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The Influence of Butene on CO Hydrogenation over Ruthenium

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Reactions of 1-C_4H_8 with H_2 and CO were investigated over Ru/SiO_2. To identify the sources of carbon in the products, ^{13}CO and unlabeled 1-C_4H_8 were used and product analysis was carried out by isotope-ratio gas chromatography–mass spectrometry. Butene undergoes extensive hydrogenation and isomerization in the absence of CO. The production of small quantities of C_1–C_3 and C_{5+} paraffins is also observed, indicating hydrogenolysis and homologation of C_4H_8. The observed product distribution is described by a chain growth scheme involving C_1 and C_4 monomer units. Butene added to synthesis gas strongly influences the reactions of CO while undergoing reactions itself. With increasing C_4H_8 partial pressure, hydrocarbon formation from CO is suppressed but the production of pentanal and pentanol via hydroformylation is enhanced. The rate of C_4H_8 homologation increases with increasing C_4H_8 pressure, resulting in higher overall rates of production of C_{5+} hydrocarbons in the $C_4H_8/H_2/CO$ reaction than those in the H_2/CO reactions. Implications of these results on the chain growth mechanism are discussed. Comparisons are made among the reactions of C_4H_8, C_2H_4, and C_3H_6 with synthesis gas. It is concluded that the efficiency of the olefin in producing monomers that are active in chain growth decreases in the order $C_2H_4 > C_3H_6 >$ 1-C_4H_8. © 1987 Academic Press, Inc.

INTRODUCTION

The influence of low-molecular-weight olefins on CO hydrogenation has been the subject of a number of studies (*1–14*) which have been reviewed previously (*15*). The addition of ethylene or propylene to synthesis gas has been found to increase the selectivity to liquid hydrocarbons over Co, Fe, and Ru catalysts (*1–5, 9, 14–16*). Using isotopically labeled olefins, it has been determined that the added olefin may participate in processes of hydrocarbon chain initiation and growth, in some cases by forming single-carbon monomer units (*1–8, 15–17*). These observations have led to investigations of chain growth processes undergone by olefins in the absence of CO. Homologation reactions of ethylene, propylene, and butene have been reported over Co, Ru, and Fe catalysts (*1, 9, 10, 15, 16, 18–23*). Our previous work focused on interactions of C_2H_4 (*15*) and C_3H_6 (*16*) with H_2 and CO over Ru/SiO_2 and on reactions of the two olefins with H_2 alone. We found that both C_2H_4 and C_3H_6 suppress the synthesis of hydrocarbons from CO but increase the overall rates of hydrocarbon production as a result of olefin homologation (*15, 16*). Homologation was also observed when each olefin reacted with H_2 in the absence of CO. Chain growth schemes which involve one- and two-carbon monomer units for C_2H_4 homologation (*15*) and one-, two-, and three-carbon monomer units for C_3H_6 homologation (*16*) were proposed.

Reactions of butene with H_2 and CO have not been investigated as thoroughly as those of ethylene or propylene. Nijs and Jacobs (*17*) observed the incorporation of butene into C_5–C_7 hydrocarbons when butene was added to synthesis gas over Ru. They report a higher extent of incorporation for 1-butene than that for methylpropene and significantly more incorporation of both olefins over RuLaY than over Ru/SiO_2 (*17*). Eidus and co-workers (*1–3*) studied the reactions of ethylene, propylene, 1-butene, 1-pentene, and 1-octene with H_2

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and CO over Co and noted that the production of hydrocarbons whose carbon number is not a multiple of that of the original olefin increases with the increasing carbon number of the reacting olefin. They propose that the primary source of single-carbon monomers for chain growth is the olefin rather than CO (*1*). Homologation of butene in the absence of CO has been observed over Co (*9*), Fe (*21*, *22*), and Ru (*18*, *23*). Kibby *et al.* (*9*) reported results of C_2H_4, C_3H_6, and 1-C_4H_8 reacting with H_2 alone over Co and found that conversions decreased in the order $C_2H_4 > C_3H_6 >$ 1-C_4H_8 but that chain growth probabilities for liquid hydrocarbons increased with the increasing carbon number of the reactant.

The objectives of this study were to investigate the effects of 1-C_4H_8 addition on the hydrogenation of CO over Ru/SiO_2 and to compare the results with those reported previously for ethylene (*15*) and propylene (*16*). Product distributions are compared for the reactions of butene with synthesis gas, the reaction of synthesis gas alone, and the reactions of butene with hydrogen. In the reactions involving both C_4H_8 and CO, the sources of carbon atoms in the products were identified by using ^{13}CO and unlabeled C_4H_8. Products were analyzed by isotope-ratio gas chromatography–mass spectrometry. The two primary issues investigated were the influence of C_4H_8 on reactions of CO to form methane, higher hydrocarbons, and oxygenates, and the participation of C_4H_8 in hydrocarbon chain growth processes. Effects of CO on reactions of butene were also examined.

EXPERIMENTAL

A 4.3% Ru/SiO_2 catalyst is used in this study. Its dispersion is 0.27 as determined by H_2 chemisorption at 373 K. Its preparation and pretreatment are discussed elsewhere (*24*). Butene (99.8%, Matheson), helium (99.999%), and carbon monoxide (88.3% ^{13}CO, 11.2% $^{13}C^{18}O$, and 0.5% ^{12}CO, Isotec) are used as received. Hydrogen is purified by passage through a Deoxo unit (Engelhard Industries) and a 5-Å molecular sieve.

Experiments are carried out at a pressure of 1 atm by introducing the reactant to the reduced catalyst (0.51 g) and allowing the reaction to continue for 15 min before product samples are taken for analysis. Details concerning the experimental procedure have been presented elsewhere (*15*). The analytical technique, which consists of a combination of capillary gas chromatography and mass spectrometry, yields both the product distribution and the ^{13}C content of each of the products. Descriptions have been given previously (*15*, *16*).

RESULTS

Reactions of H_2 and C_4H_8

Butene reacting with hydrogen over Ru produces, in addition to *n*-butane and other C_4 isomers, C_1–C_3 and C_{5+} hydrocarbons which are primarily *n*-paraffins. The distribution of products, except butenes and butanes, is shown in Fig. 1 for an equimolar feed of H_2 and 1-C_4H_8 at 493 K and 0.80 atm. Conversions of butene under these reaction conditions are 0.62 to butane, 0.34 to butene isomers, and 0.042 to other hydrocarbons. Of these other hydrocarbons, methane is the most abundant. An interesting feature of the C_{5+} product distribution is the high C_8 rate compared with the monotonically decreasing rates of C_5–C_7 hydrocarbons.

Figure 2 shows the proportions of linear olefins and paraffins and branched products in each of the C_2–C_6 fractions. Normal paraffins predominate, comprising more than 80% of each product except C_4. With decreasing H_2/C_4H_8 feed ratios, branched products become somewhat more abundant. At $H_2/C_4H_8 = 0.25$, for example, the C_6 product consists of 0.04 linear olefin, 0.61 *n*-paraffin, and 0.35 branched species. The fractional conversions of butene to butane, C_1–C_3 hydrocarbons, and C_{5+} hydrocarbons are given in Table 1. As the H_2/C_4H_8 feed ratio decreases from 1.0 to

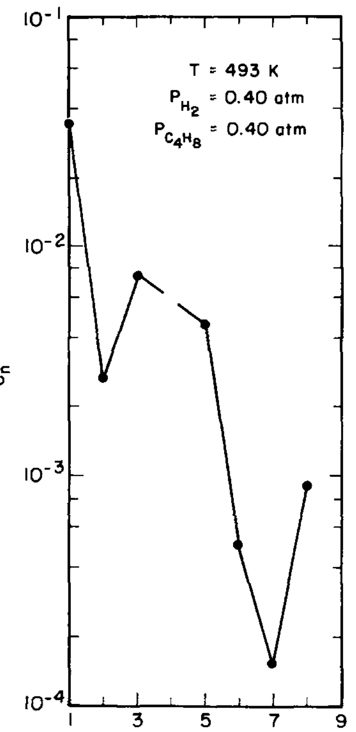


FIG. 1. Distribution of C_1 through C_8 hydrocarbons produced by reaction of H_2 and C_4H_8 at 493 K. $P_{H_2} = P_{C_4H_8} = 0.40$ atm.

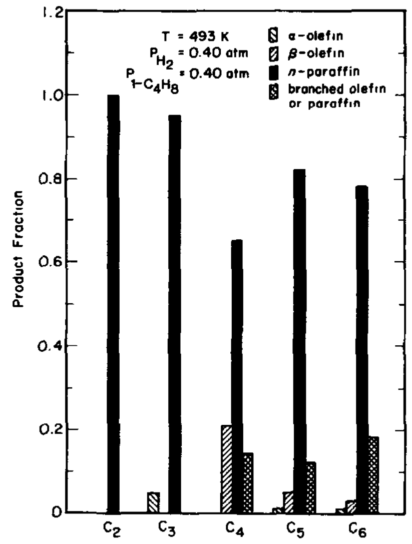


FIG. 2. Proportions of linear olefin, linear paraffin, and branched products observed in the reactions of H_2 and C_4H_8.

0.25, the conversion of butene to hydrocarbons other than C_4 decreases from 0.042 to 0.0051. It is interesting to note that, at the same time, conversion to heavier (C_{5+}) relative to lighter (C_{1-3}) products doubles.

Reaction of H_2 and CO

Figure 3 shows the hydrocarbon product distribution for the reaction of a 2 : 1 H_2 : CO feedstream under the same conditions as those used for the H_2/C_4H_8 reaction in Fig. 1. The rates of formation of C_{3+} products decrease linearly with carbon number on a lognormal scale. Under these conditions, the conversion of CO is 0.078 and the chain growth probability, α, for C_{3+} products is 0.53. The relative amounts of linear olefins and paraffins and branched products are shown in Fig. 4. The α-olefin content is low and generally decreases with increasing carbon number for C_{3+} products. The *n*-paraffin content is high in the light gases, while branched products constitute the largest fraction of the heavier products.

TABLE 1

Conversion of 1-C_4H_8 to Products in the Reaction of H_2 and C_4H_8

Feed H_2/C_4H_8	C_4H_{10}	C_4H_8 isomers	C_{1-3}	C_{5+}	Conv. to C_{5+}/ conv. to C_{1-3}
1.0	6.2×10^{-1}	3.4×10^{-1}	2.7×10^{-2}	1.5×10^{-2}	0.56
0.75	4.9×10^{-1}	2.0×10^{-1}	1.9×10^{-2}	1.2×10^{-2}	0.63
0.50	3.2×10^{-1}	1.5×10^{-1}	8.7×10^{-3}	5.9×10^{-3}	0.68
0.25	1.0×10^{-1}	1.5×10^{-1}	2.3×10^{-3}	2.8×10^{-3}	1.2

Note. Reaction conditions: feed $P_{C_4H_8} = 0.40$ atm; $T = 493$ K.

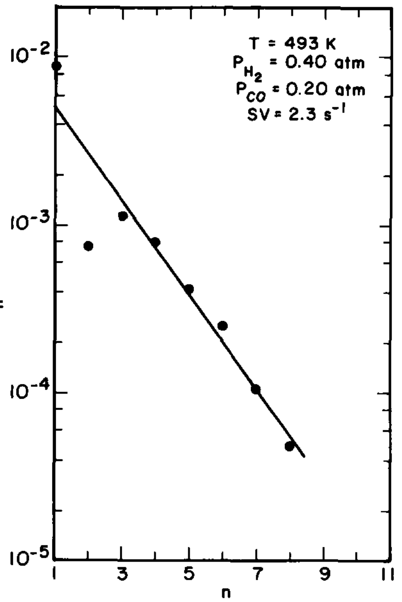


FIG. 3. Distribution of C_1 through C_8 hydrocarbons produced by reaction of H_2 and CO at 493 K. P_{H_2} = 0.40 atm; P_{CO} = 0.20 atm.

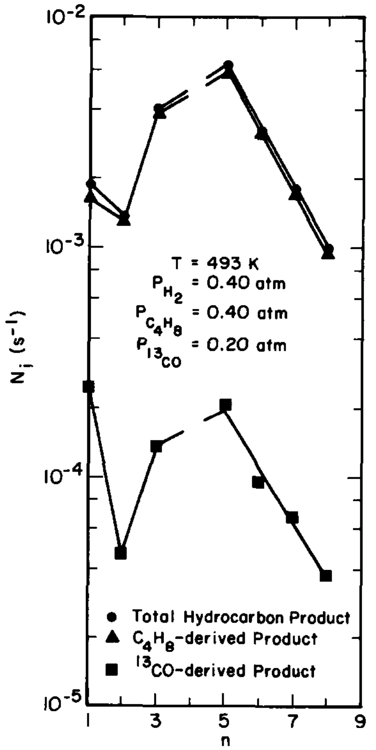


FIG. 5. Distributions of C_4H_8-derived and ^{13}CO-derived hydrocarbons produced by reaction of H_2, C_4H_8, and ^{13}CO at 493 K. P_{H_2} = $P_{C_4H_8}$ = 0.40 atm; P_{CO} = 0.20 atm.

Reactions of H_2, C_4H_8, and CO

A feed consisting of 0.40 atm H_2, 0.40 atm C_4H_8, and 0.20 atm ^{13}CO was used as a base case in the following series of experiments. Figure 5 shows the distribution of products other than oxygenates resulting from the reaction of this mixture at 493 K. The rates of C_4H_8- and ^{13}CO-derived hydrocarbons were determined from the combustion analysis of each product. It was found that 13% of the methane and 3.4% (±0.4) of the carbon atoms in C_{2+} products derive from CO. It is of interest that the fraction of CO-derived carbon is virtually independent of carbon number except in the case of methane. The conversions of butene are 0.13 to *n*-butane and 0.040 to C_{1-3} and C_{5+} hydrocarbons. The conversion of CO to hydrocarbons is 0.014, compared with 0.078 in the reaction of CO and H_2 alone.

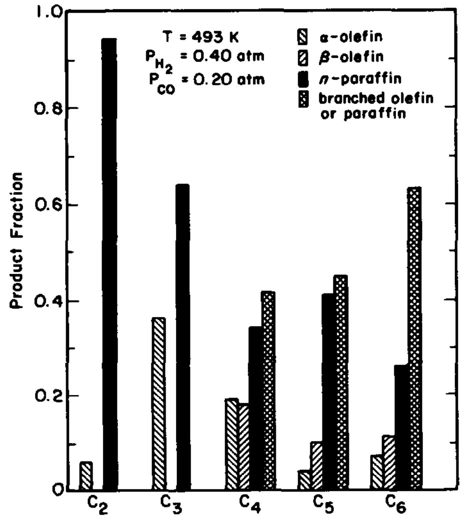


FIG. 4. Proportions of linear olefin, linear paraffin, and branched products observed in the reaction of H_2 and CO.

The oxygenates pentanol-1, pentanal, and in some cases 2-methylbutanal are produced in the reaction of H_2, C_4H_8, and CO. Each of these products contains 20% (±2) CO-derived carbon. The total rate of production of oxygenates is comparable to the synthesis rate of C_7 or C_8 hydrocarbons, although in the reaction of CO and H_2 alone the oxygenates are not produced at measurable rates. The conversions of CO and C_4H_8 to the C_5-containing oxygenates are 4.4 × 10^{-3} and 2.2 × 10^{-3}, respectively.

The source of synthesized hydrocarbons in the present reaction is primarily butene, as noted above, but the rates of production of C_4H_8-derived hydrocarbons are different in the presence of CO from those in the absence of CO. The effects of CO on the product distribution are seen by comparing Figs. 1 and 5. The presence of CO reduces the rates of formation of methane, and, to a lesser extent, ethane and propane, and it enhances the production of C_{5+} hydrocarbons. In the presence of CO, the rates of formation of C_{5+} products decrease in a lognormal fashion with carbon number, in a manner similar to that of an Anderson–Schulz–Flory distribution. The apparent chain growth probability for C_{5+} products is 0.53. In addition to the effects of CO which are apparent from Figs. 1 and 5, the hydrogenation of butene to butane is suppressed when CO is added to the feed, as shown in Table 2. In the absence of CO (Fig. 1) the conversion of C_4H_8 to C_4H_{10} is 0.13. The change in the structural composition of the product is seen by comparing Figs. 6 and 2. When CO is present, the product consists primarily of linear olefins rather than linear paraffins. The proportion which is branched increases slightly upon the addition of CO to the feed.

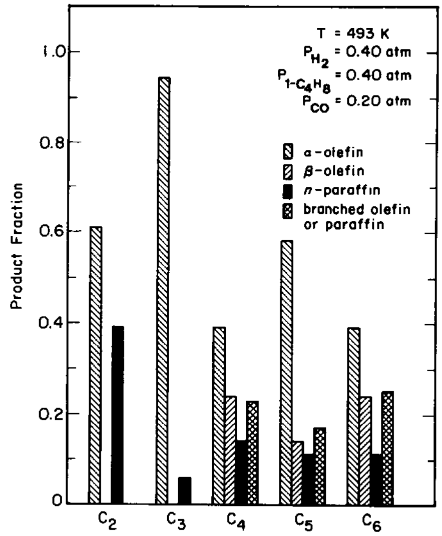


FIG. 6. Proportions of linear olefin, linear paraffin, and branched products observed in the reaction of H_2, C_4H_8, and CO.

The rates of production of C_1–C_3 and C_5–C_8 hydrocarbons are shown as functions of P_{CO} in Fig. 7. The methane rate is reduced by a factor of 9 when 0.02 atm CO is present in the H_2/C_4H_8 feed and by a factor of 18 for $P_{CO} = 0.20$ atm, compared with the reaction of H_2 and C_4H_8 alone. The rates of formation and C_2 and C_3 hydrocarbons exhibit weak negative dependences on P_{CO}. For C_{5+} products, the rates increase

TABLE 2

Effects of P_{CO} on the Conversion of C_4H_8 and CO to Products in the Reaction of H_2, C_4H_8, and CO

Feed P_{CO}(atm)	Conversion of C_4H_8 to:				Conversion of CO to:	
	C_4H_{10}	C_4H_8 isomers	$C_{1\text{-}3} + C_{5+}$	Oxygen	HC	Oxygen
0	6.2 × 10^{-1}	3.4 × 10^{-1}	4.2 × 10^{-2}	0	—	—
0.02	4.8 × 10^{-1}	5.2 × 10^{-1}	4.8 × 10^{-2}	4.4 × 10^{-4}	4.8 × 10^{-2}	8.4 × 10^{-3}
0.05	3.8 × 10^{-1}	5.7 × 10^{-1}	5.2 × 10^{-2}	1.1 × 10^{-3}	2.7 × 10^{-2}	9.1 × 10^{-3}
0.12	1.2 × 10^{-1}	4.5 × 10^{-1}	4.0 × 10^{-2}	1.8 × 10^{-3}	1.7 × 10^{-2}	6.0 × 10^{-3}
0.20	1.3 × 10^{-1}	4.4 × 10^{1}	4.0 × 10^{-2}	2.2 × 10^{-3}	1.4 × 10^{-2}	4.4 × 10^{-3}

Note. Reaction conditions: feed $P_{C_4H_8} = 0.40$ atm; feed $P_{H_2} = 0.40$ atm; $T = 493$ K.

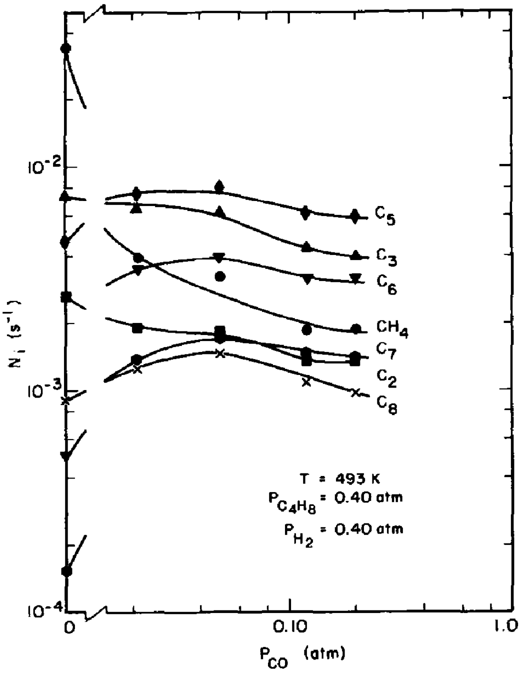


FIG. 7. Influence of P_{CO} on the rates of production of C_1 through C_8 hydrocarbons. $P_{H_2} = P_{C_4H_8} = 0.40$ atm.

by factors ranging from approximately 1.5 (for C_5 and C_8) to 9 (for C_7) when 0.02 atm CO is added to the feed, and the C_{5+} rates all pass through weak maxima as P_{CO} is increased further. The conversions of C_4H_8 and CO corresponding to this series of experiments are given in Table 2. As mentioned earlier, hydrogenation of butene is suppressed by CO, but at the highest P_{CO} studied the conversion is 0.13 to butane and 0.04 to other products.

The rates of formation of oxygenates are shown as functions of CO partial pressure in Fig. 8. Except for small quantities of the isomer 2-methylbutanal formed at high P_{CO}, no other oxygenates are produced at measurable rates. At $P_{CO} = 0.20$ atm, the conversion of CO to oxygenates is 4.4×10^{-3}, compared with 1.4×10^{-2} to hydrocarbons.

Figure 9 shows the effects of adding C_4H_8 to a H_2/CO feed, and Table 3 gives the corresponding conversions of CO and C_4H_8. Methane formation is inhibited and C_{2+} hydrocarbon production is enhanced by the presence of C_4H_8 in the feed. At a CO/C_4H_8 feed ratio of 1.0, the rate of methane formation is lower by a factor of 2 and the rate of formation C_5 hydrocarbons is higher by a factor of 16, compared with synthesis rates in the H_2/CO reaction. At the same time, the conversion of CO to all

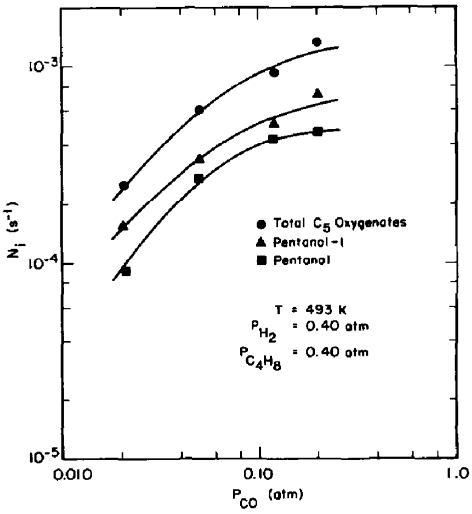


FIG. 8. Influence of P_{CO} on the rates of production of C_5 oxygenates. $P_{H_2} = P_{C_4H_8} = 0.40$ atm.

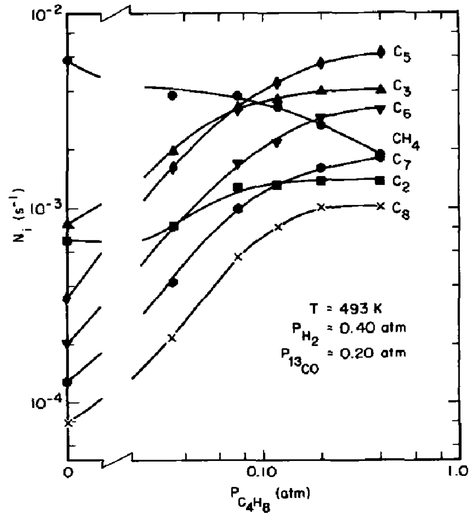


FIG. 9. Influence of $P_{C_4H_8}$ on the rates of production of C_1 through C_8 hydrocarbons. $P_{H_2} = 0.40$ atm; $P_{CO} = 0.20$ atm.

TABLE 3

Effects of $P_{C_4H_8}$ on the Conversions of C_4H_8 and CO to Products in the Reaction of H_2, C_4H_8, and CO

Feed $P_{C_4H_8}$ (atm)	Conversion of C_4H_8 to:				Conversion of CO to:	
	C_4H_{10}	C_4H_8 isomers	$C_{1-3} + C_{5+}$	Oxygen	HC	Oxygen
0	—	—	—	—	7.8×10^{-2}	—
0.028	1.9×10^{-1}	5.2×10^{-1}	2.0×10^{-1}	1.8×10^{-3}	3.4×10^{-2}	2.5×10^{-4}
0.075	2.2×10^{-1}	4.8×10^{-1}	1.2×10^{-1}	1.7×10^{-3}	2.0×10^{-2}	6.4×10^{-4}
0.12	2.0×10^{-1}	4.8×10^{-1}	8.6×10^{-2}	2.7×10^{-3}	1.9×10^{-2}	1.6×10^{-3}
0.20	1.7×10^{-1}	4.7×10^{1}	7.5×10^{-2}	3.1×10^{-3}	1.3×10^{-2}	3.1×10^{-3}
0.40	1.3×10^{-1}	4.4×10^{-1}	4.0×10^{-2}	2.2×10^{-3}	1.4×10^{-2}	4.4×10^{-3}

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

hydrocarbons is lower by a factor of 6 in the $H_2/C_4H_8/CO$ reaction than in the H_2/CO reaction. The inhibition by C_4H_8 of the H_2/CO synthesis reaction is shown in Fig. 10. For the 2 : 1 : 1 $H_2 : C_4H_8 : CO$ reactions cited above, the rate of methane synthesis from CO is lower by a factor of 16 and the rate of C_5 hydrocarbon synthesis from CO is lower by a factor of 1.6 than that in the H_2/CO reaction. The negative dependences of the production of CO-derived C_1–C_3 hydrocarbons on $P_{C_4H_8}$ are nearly parallel and are stronger than the corresponding relationships involving C_5 and C_6 hydrocarbons.

Figure 11 shows the effect of C_4H_8 partial pressure on the rates of formation of C_5 oxygenates. The linear aldehyde and normal alcohol, which constitute more than 80% of the oxygenate produced, exhibit strong positive dependences on $P_{C_4H_8}$. The rate of production of the branched aldehyde

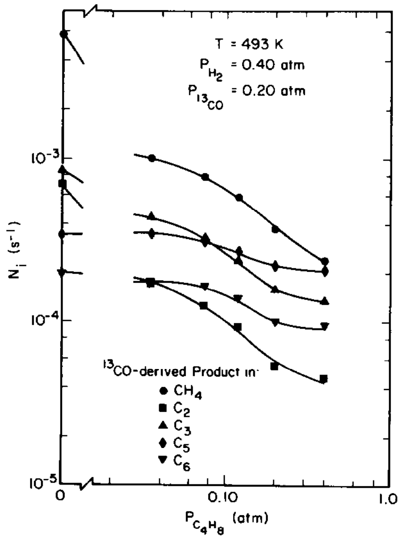


FIG. 10. Influence of $P_{C_4H_8}$ on the rates of production of ^{13}CO-derived hydrocarbons. $P_{H_2} = 0.40$ atm; $P_{CO} = 0.20$ atm.

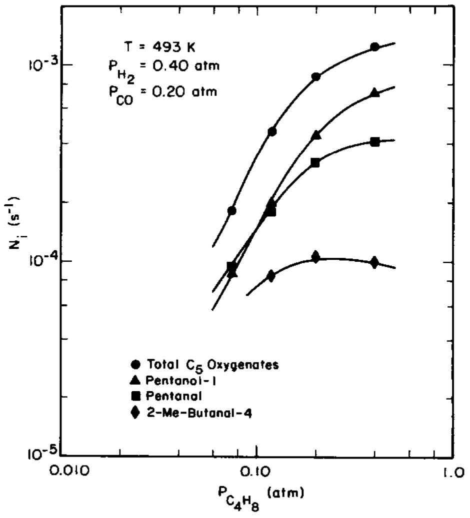


FIG. 11. Influence of $P_{C_4H_8}$ on the rates of production of C_5 oxygenates. $P_{H_2} = 0.40$ atm; $P_{CO} = 0.20$ atm.

is slow and nearly independent of butene pressure.

The distributions of C_4H_8- and ^{13}CO-derived hydrocarbon products are shown in Fig. 12 for the reaction of 0.60 atm synthesis gas and 0.028 atm butene. The methane produced contains 28% ^{13}C. For the higher hydrocarbons, the ^{13}C content ranges from 22% for C_2, C_3, and C_5, to 33% for C_8, in a monotonically increasing fashion. The conversion of butene to butane is 0.19 and to C_1–C_3 and C_{5+} hydrocarbons is 0.20, while the conversion of CO to hydrocarbons is 0.034. Conversions to oxygenates are 1.8×10^{-3} for C_4H_8 and 2.5×10^{-4} for CO.

Figure 13 shows the rates of hydrocarbon production as functions of P_{H_2}, and the conversions of C_4H_8 and CO are given in Table 4. The rate of methane formation increases rapidly with P_{H_2}, and the dependence of rate on P_{H_2} increases with increasing carbon number. As a result, a product having a high average molecular weight is favored by high H_2 pressures.

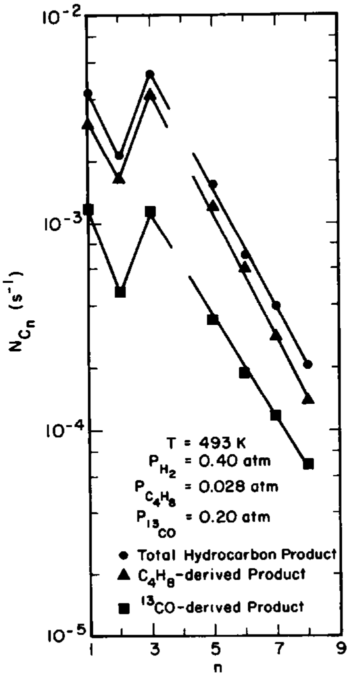


FIG. 12. Distribution of C_4H_8-derived and ^{13}CO-derived hydrocarbons. $P_{H_2} = 0.40$ atm; $P_{CO} = 0.20$ atm; $P_{C_4H_8} = 0.028$ atm.

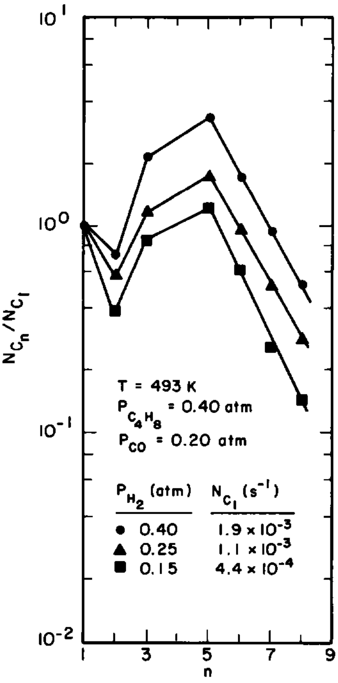


FIG. 13. Effects of H_2 partial pressure on the distribution of C_1 through C_8 hydrocarbon products. $P_{C_4H_8} = 0.40$ atm; $P_{CO} = 0.20$ atm; $T = 493$ K.

DISCUSSION

Comparison with Previous Studies

Investigations of ethylene and propylene reacting with H_2 in the presence and absence of CO have been reported previously (*15, 16*). In the absence of CO, both olefins undergo significant hydrogenation. Products of homologation and hydrogenolysis are also observed. Ethylene is six to seven times more active for homologation relative to hydrogenolysis than propylene is. Both olefins exhibit increasing conversions to products of homologation (C_{n+}) and of hydrogenolysis (C_{n-}) with an increasing H_2/olefin feed ratio. The product distributions are similar in that methane is the most abundant product other than the corresponding paraffin and in that synthesis rates decrease with carbon number in a nonmonotonic fashion. The product distributions differ in shape: for C_2H_4, products with an even number of carbon atoms are

TABLE 4

Effects of P_{H_2} on the Conversions of C_4H_8 and CO to Products in the Reaction of H_2, C_4H_8, and CO

Feed P_{H_2}(atm)	Conversion of C_4H_8 to:			Conversion of CO to:	
	C_4H_{10}	$C_{1-3} + C_{5+}$	Oxygen	HC	Oxygen
0.15	3.5×10^{-2}	4.3×10^{-3}	2.0×10^{-4}	1.2×10^{-3}	4.4×10^{-4}
0.25	6.1×10^{-2}	1.4×10^{-2}	6.4×10^{-4}	4.6×10^{-3}	1.2×10^{-3}
0.40	1.3×10^{-1}	4.0×10^{-2}	2.2×10^{-3}	1.4×10^{-2}	4.4×10^{-3}

Note. Reaction conditions: feed $P_{C_4H_8} = 0.40$ atm; feed $P_{CO} = 0.20$ atm; $T = 493$ K.

favored, while for C_3H_6, C_4, and C_9 synthesis rates are anomalously high. Chain growth schemes involving one- and two-carbon monomer units in the case of C_2H_4, and one-, two-, and three-carbon units in the case of C_3H_6 are shown to describe the observed product distributions. In the presence of CO, homologation is enhanced relative to hydrogenolysis and hydrogenation is suppressed. The ratio of the conversion to C_{n+} relative to C_{n-}hydrocarbons remains higher for C_2H_4 than for C_3H_6 by a factor of 6. Olefin addition to synthesis gas was found to suppress hydrocarbon synthesis from CO, ethylene being more effective than propylene by a factor of 3, but overall synthesis rates are higher in the olefin/H_2/CO reactions than in the CO/H_2 reaction as a result of olefin homologation. Similar product distributions were observed in the two olefin/H_2/CO reactions.

Butene reacting with H_2 in the absence of CO undergoes reactions similar to those observed for ethylene and propylene. Hydrogenation or, in the case of butene, hydrogenation and isomerization account for more than 95% of the olefin converted to products. Total conversions to other hydrocarbons are similar for the three olefins. The olefin reactions differ, however, in the distributions of the C_{n-} and C_{n+} products. Butene is five times lower than ethylene and slightly higher than propylene in its selectivity to homologation relative to hydrogenolysis. The ratio of conversions to C_{n+} relative to C_{n-} products decreases with an increasing H_2/olefin feed ratio in a similar manner for all three olefins. In terms of the C_{n-} and C_{n+} product distributions, butene is distinctive in that it produces C_3, C_5, and C_8 hydrocarbons at anomalously high rates, in contrast to the distributions discussed earlier for the C_2H_4/H_2 and C_3H_6/H_2 reactions. For all three olefin/H_2 reactions, methane is the most abundant product. For an olefin/H_2 feed ratio of one, butene produces almost entirely *n*-paraffins, while C_3H_6 produces both *n*-paraffins and branched species and C_2H_4 yields primarily olefins and branched species.

Homologation of butene in the absence of CO has been observed by Huang and Ekerdt (*23*) over Ru/SiO_2 and by Kibby (*9*) *et al.* over Co catalysts. The normalized product distribution for C_1–C_6 hydrocarbons reported by Huang and Ekerdt (*23*) is remarkably similar to that reported here, with the exception of the C_2 product, which was formed at a relative rate nearly an order of magnitude higher than that in the present study. It is interesting that the strong similarity exists, however, given the higher H_2/C_4H_8 feed ratio of 11 and lower temperature of 423 K that were used. The authors suggest that homologation occurs via methylene addition to surface alkenes (*23*). The product distribution observed by Kibby *et al.* (*9*) for the H_2/C_4H_8 reaction is quite similar to that observed for the H_2/C_4H_8/CO reaction in the present study. That is, the synthesis rates of C_{1-3} hydrocarbons are lower than that of C_5, which is the most abundant non-C_4 product, and the rates of production of C_{5+} hydrocarbons decrease in a lognormal fashion with carbon number. Such similarities also exist between the H_2/C_2H_4 and the H_2/C_3H_6 reactions of Kibby *et al.* (*9*) and the $H_2/C_2H_4/CO$ and $H_2/C_3H_6/CO$ reactions, respectively, of our previous studies (*15, 16*). Kibby *et al.* (*9*) propose no scheme by which homologation occurs but suggest that an O_2 impurity in the olefin feedstream might be responsible for initiating the reaction. This work and our previous studies (*15, 16*), as well as other investigations of olefin homologation (*1, 10, 18–23*), clearly indicate that the reaction does not require the presence of O_2 for initiation. An impurity of CO in the feedstream, however, might explain the strong similarity between the olefin homologation reaction observed by Kibby *et al.* (*9*) and that of the present work.

Butene reacting with H_2 in the presence of CO exhibits selectivities to homologation relative to hydrogenolysis which are about 3 times lower than those of C_3H_6 and 15 times lower than those of C_2H_4 (*15, 16*). However, the distribution of C_{n+} products is the same for the three reactions, i.e., a lognormal relationship between rate and carbon number with nearly identical values of the apparent chain growth probability. The suppression by CO of olefin hydrogenation is less effective for butene than for ethylene by a factor of 3 and is about equally effective for butene and propylene. With the increasing pressure of CO, the synthesis rates of C_{n+} hydrocarbons exhibit weak maxima in the case of butene homologation, while they exhibit stronger maxima for C_3H_6 and level off at high values for C_2H_4. The addition of C_4H_8 or C_3H_6 to synthesis gas suppresses hydrocarbon synthesis from CO with equal effectiveness (*16*). Oxygenates, comprising the alcohol $C_{n+1}H_{2n+3}OH$ and the aldehyde $C_{n+1}H_{2n+2}O$, are produced in the three $C_nH_{2n}/H_2/CO$ reactions. The rate of oxygenate production in the C_4H_8 reaction is similar to that in the C_3H_6 reaction and about three times lower than that in the C_2H_4 reaction (*15, 16*). The incorporation of C_4H_8 into C_5–C_7 products of the CO/H_2 reaction was observed by Nijs and Jacobs (*17*) over Ru. From changes in the amounts of isomer present in the products, the authors conclude that chain growth occurs primarily by "end-to-end attachment" of methylene to surface alkene (*17*). They also speculate that an alcohol intermediate is formed from the added alkene and water prior to incorporation (*17*).

Reactions of H_2 and C_4H_8

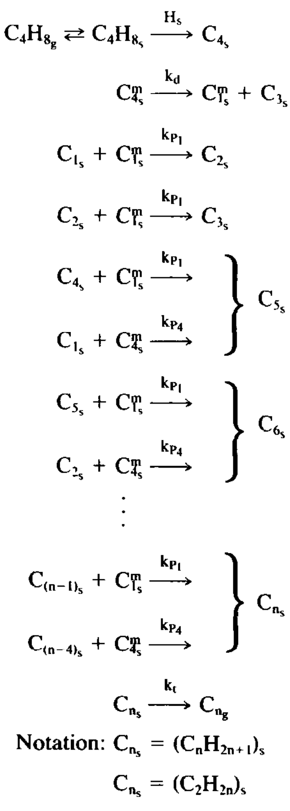
The data of Table 1 show that butene, reacting with H_2 in the absence of CO, undergoes hydrogenation, isomerization, hydrogenolysis, and homologation. Hydrogenation and isomerization dominate the reactions. The rates of homologation and hydrogenolysis are approximately equal at the lowest H_2/C_4H_8 feed ratio. As the H_2/C_4H_8 feed ratio increases, the rate of hydrogenolysis increases more rapidly than the rate of homologation.

Hydrogenolysis, hydrogenation, and isomerization of butene can be described by the following scheme:

$$\begin{tikzcd}
C_4H_{8_g} \arrow[r, shift left] & C_4H_{8_s} \arrow[l, shift left] \arrow[r, "H_s"] \arrow[d] & C_4H_{9_s} \arrow[r, "H_s"] \arrow[d, shift right, "xH_s"'] & C_4H_{10_g} \\
& \begin{matrix} C_4H_{8_g} \\ \text{isomers} \end{matrix} & C_4H_{(9-x)_s} + xH_2 \arrow[u, shift right] \arrow[d] & \\
& & CH_y \arrow[r, "H_s"] & CH_{4_g} \\
& & + & \\
& & C_3H_2 \arrow[r, "H_s"] & C_3H_{8_g}
\end{tikzcd}$$

Butene adsorbs to form either a π-bonded or a di-σ-bonded species. Isomerization occurs via a double-bond shift or surface rearrangement, followed by desorption. Addition of H_s produces a butyl species which may undergo either further hydrogenation to form butane or loss of H_s and subsequent degradation. Dehydrogenation of a surface alkyl followed by C–C bond scission has been proposed by Sinfelt (*25*) for C_2H_6 hydrogenolysis. The formation from the C_4 surface species of CH_y and C_3H_z follow from the work of Osterloh *et* *al.* (*26*), who propose that hydrogenolysis of higher alkenes occurs by the stepwise loss of methylene from the surface alkyl to form the next lower homologous surface alkyl. According to the authors, the stepwise deinsertion mechanism is consistent with the product distribution observed in the hydrogenolysis of 1-octene over Ru (*26*). In the scheme above, the C_3H_z species is not permitted to undergo further degradation. Instead, C_3H_z and CH_y may undergo hydrogenation to form propane and methane, respectively, or they may participate in chain growth processes via homologation.

A series of reactions describing butene homologation is presented in Scheme I. Adsorbed butene is assumed to undergo C–C bond scission to form one- and three-carbon units designated C_{1_s} and C_{3_s}, as discussed above. The monomer units for the chain growth process are assumed to be one- and four-carbon units, designated $C_{1_s}^{m}$ and $C_{4_s}^{m}$, which may be viewed as CH_{2_s} and $C_4H_{8_s}$. Chain growth is initiated by both C_{1_s} and C_{4_s} species. These chain initiators may be the alkyl groups CH_{3_s} and $C_4H_{9_s}$, respectively. Propagation of chain growth occurs by the addition of a monomer unit, first to a chain initiator and then to a hydrocarbon chain, C_{n_s}. Chain growth is terminated by either reductive elimination to form a paraffin or β-hydride abstraction to form the α-olefin.



$$C_4H_{8_g} \rightleftarrows C_4H_{8_s} \xrightarrow{H_s} C_{4_s}$$

$$C_{4_s}^{m} \xrightarrow{k_d} C_{1_s}^{m} + C_{3_s}$$

$$C_{1_s} + C_{1_s}^{m} \xrightarrow{k_{p_1}} C_{2_s}$$

$$C_{2_s} + C_{1_s}^{m} \xrightarrow{k_{p_1}} C_{3_s}$$

$$\left.\begin{array}{l} C_{4_s} + C_{1_s}^{m} \xrightarrow{k_{p_1}} \\ C_{1_s} + C_{4_s}^{m} \xrightarrow{k_{p_4}} \end{array}\right\} C_{5_s}$$

$$\left.\begin{array}{l} C_{5_s} + C_{1_s}^{m} \xrightarrow{k_{p_1}} \\ C_{2_s} + C_{4_s}^{m} \xrightarrow{k_{p_4}} \end{array}\right\} C_{6_s}$$

$$\vdots$$

$$\left.\begin{array}{l} C_{(n-1)_s} + C_{1_s}^{m} \xrightarrow{k_{p_1}} \\ C_{(n-4)_s} + C_{4_s}^{m} \xrightarrow{k_{p_4}} \end{array}\right\} C_{n_s}$$

$$C_{n_s} \xrightarrow{k_t} C_{n_g}$$

Notation: $C_{n_s} = (C_nH_{2n+1})_s$

$C_{n_s} = (C_2H_{2n})_s$

SCHEME I

A relationship between relative rate and carbon number can be developed using the scheme presented above. It is assumed that the surface coverages of the chain initiators, designated θ_1 and θ_4, and of the monomer units, designated θ_1^{m} and θ_4^{m}, are constant and independent. Specific rates of propagation and of termination are assumed to be independent of chain length. The rate of formation of a hydrocarbon containing n carbon atoms is given by

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

where k_t is the rate coefficient for chain termination and θ_n is the surface coverage by chains containing n carbon atoms. To develop relationships between rates and surface coverages by monomer units, the following steady-state balances are written for C_2, C_3, and C_{5+} surface species, respectively:

$$0 = k_{p_1}\theta_1^{m}\theta_1 - k_{p_1}\theta_1^{m}\theta_2 - k_{p_4}\theta_4^{m}\theta_2 - k_t\theta_2 \qquad [2]$$

$$0 = k_d\theta_4^{m} + k_{p_1}\theta_1^{m}\theta_2 - k_{p_1}\theta_1^{m}\theta_3 - k_{p_4}\theta_4^{m}\theta_3 - k_t\theta_3 \qquad [3]$$

$$0 = k_{p_1}\theta_1^{m}\theta_{n-1} + k_{p_4}\theta_4^{m}\theta_{n-4} - k_{p_1}\theta_1^{m}\theta_n - k_{p_4}\theta_4^{m}\theta_n - k_t\theta_n \quad (n \geq 5). \qquad [4]$$

In these equations, k_{p_1} and k_{p_4} are the rate coefficients for chain propagation via $C_{1_s}^{m}$ and $C_{4_s}^{m}$, and k_d is the rate coefficient for the dissociation of $C_{4_s}^{m}$ to form $C_{1_s}^{m}$ and C_{3_s}. Equations [2]–[4] can be rewritten as

$$0 = \theta_2 - \alpha_1\theta_1 \qquad [5]$$

$$0 = \theta_3 - \alpha_1\theta_2 - \eta\alpha_4 \qquad [6]$$

$$0 = \theta_n - \alpha_1\theta_{n-1} - \alpha_4\theta_{n-4} \quad (n \geq 5), \qquad [7]$$

where α_1, α_4, and η are defined as

$$\alpha_1 = k_{p_1}\theta_{1_s}^{m}/(k_{p_1}\theta_{1_s}^{m} + k_{p_4}\theta_{4_s}^{m} + k_t) \qquad [8]$$

$$\alpha_4 = k_{p_4}\theta_{4_s}^{m}/(k_{p_1}\theta_{1_s}^{m} + k_{p_4}\theta_{4_s}^{m} + k_t) \qquad [9]$$

$$\eta = k_d/k_{p_4}. \qquad [10]$$

The parameters α_1 and α_4 represent probabilities of chain growth via the monomers $C_{1_s}^{m}$ and $C_{4_s}^{m}$, respectively, and η represents the rate at which $C_{4_s}^{m}$ undergoes dissociation relative to its rate of chain propagation.

The carbon number distribution of products can be calculated by combining Eq. [1] with Eqs. [5]–[7]. If the rates of formation of C_{2+} hydrocarbons are normalized to the methane rate, then the model parameters are α_1, α_4, η, and the ratio of surface coverages by chain initiators θ_4/θ_1. It is noted that an Anderson–Schulz–Flory distribution results for values of θ_4/θ_1, α_4/α_1, and $\eta\theta_4$ approaching zero. If α_1 dominates α_4 but θ_4/θ_1 is high, then lognormal decreases in rate with carbon number are calculated for the C_{1-3} and C_{5+} portions of the curve. On the other hand, if α_4 dominates α_1, then the calculated rates of C_5 and C_8 production are generally high and, if the value of $\eta\alpha_4$ is also significant, high C_3 and C_7 rates are calculated.

A fit of Eqs. [1] and [5]–[7] to the data of Fig. 1 is presented in Fig. 14. A good agreement between theory and experiment is obtained using the parameter values shown. The high value of α_1/α_4 suggests that propagation of chain growth by $C_{1_s}^{m}$ occurs more rapidly than chain propagation by $C_{4_s}^{m}$. However, chain growth is initiated more frequently by C_{4_s} than by C_{1_s} species, as reflected in the high value of θ_4/θ_1. The magnitude of the parameter η implies that $C_{4_s}^{m}$ dissociates to form $C_{1_s}^{m}$ and C_{3_s} at a rate comparable to its rate of chain propagation.

Reactions of H_2, C_4H_8, and CO

The strong influence of CO on reactions of C_4H_8 and H_2 is seen in Figs. 1 and 5 and Table 2. Hydrogenolysis proceeds less rapidly and homologation more rapidly in the presence of CO than in its absence. However, the sum of the two rates is affected very little by CO. These two observations, taken together with the schemes for hydrogenolysis and homologation presented earlier, imply that CO has little effect on the formation of $C_4H_{(9-x)}$ but it has a significant effect on the reactions of CH_y and other surface species. For these species, competition exists between chain propagation and chain termination. It is likely that suppression by CO of reductive elimination increases the probability that a surface hydrocarbon will undergo chain growth, thus increasing the average molecular weight of the product. This effect is apparently less significant for butene than for either ethylene or propylene (*15, 16*).

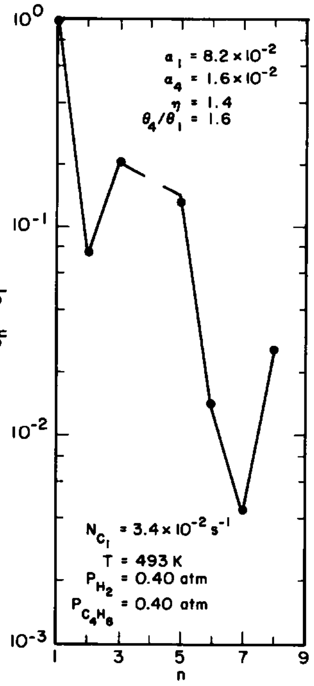


FIG. 14. Comparison of calculated and experimental product dsitributions for the reaction of H_2 and C_4H_8.

It is difficult to infer from the present results the influence of CO on the production of methylene from adsorbed butene. Although the rate of methane formation falls dramatically with the addition of CO, it is unlikely that methylene formation is reduced. In fact, one might speculate that the relative rate of chain propagation via (C_4H_8-derived) $C_{1_s}^{m}$ is higher when CO is present. This idea follows from the observation that the C_{5+} product distribution is consistent with a high value of α_1/α_4 in the butene homologation scheme discussed earlier. However, dominance of methylene addition in the $H_2/C_4H_8/CO$ reaction must be considered speculation since a unique set of chain growth parameters does not describe the observed results.

Butene added to the synthesis gas feed both affects the reactions of CO and undergoes reaction itself. These results are apparent in Table 3 and Figs. 9–11. As the partial pressure of butene in the feed increases, the contribution of CO to chain growth is suppressed. It is likely that the rapid reaction of adsorbed CO and C_4H_8 to form C_5 oxygenates reduces the rate of CO dissociation to form monomer units for hydrocarbon chain growth. While the rate of hydrocarbon synthesis from CO decreases with increasing $P_{C_4H_8}$, the rate of hydrocarbon synthesis from C_4H_8 increases. It is concluded from this result that C_4H_8 is a more efficient source of monomer for chain growth than CO is. In terms of higher hydrocarbon synthesis, the efficiency of monomer production and subsequent chain growth increases in the order $CO < C_4H_8 < C_3H_6 < C_2H_4$ (*15, 16*). At high butene pressures, the fraction of CO-derived carbon atoms in the C_{2+} product does not vary with carbon number. This result suggests that similar reaction pathways for chain growth are taken by CO- and C_4H_8-derived monomer units. At low butene pressures (see Fig. 12), it was observed that the fraction of CO-derived carbon atoms increases with carbon number for C_{5+} products. It is possible that CO-derived $C_{1_s}^{m}$ undergoes chain growth more rapidly relative to C_4H_8-derived $C_{1_s}^{m}$ than at higher $P_{C_4H_8}$ as a result of low surface coverage by C_4H_8-derived $C_{1_s}^{m}$. In this case, butene may act primarily to initiate chain growth via C_{4_s} and to form lighter products by degradation of C_{4_s}. The increase in hydrocarbon synthesis rates with increasing butene pressure is probably the result of higher surface coverages by butene and thus by its chain initiators and monomer units. It is observed that these rates level off at high $P_{C_4H_8}$. Under these conditions, the coverage by C_4H_{8s} may be high enough to inhibit hydrogen adsorption, thereby inhibiting homologation and hydrogenolysis.

CONCLUSIONS

Butene reacting with H_2 over Ru undergoes hydrogenation, isomerization, hydrogenolysis, and homologation. Degradation of adsorbed C_4H_8 produces C_{1_s} species, which are taken to be precursors of CH_4 and of higher hydrocarbons through homologation. A chain growth mechanism involving C_1 and C_4 monomer units describes the observed product distribution.

The addition of C_4H_8 to synthesis gas strongly influences the reactions of CO. Hydrocarbon formation from CO is suppressed and hydroformylation to form pentanal and pentanol is enhanced. Compared with ligher olefins, C_4H_8 is equally as effective as C_3H_6 and three times less effective than C_2H_4 in reducing hydrocarbon formation from CO. The presence of CO suppresses hydrogenation of C_4H_8 to form C_4H_{10} and enhances homologation relative to hydrogenolysis. At high partial pressures of C_4H_8 and CO, rates of hydrocarbon production are higher than those observed for either the reaction of synthesis gas alone or the reaction of C_4H_8 with H_2. The product distribution in this case is similar to that observed in the $C_3H_6/CO/H_2$ and $C_2H_4/CO/H_2$ reactions. Similar reaction pathways, which might include significant participation of C_1 monomers in chain growth, may be involved in the three reactions.

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