_1^m \theta_n - k_{p_2} \theta_2^m \theta_n - k_{p_3} \theta_3^m \theta_n - k_t \theta_n. \quad [2]$$

In this equation, the terms k_{p_1} , k_{p_2} , and k_{p_3}

represent rate coefficients for chain propagation by C_1^m , C_2^m , and C_3^m . Equation [2] can be rewritten as

$$\theta_n = \alpha_1 \theta_{n-1} + \alpha_2 \theta_{n-2} + \alpha_3 \theta_{n-3}, \quad [3]$$

where α_1 , α_2 , α_3 are defined as

$$\begin{aligned} \alpha_1 &= \frac{k_{p_1} \theta_1^m}{k_{p_1} \theta_1^m + k_{p_2} \theta_2^m + k_{p_3} \theta_3^m + k_t} \\ \alpha_2 &= \frac{k_{p_2} \theta_2^m}{k_{p_1} \theta_1^m + k_{p_2} \theta_2^m + k_{p_3} \theta_3^m + k_t} \\ \alpha_3 &= \frac{k_{p_3} \theta_3^m}{k_{p_1} \theta_1^m + k_{p_2} \theta_2^m + k_{p_3} \theta_3^m + k_t} \end{aligned} \quad [4]$$

Thus α_1 , α_2 , and α_3 represent probabilities of chain growth via the monomers C_1^m , C_2^m , and C_3^m , respectively.

The product distribution can be calculated by combining Eq. [1] with Eq. [3] written for $n \geq 4$. It is convenient to normalize the product distribution to the methane rate. In this case the parameters are the chain growth probabilities α_1 , α_2 , and α_3 , and the ratios of surface coverages by chain initiators, θ_2/θ_1 and θ_3/θ_1 . The calculated product distribution is, in general, not monotonic. The extent to which the rates oscillate as a function of carbon number depends largely on the magnitudes of α_2/α_1 and α_3/α_1 . A large value of α_3/α_1 relative to α_2/α_1 , for example, yields a product distribution with anomalously high C_6 and C_9 rates. Dominance of either θ_3/θ_1 or θ_2/θ_1 has a similar but less dramatic influence on the form of the calculated product distribution.

A fit of Eq. [3] to the data presented in Fig. 1 is shown in Fig. 13. Good agreement of theory and experiment is obtained using the parameter values shown. The value of θ_2/θ_1 is set at the experimentally observed value of N_{C_2}/N_{C_1} . The calculated parameter values suggest that chain propagation occurs most rapidly via C_1^m and least rapidly via C_2^m . On the other hand, initiation of chain growth occurs most frequently at C_3 and least frequently at C_2 .

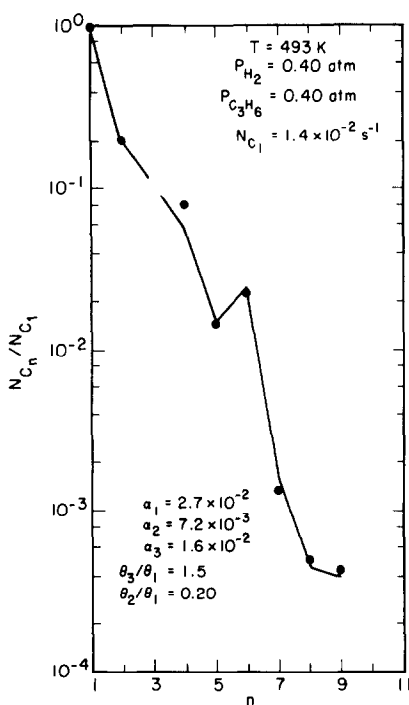


FIG. 13. Comparison of calculated and experimental product distributions for the reaction of H_2 and C_3H_6 .

Reactions of H_2 , C_3H_6 , and CO

The presence of CO has a strong influence on the reactions of C_3H_6 and H_2 . While the total production from C_3H_6 of C_1 , C_2 , and C_{4+} hydrocarbons changes very little with the addition of CO (see Table 2), the selectivity shifts dramatically to higher-molecular-weight products (Figs. 1 and 5). The former result implies that CO has little influence on the formation of $C_3H_{(7-x)}$ species which act as precursors of homologation and hydrogenolysis products. However, the probability of chain growth by any of the one-, two-, or three-carbon monomer units formed from these species is higher because CO inhibits reductive elimination. From the shift to a monotonic product distribution, it is inferred that the relative rates of chain propagation by the various monomer units also change when CO is present. However, many combina-

tions of the relevant parameters result in a lognormal distribution of C_{4+} products, so it is difficult to speculate on the effects of CO on individual steps in the reaction scheme involved in C_3H_6 homologation.

The results presented in Figs. 9 and 10 and Table 3 show the effects of C_3H_6 on CO hydrogenation. With increasing partial pressure of C_3H_6 in the feed, the conversion of CO to hydrocarbons decreases and the rates of formation of hydrocarbons from C_3H_6 increase. The implication of these results is that C_3H_6 acts more efficiently than CO does to provide intermediates for hydrocarbon chain growth. Taken together with the results cited earlier regarding C_2H_4 , the data shown in Figs. 9 and 10 also suggest that C_3H_6 is a less efficient source of hydrocarbon intermediates than C_2H_4 . The similarity between the C_{n+} product distributions of the olefin/ H_2 /CO reactions and that of the H_2 /CO reaction implies that hydrocarbon chain growth involving CO-, C_2H_4 -, and C_3H_6 -derived intermediates may proceed along similar reaction pathways. This conclusion is supported by the results of the combustion analysis shown in Fig. 5, in which the CO- and C_3H_6 -derived C_{4+} product distributions are nearly parallel. The suppression by C_3H_6 of hydrocarbon synthesis from CO may be the result of rapid hydroformylation and thus lower rates of CO dissociation and chain growth. It is observed that the suppression of hydrocarbon formation from CO is lower by a factor of 3 for C_3H_6 compared with C_2H_4 , and that the formation of oxygenates is lower by a factor of 3 to 4 for C_3H_6 / H_2 /CO compared with C_2H_4 / H_2 /CO. It is likely that, at high olefin partial pressures, this difference in reactivities is related to a higher coverage by adsorbed hydrogen in the C_3H_6 / H_2 /CO reaction than in the C_2H_4 / H_2 /CO reaction. This argument is supported by the observations that olefin hydrogenation is more rapid for C_3H_6 than for C_2H_4 and that olefin homologation rates decrease at high olefin partial pressures for C_2H_4 but not for C_3H_6 .

CONCLUSIONS

Propylene reacting with H_2 over Ru undergoes homologation, hydrogenation, and hydrogenolysis in the absence of CO. Except for C_3H_8 , the rates of production of hydrocarbons decrease in a nonmonotonic fashion with carbon number. A scheme for homologation involving one-, two-, and three-carbon monomer units accurately describes the product distribution.

The addition of propylene to synthesis gas suppresses the reaction of CO to form hydrocarbons and increases the rate of hydroformylation to form butanal and butanol. Compared with ethylene, propylene is less efficient by approximately a factor of 3 in suppressing hydrocarbon synthesis from CO. Homologation of propylene proceeds in the presence of CO, yielding higher rates of C_{4+} hydrocarbon production than in the reaction of CO and H_2 alone. The effects of CO on reactions of C_3H_6 are to increase the selectivity to C_{4+} products relative to CH_4 and C_2H_6 and to decrease the conversion to C_3H_8 . The distribution of C_{4+} products observed in the $C_3H_6/CO/H_2$ reaction is similar to that observed in the $C_2H_4/CO/H_2$ reaction, suggesting that chain growth via the two olefins proceeds along similar reaction pathways.

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