JOURNAL OF CATALYSIS 78, 165–181 (1982)

Hydrogenation of Carbon Monoxide over Ruthenium: Detection of Surface Species by Reactive Scavenging

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Received February 5, 1982; revised June 17, 1982

Hydrocarbon species produced on the surface of a Ru/SiO_2 catalyst during CO hydrogenation have been detected by analysis of the products formed when these species react with cyclohexene, benzene, cyclopentene, or *cis*-2-butene, added in low concentration to the synthesis gas mixture. The presence of adsorbed methylene groups is strongly supported by the formation of norcarane and 1,2-dimethylcyclopropane from cyclohexene and *cis*-2-butene, respectively, and by the formation of ethylcyclopropane from 1-butene produced by the isomerization of *cis*-2-butene. Methyl and higher-molecular-weight alkyl groups are detected through the observation of alkyl derivatives of cyclohexene and benzene when cyclohexene or benzene is used as the scavenger. The addition of a scavenger to the synthesis gas is found to decrease the formation of higher-molecular-weight hydrocarbons produced by CO hydrogenation. This suggests that the species removed by the scavenger are intermediates in the process of hydrocarbon chain growth.

INTRODUCTION

A number of recent investigations (*1–14*) concerned with CO hydrogenation over Group VIII metals have suggested that CH_x (x = 1–3) species present on the catalyst surface play a vital role in the formation of methane and higher-molecular-weight hydrocarbons. These species are assumed to be formed via the dissociation of adsorbed CO followed by stepwise hydrogenation of the atomic carbon thus released. Biloen *et al.* (*3–5*) and Bell and co-workers (*6–10*) have proposed that CH_3 groups can act as precursors to methane as well as chain initiators for the formation of higher-molecular-weight hydrocarbons. Chain growth is envisioned to begin with the insertion of a methylene group into the metal–carbon bond of a methyl group. Further addition of methylene groups propagates the chain growth. Termination of the alkyl chains takes place either by elimination of a β-hydrogen atom, to form an α-olefin, or by hydrogen addition to the α-carbon of the chain, to form a normal alkane.

Kellner and Bell (*9, 10*) have demonstrated that the proposed mechanism can be used to interpret the kinetics observed for the synthesis of methane, and C_{2+} olefins and paraffins, over Ru/SiO_2 and Ru/Al_2O_3 catalysts, as well as the nature of the H_2/D_2 isotope effects observed over these catalysts. Further evidence supporting the mechanism has come from the recent work of Brady and Pettit (*12, 13*). These authors have shown that a spectrum of hydrocarbon products, resembling that observed during CO hydrogenation, can be obtained upon passage of diazomethane and hydrogen over supported Ni, Fe, Co, and Ru catalysts. To explain these results it was proposed that diazomethane decomposes to produce surface methylene groups, which then add hydrogen to form methyl groups. The formation of methane and C_{2+} hydrocarbons was taken to occur as described above.

Several spectroscopic studies have been undertaken in an attempt to detect the intermediates involved in hydrocarbon synthesis. Blyholder and Neff (*15*) have reported infrared evidence for CH and OH bands on the surface of an Fe/SiO_2 catalyst

0021-9517/82/110165-17$02.00/0

heated in a mixture of CO and H_2. These bands were ascribed to M=C(OH)R and M—CH_2R species; however, the evidence for the first of these structures has been questioned by King (*16*). Extensive efforts have been carried out with Ru/SiO_2 and Ru/Al_2O_3 catalysts by Dalla Betta and Shelef (*17*), King (*16*), Ekerdt and Bell (*6*), Kellner and Bell (*18*), and Yamasaki *et al.* (*14*). While each of these investigations produced strong evidence for the presence of hydrocarbon moieties, differing conclusions were reached regarding the location of the hydrocarbon species and their role in the synthesis process. Dala Betta and Shelef (*17*) and Kellner and Bell (*18*) concluded that the species observed are due to the accumulation of reaction products on the catalyst support. Ekerdt and Bell (*6*) and King (*16*) proposed that the hydrocarbons are attached to the surface of Ru but indicated that the species are not likely to be reaction intermediates. Yamasaki *et al.* (*14*), on the other hand, has recently suggested that the observed species are attached to the metal and represent a reservoir of alkyl groups which undergo release of CH_2 units during hydrogenation of the catalyst, following a reaction.

As an alternative to spectroscopic techniques for detecting the intermediates involved in CO hydrogenation, one might consider addition to the synthesis gas of a reagent which would react with one or more of the intermediates to produce distinctive products. The earliest demonstrations of this approach were carried out by Eidus (*19*). The addition of benzene to the synthesis gas passed over either a Co–Ni or Fe–Cu catalyst resulted in the formation of toluene. Since toluene was not observed in the absence of benzene addition, it was concluded that this product was formed via a hydrocondensation reaction of benzene with surface CH_2 or CH_3 groups. Subsequent studies (*20, 21*) conducted with a Co–ThO_2–kieselguhr catalyst led to the observation of a small amount of cycloheptatriene, in addition to toluene, strongly suggesting the presence of CH_2 species over this catalyst. Scavenging experiments were also conducted over this catalyst using cyclohexene (*19*), cyclopentene (*22, 23*), 1-pentene (*24*), 2-pentene (*25*), 1,3-butadiene (*26*), and 1,3-cyclopentadiene (*26*). In each case, derivatives of the scavenger resulting from methylene or methyl hydrocondensation with the scavenger were observed.

It is significant to note that the mechanistic interpretations given by Eidus *et al.* (*19–26*) to explain the results of their experiments were not supported by any precedents for similar chemistry observed with organometallic complexes, since at the time of publication such evidence was unavailable. Only relatively recently have advances in synthetic organometallic chemistry and product identification led to unambiguous examples for alkylidene and alkyl species as ligands associated with both mono- and polynuclear metal complexes (*27, 28*). The reaction of such ligands with low-molecular-weight olefins to produce distinctive products has now been observed in a significant number of instances (*29–37*). In most cases, alkylidene ligands react with an olefin or other alkene to form an alkylcyclopropane. This corresponds to the addition of the carbene across the double bond of the olefin or alkene. The formation of higher-molecular-weight olefins via transfer of an alkylidene group has also been observed (*32–35, 37*). Finally, Evit and Bergman (*37*) have reported the reaction of $(Cp)(Ph_3P)Co(CD_3)_2$ with C_2H_4 to produce $CD_3CH=CH_2$ and CD_3H, thereby demonstrating the scavenging of an alkyl group by an olefin.

In most of the experiments conducted by Eidus *et al.* (*19–26*), the scavenging reagent constituted 10 to 50% of the total gas feed. While not demonstrated in those studies, it could reasonably be expected that such massive additions of hydrocarbon would substantially perturb the surface concentrations of the intermediates involved in hydrocarbon synthesis, and hence seriously alter the kinetics of the synthesis process.

To avoid such perturbations, it would be preferable to use much smaller concentrations of the added reagent (i.e., $\leq 2\%$). Experiments carried out under such circumstances have been reported by Ekerdt and Bell (*7*). The addition of 1.8% ethylene to the synthesis gas feed resulted in a 3.6-fold increase in the production of propylene. When cyclohexene was used as the scavenger ($\sim 2\%$), 1-methylcyclohexene, 3-methylcyclohexene, ethylcyclohexene, and methyl-, ethyl-, propyl-, and butylcyclohexane were formed. Moreover, the addition of cyclohexene was found to suppress the extent of hydrocarbon chain growth during CO hydrogenation. While the exact nature of the species present on the catalyst surface could not be determined from these results, strong evidence was obtained for the presence of both alkylidene and alkyl groups. The present work was undertaken with three objectives in mind: to determine the effects of scavenger composition on the reactivity of the scavenger and the nature of the products obtained; to study the effects of reaction conditions on the conversion of each scavenger to products; and to evaluate the effects of scavenger addition on the distribution of hydrocarbons produced via CO hydrogenation. All of these studies were carried out with a Ru/SiO_2 catalyst.

EXPERIMENTAL

A 4.3% Ru/SiO_2 catalyst was used for the present investigations. Details concerning the preparation and initial reduction of this catalyst have been presented previously (*6*). The dispersion of ruthenium was determined to be 0.22 by CO chemisorption and is in reasonably good agreement with the value of 0.17 determined from transmission electron micrographs.

Carbon monoxide (99.8%) was passed through a dry-ice/acetone trap to remove iron carbonyl and a trap packed with 5-Å molecular sieve to remove water. Hydrogen (99.999%) was purified of traces of oxygen by passage through a Deoxo unit (Engelhard Industries, Inc.) and then passed through a trap packed with 5-Å molecular sieve to remove water. Helium (99.998%) was passed through an Oxy-sorb trap (Alltech Associates) and a trap filled with 5-Å molecular sieve to remove traces of oxygen and water, respectively.

The following compounds were used as scavengers: cyclohexene (MCB—99.5% purity); benzene (MCB—99.8% purity); cyclopentene (Aldrich—99.6% purity); *cis*-2-butene (Union Carbide—99.3% purity). Each of these compounds was used as received without further purification.

The apparatus used for these studies is similar to that described by Ekerdt and Bell (*6, 7*). The central part of this apparatus is a glass microreactor, containing 0.210 g of the catalyst (+120, −80 mesh), heated in a fluidized sand bath and supplied with reactants from a flow manifold. The scavenging reagent was admitted to the reactor by passing the synthesis gas through a gas saturation bottle containing a small amount of the scavenging reagent. The partial pressure of the scavenger in the reactor feed was controlled by the temperature at which the gas saturation bottle was maintained.

Products from the reactor were analyzed by gas chromatography. Analyses for C_1 through C_5 hydrocarbons were conducted off-line using a chromatograph containing a pair of 0.125-cm-o.d. × 0.91-m stainless-steel columns packed with Chromosorb 106 and equipped with flame ionization detectors. Typically, a 2.5-cm^3 sample of reaction products was injected into this chromatograph from a gas-tight syringe equipped with a Chaney adapter. Products containing more than four carbon atoms were analyzed on-line using a chromatograph (equipped with a flame ionization detector), containing a 0.23-mm-i.d. × 50-m fused-silica capillary column coated internally with SE-54. A variation on the Grob injection technique (*38*) was employed to introduce the gas sample into this chromatograph.

The peaks appearing in the chromatograms obtained from the capillary column were identified with gas chromatography/mass spectrometry using a Finnigan model 4023B gas chromatograph/mass spectrometer (GC/MS). The quality of the identification for each chromatographic peak was characterized by three parameters: the purity, the forward fit, and the reverse fit. Each of these parameters ranges from zero (no fit) to 1000 (perfect fit). The purity represents the extent to which the sample mass spectrum contains peaks which do not appear in the library spectrum of the assigned compound. The forward fit provides a measure of the extent to which the sample peak positions and intensities agree with those of the library spectrum. The reverse fit represents the extent to which the peak positions and intensities of the library spectrum coincide with those of the mass spectrum of the sample. The most useful of these parameters is the forward fit, since it is least dependent upon spectral noise and instrument operating conditions.

Assignment of a chromatographic peak was initiated by consideration of the ten best matches between the mass spectrum of the unknown peak and spectra in the library of the GC/MS. The library compound having the highest forward fit above 750 was then selected as the most likely match to the sample peak. If several library compounds had forward fit values agreeing to within 10%, identification was based upon the values of the reverse fit and purity. To confirm the identification thus obtained, a chromatogram was taken of a calibration mixture made up of *n*-hexane or *n*-butane and the pure component selected by the GC/MS. The relative retention index of the pure component (defined as the ratio of the retention time of the pure component to that of either *n*-hexane or *n*-butane) was then compared to that of the peak under consideration in the chromatogram of the reaction products. If the ratio of the relative retention indices was within 2% of unity, then the identification proposed by the GC/MS was taken to be confirmed.

Prior to each experiment, the catalyst was reduced in pure hydrogen at 498 K for 1 hr. The synthesis gas was then substituted for the flow of hydrogen and reaction was allowed to proceed for 10 min prior to taking a sample for product analysis. For those experiments in which a scavenger was introduced, the reagent was added to the feed stream after the reaction had proceeded for 9 min. After three experiments were completed, the catalyst was reduced at 573 K for 8 hr. This procedure was found to restore the catalyst activity to within 4% of the reference activity.

RESULTS AND DISCUSSION

Identification of Synthesis Products

Prior to introducing any of the scavenging reagents, experiments were conducted with CO and H_2 alone to establish the composition of the products formed via CO hydrogenation. Figure 1 illustrates a typical capillary gas chromatogram. The identity of each of the numbered peaks appearing in Fig. 1 was determined using the GC/MS and is listed in Table 1. With the exception of peaks 8, 9, and 15 all of the products are either olefins or paraffins, and both linear and branched hydrocarbons are observed.

Scavenging by Cyclohexene

Chromatograms a and b in Fig. 2 characterize the C_5 through C_8 products observed in the absence and presence of cyclohexene in the feed, and chromatogram c characterizes a calibration mixture consisting of pure components. Comparison of chromatograms a and b indicates that the addition of cyclohexene produces five new peaks which are not present in the absence of the scavenger. The identities of these peaks were established from GC/MS analyses and comparisons of the relative retention indices for each peak with those of known compounds. Table 2 indicates that the five peaks can be assigned to cyclohexane, cyclohexene, methylcyclohexane, methylcyclohexene, and norcarane. The GC/MS

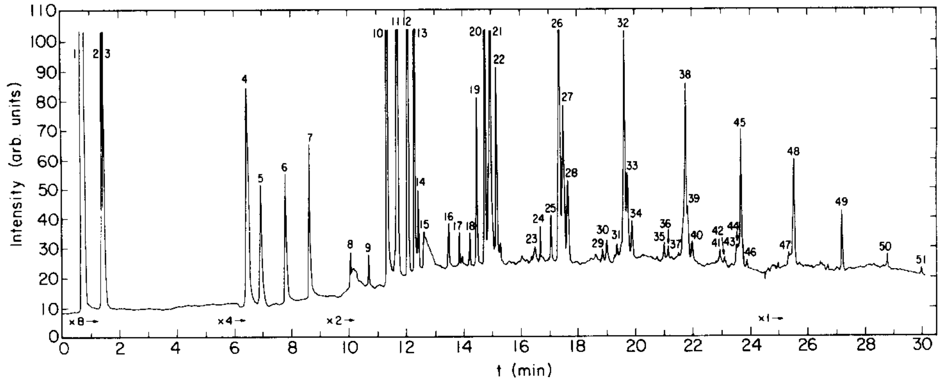

FIG. 1. Chromatogram of reaction products: $T = 498$ K; $p = 1$ atm; $H_2/CO = 3$; $Q = 122$ STP cm^3/min.

TABLE 1

Identity of the Numbered Peaks Appearing in Fig. 1

Peak number	Compound	Peak number	Compound
1	Methane	31	1-Octene
2	Ethylene, ethane	32	*n*-Octane
3	Propylene, propane	33	2-Methyl-1-heptene
4	1-Butene	34	2-Octene
5	*n*-Butane	35	Dimethylheptenes[a]
6	2-Methylpropylene	36	Methyloctanes[a]
7	2-Butene	37	1-Nonene
8	Methanol	38	*n*-Nonane
9	Acetaldehyde	39	2-Methyl-1-octene
10	1-Pentene	40	2-Nonene
11	*n*-Pentane	41	Dimethyloctenes[a]
12	2-Methyl-1-butene	42	Methylnonanes[a]
13	2-Pentene	43	1-Decene
14	2-Methyl-2-butene	44	Decenes[a]
15	3-Pentanone[b]	45	*n*-Decane
16	3,3-Dimethylbutene	46	2-Decene
17	Methylpentanes	47	Undecenes[a]
18	2,3-Dimethylbutene	48	*n*-Undecane
19	1-Hexene	49	*n*-Dodecane
20	*n*-Hexane	50	*n*-Tridecane
21	2-Methyl-1-pentene	51	*n*-Tetradecane
22	2-Hexene		
23	Dimethylpentenes[a]		
24	Methylhexanes[a]		
25	1-Heptene		
26	*n*-Heptane		
27	2-Methyl-1-hexene		
28	2-Heptene		
29	Dimethylhexenes[a]		
30	Methylheptanes[a]		

[a] Mixture of isomers.

[b] GC/MS identification not conclusive.

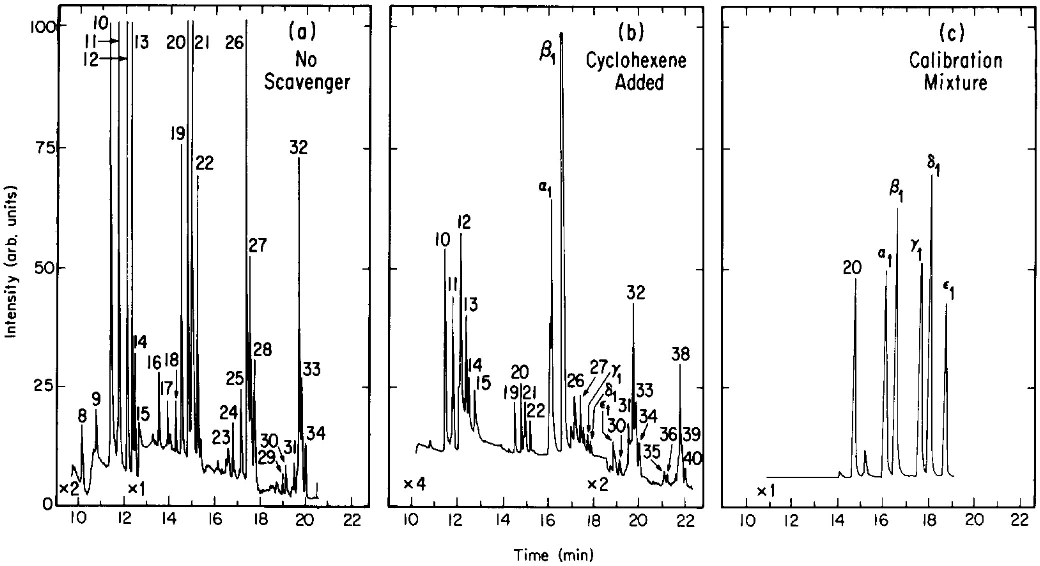

FIG. 2. Chromatograms used to identify the products formed during cyclohexene scavenging.

analyses also showed evidence for ethyl-, propyl-, and butylcyclohexane.

With the exception of norcarane, the products reported in Table 2 are identical to those observed by Ekerdt and Bell (*7*) over a Ru/SiO_2 catalyst and by Eidus (*19*) over supported Co catalysts. The failure of either of these previous studies to observe norcarane is most likely due to the choice of experimental conditions and procedures. The work of Ekerdt and Bell (*7*) was conducted using an open-loop recycle system. Repeated recirculation of the products over the catalyst in that system could have resulted in the isomerization of norcarane to methylcyclohexene, and subsequent hydro-

TABLE 2

Identification of Chromatographic Peaks for Cyclohexene and Cyclohexene Derivatives

Peak[a]	Compound	Forward fit	Reverse fit	Ratio relative retention indices (sample/calibration mixture)[b]
α_1	Cyclohexane	991	966	1.02
β_1	Cyclohexene	994	977	1.01
γ_1	Methylcyclohexane	987	963	1.00
δ_1	1-Methylcyclohexene	993	854	0.97
—	3-Methylcyclohexene[c]	966	906	
ε_1	Norcarane	822	830	1.01
—	Ethylcyclohexane[d]	985	921	—
—	Propylcyclohexane[d]	935	872	—
—	Butylcyclohexane[d]	875	903	—

[a] Peaks appearing in Fig. 2.

[b] See text for definition of relative retention index.

[c] Present in very small concentrations in the sample taken for GC/MS analysis.

[d] Identified solely on the basis of GC/MS analysis.

genation of this product to methylcyclohexane. The work of Eidus (*19*) was carried out at low space velocities and here too isomerization of norcarane to methylcyclohexene may have occurred.

The complete absence of cyclic compounds from the products observed during CO hydrogenation over the catalyst, in the absence of cyclohexene, indicates that the products listed in Table 2 arise as a direct consequence of cyclohexene addition. The question to be addressed next is whether the additional carbon atoms required to form norcarane and the alkyl derivatives of cyclohexene and cyclohexane derive from intermediates of CO hydrogenation or from the cracking of cyclohexene. To exclude the latter possibility, a series of experiments was carried out in which cyclohexene and hydrogen, diluted with helium, were passed over the catalyst in the absence of CO. Product analysis showed that 95% of the cyclohexene was converted to cyclohexane with no evidence for the formation of any other products. Additional experiments were conducted in which perfluorocyclohexene was added to the synthesis gas. The only new product observed in this case was $CH_3(H)C_6F_{10}$. Thus, the results of both experiments strongly suggest that the formation of norcarane and the alkyl derivatives of cyclohexene and cyclohexane occurs through the reaction of cyclohexene with hydrocarbon intermediates formed on the catalyst surface from CO and H_2.

Table 3 summarizes the effects of reaction conditions on the conversion of cyclohexene to products, as well as the conversion of CO to C_1 through C_{14} hydrocarbons. In all of these experiments the inlet concentration of cyclohexene was maintained near 0.9%. For a total flow rate of 122 STP cm^3/min, the CO conversion increases from 4.4 to 7.0% as the H_2/CO ratio increases from 3 to 9. The principal product obtained from cyclohexene is cyclohexane, and the conversion to this product rises from 10 to 22% as the H_2/CO ratio increases. The conversion of cyclohexene to products containing seven carbon atoms is on the order of a few hundredths of a percent or less. Norcarane is the principal C_7 product formed. The conversion of cyclohexene to norcarane is not a strong function of the H_2/CO ratio and appears to pass through a shallow maximum as the H_2/CO ratio is increased. Methylcyclohexene and methylcyclohexane are produced in nearly equivalent concentrations and the conversion of cyclohexene to each of these products increases monotonically with increasing H_2/CO ratio.

Increasing the gas flow rate from 37 to 403 STP cm^3/min, at an H_2/CO ratio of 3, causes the CO conversion to decrease from 22 to 2.1% and the conversion of cyclohex-

TABLE 3

Effects of Reaction Conditions on the Concentration of Cyclohexene and Cyclohexene Derivatives

T (K)	498	498	498	498	498	498
H_2/CO	3	6	9	3	3	3
Q (STP cm^3/min)	122	122	122	37	122	403
Mole fraction C_6H_{10}	8.5×10^{-3}	8.5×10^{-3}	8.6×10^{-3}	8.6×10^{-3}	8.5×10^{-3}	9.1×10^{-3}
X_{CO} with C_6H_{10} added	4.4×10^{-2}	5.3×10^{-2}	7.0×10^{-2}	2.2×10^{-1}	4.4×10^{-2}	2.1×10^{-2}
X_{CO} without C_6H_{10} added	5.0×10^{-2}	5.8×10^{-2}	7.4×10^{-2}	2.3×10^{-1}	5.0×10^{-2}	2.4×10^{-2}
$[P]/[C_6H_{10}]$						
Cyclohexane	1.0×10^{-1}	1.7×10^{-1}	2.0×10^{-1}	2.0×10^{-1}	1.0×10^{-1}	8.0×10^{-2}
Norcarane	3.6×10^{-4}	5.9×10^{-4}	4.3×10^{-4}	3.0×10^{-5}	3.6×10^{-4}	4.1×10^{-4}
Methylcyclohexene	1.9×10^{-5}	4.1×10^{-5}	8.7×10^{-5}	2.2×10^{-5}	1.9×10^{-5}	1.7×10^{-5}
Methylcyclohexane	2.1×10^{-5}	3.3×10^{-5}	1.1×10^{-4}	6.8×10^{-5}	2.1×10^{-5}	2.3×10^{-5}

ene to cyclohexane to decrease from 20 to 8%. The conversion of cyclohexene to c-C_7 products is virtually the same for flow rates of 122 and 403 STP cm^3/min. When the flow rate is reduced to 37 STP cm^3/min, the conversion to norcarane decreases by an order of magnitude. The conversion to methylcyclohexane increases by a factor of 3.4, but the conversion to methylcyclohexene increases only slightly over that observed at a flow rate of 122 STP cm^3/min.

A possible mechanism for the interaction of cyclohexene with hydrocarbon moieties present on the catalyst surface is illustrated in Fig. 3. The formation of norcarane is envisioned to proceed through a metallocycle produced by the reaction of a surface methylene group with adsorbed cyclohexene. The indicated sequence of steps is similar to that proposed by Grubbs and Miyashita (*35*) to explain the formation and decomposition of nickel metallocycles. Three pathways can be proposed for the formation of 1-methylcyclohexene. The first involves the isomerization of intermediate **1** to produce intermediate **2**, via an intramolecular shift of hydrogen. Intermediate **2** is then the precursor to 1-methylcyclohexene. The second possibility is that 1-methylcyclohexene is formed by the addition of a surface methyl group to cyclohexene. The sequence of steps for this process, illustrated in Fig. 3, parallels that proposed by Evit and Bergman (*37*) to explain the reaction of ethylene with a methyl ligand attached to a cobalt complex. The third alternative is that 1-methylcyclohexene is formed via the isomerization of norcarane. The presence of 3-methylcyclohexene is somewhat surprising, since it is not expected as a primary product of the reaction of cyclohexene with either methylene or methyl groups. It is more likely that this product is produced by the isomerization of 1-methylcyclohexene. Finally, Fig. 3 shows two alternative pathways for the formation of methylcyclohexane. The first involves the addition of a hydrogen atom to the α-carbon atom of intermediate **3**, which is formed upon interaction of a surface methyl group with cyclohexene. The second alternative is the hydrogenation of either 1- or 3-methylcyclohexene.

The formation of higher-molecular-weight alkylcyclohexanes may occur via a mechanism similar to that shown in Fig. 3 for the formation of methylcyclohexane. It is also possible that an alkylcyclohexene is formed first which then rapidly undergoes hydrogenation. The present results do not permit discrimination between these two possibilities.

Scavenging by Benzene

Selected portions of the chromatograms obtained in the absence and presence of

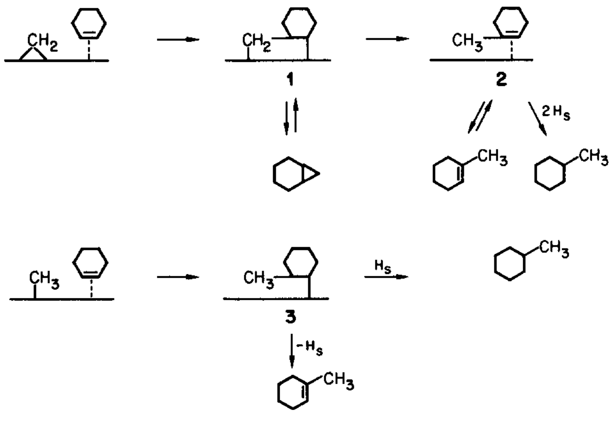

FIG. 3. Proposed mechanism for cyclohexene scavenging.

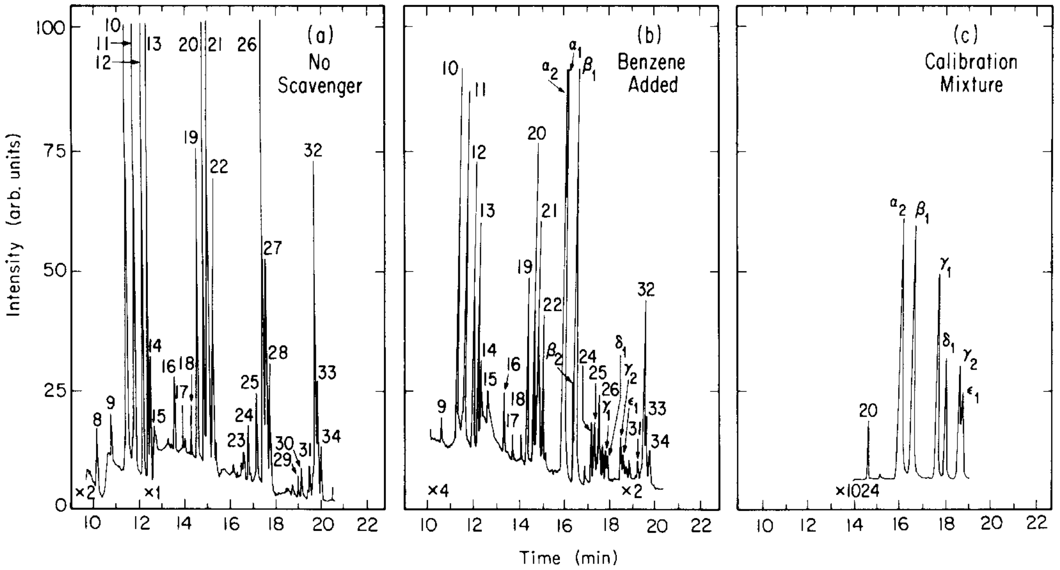

FIG. 4. Chromatograms used to identify the products formed during benzene scavenging.

benzene are shown in Fig. 4, together with the chromatogram for an appropriate calibration mixture. Comparison of chromatograms a and b shows that eight new peaks appear in the chromatogram upon addition of benzene to the feed. The identities of these peaks were determined by GC/MS analysis and by a comparison of the relative retention index for each peak with those of known compounds. As noted in Table 4,

TABLE 4

Identification of Chromatographic Peaks for Benzene and Benzene Derivatives

Peak[a]	Compound	Forward fit	Reverse fit	Ratio relative retention indices (sample/calibration mixture)[b]
α_2	Benzene	997	985	0.96
α_1	Cyclohexane	990	970	1.00
β_2	Cyclohexadiene[c]	983	991	—
β_1	Cyclohexene	994	977	0.97
γ_1	Methylcyclohexane	988	972	1.04
δ_1	1-Methylcyclohexene	977	863	0.99
—	3-Methylcyclohexene	976	875	—
ϵ_1	Norcarane	820	831	0.98
γ_2	Toluene	991	976	0.99
—	*ortho*-Xylene[d]	963	952	—
—	Ethylbenzene[d]	951	876	—
—	Propylbenzene[d]	891	672	—
—	Butylbenzene[d]	826	523	—

[a] Peaks appearing in Fig. 4.

[b] See text for definition of relative retention index.

[c] Identified solely on the basis of GC/MS analysis.

[d] Present in very small concentrations in the sample taken for GC/MS analysis.

the new peaks can be assigned to benzene, cyclohexadiene, cyclohexene, cyclohexane, toluene, methylcyclohexane, methylcyclohexene, and norcarane. The GC/MS analyses also showed evidence of small quantities of *ortho*-xylene and ethyl-, propyl-, and butylbenzene.

The appearance of toluene as one of the products formed by the interaction of benzene with species produced by the hydrogenation of CO is in good agreement with the observations reported by Eidus *et al.* (*19–21*) in studies conducted using a supported Co catalyst. While a small amount of cycloheptatriene was also found in those studies, none could be detected here. It should be noted that detection of very small amounts of cycloheptatriene in the presence of toluene would have been virtually impossible since toluene and cycloheptatriene have similar boiling points and virtually indistinguishable mass spectrometric cracking patterns.

The effects of reaction conditions on the conversion of benzene to products and the conversion of CO to C_1 through C_{14} hydrocarbons is given in Table 5. It is noted that in all of these experiments the feed concentration of benzene was between 0.9 and 1.5%. As was observed in the case with cyclohexene addition, the presence of the scavenger has relatively little effect on the CO conversion or its dependence on either the H_2/CO ratio or the total flow rate.

Between 96 and 98% of the benzene added to the feed is converted to cyclohexane. The small amounts of cyclohexadiene and cyclohexene observed are formed as intermediates during benzene hydrogenation. The conversion to these products passes through a maximum as either the H_2/CO ratio or the total flow rate is increased. The C_7 product obtained from benzene in the highest concentration is toluene. The conversion of benzene to toluene increases as either the H_2/CO ratio decreases or the flow rate increases. It is interesting to note that methylcyclohexane is also observed in relatively high concentration. The conversion to this product passes through a minimum as the H_2/CO ratio increases but decreases monotonically with increasing flow rate. A similar pattern is exhibited by methylcyclohexene.

The decline in the conversion of benzene to toluene with either increasing H_2/CO or decreasing feed flow rate, noted in Table 5, parallels the decrease in the concentration of benzene over the catalyst and clearly indicates that toluene is formed via reaction

TABLE 5

Effects of Reaction Conditions on the Concentration of Products Formed from Benzene

T (K)	498	498	498	498	498	498
H_2/CO	3	6	9	3	3	3
Q (STP cm^3/min)	122	122	122	37	122	403
Mole fraction C_6H_6	1.1×10^{-2}	1.2×10^{-2}	1.1×10^{-2}	9.0×10^{-3}	1.1×10^{-2}	1.5×10^{-2}
X_{CO} with C_6H_6 added	4.3×10^{-2}	5.1×10^{-2}	6.0×10^{-2}	1.9×10^{-1}	4.3×10^{-2}	2.2×10^{-2}
X_{CO} without C_6H_6 added	5.0×10^{-2}	5.8×10^{-2}	7.4×10^{-2}	2.3×10^{-1}	5.0×10^{-2}	2.4×10^{-2}
$[P]/[C_6H_6]$						
Cyclohexane	9.6×10^{-1}	9.7×10^{-1}	9.8×10^{-1}	9.6×10^{-1}	9.6×10^{-1}	9.7×10^{-1}
Cyclohexadiene	3.6×10^{-3}	—	—	5.0×10^{-5}	3.6×10^{-3}	6.0×10^{-4}
Cyclohexene	6.9×10^{-3}	1.3×10^{-2}	3.8×10^{-3}	4.2×10^{-3}	6.9×10^{-3}	6.9×10^{-4}
Toluene	1.6×10^{-2}	1.3×10^{-2}	6.9×10^{-3}	1.3×10^{-2}	1.6×10^{-2}	2.6×10^{-2}
Norcarane	8.1×10^{-4}	1.6×10^{-3}	1.1×10^{-3}	4.7×10^{-3}	8.1×10^{-4}	3.6×10^{-4}
Methylcyclohexene	1.5×10^{-3}	1.3×10^{-3}	1.5×10^{-3}	7.0×10^{-3}	1.5×10^{-3}	7.2×10^{-4}
Methylcyclohexane	1.0×10^{-2}	3.2×10^{-3}	6.0×10^{-3}	1.3×10^{-2}	1.0×10^{-2}	5.2×10^{-4}

of benzene with one or more surface species. The nature of the adsorbed species cannot be established unambiguously. One possibility is that toluene is formed by insertion of a CH_2 group into one of six carbon–hydrogen bands of benzene. As an alternative one can envision the direct alkylation of benzene by a surface CH_3 group. Such a mechanism might also explain the formation of the other alkylbenzenes observed in GC/MS analyses of the reaction products. The possibility that cycloheptatriene, formed via CH_2 insertion into the benzene ring, might act as a precursor to toluene seems unlikely in the light of the results obtained by Eidus *et al.* (*21*). These authors observed that the isomerization of cycloheptatriene to toluene proceeded to only about 1% when cycloheptatriene was passed over a Co/ThO_2/kieselguhr catalyst in the presence of H_2 or a mixture of H_2 and CO.

The pathway by which norcarane benzene reacts to form norcarane cannot be established unambiguously from the present results. It seems unlikely that this product is formed through the direct reaction of a CH_2 group with adsorbed benzene and subsequent hydrogenation of the adduct, since there appears to be no precedent for such chemistry. A more plausible suggestion is that adsorbed benzene undergoes partial hydrogenation to form adsorbed cyclohexene, which then interacts with a CH_2 group to form norcarane.

The appearance of methylcyclohexene and methylcyclohexane might also be ascribed to reactions involving cyclohexene. However, comparison of Tables 3 and 5 suggests that this conclusion may not be correct, since the ratio of norcarane to either methylcyclohexene or methylcyclohexane is considerably larger when cyclohexene rather than benzene is used as the scavenger. This observation implies that most of the methylcyclohexene and methylcyclohexane reported in Table 5 may arise from the stepwise hydrogenation of toluene or its precursor.

Scavenging by Cyclopentene

Chromatograms a and b, shown in Fig. 5, were obtained in the absence and presence, respectively, of cyclopentene in the feed gas. Examination shows that chromatogram b contains six peaks not present in chromatogram a. These peaks are listed in Table 6 and are assigned to cyclopen-

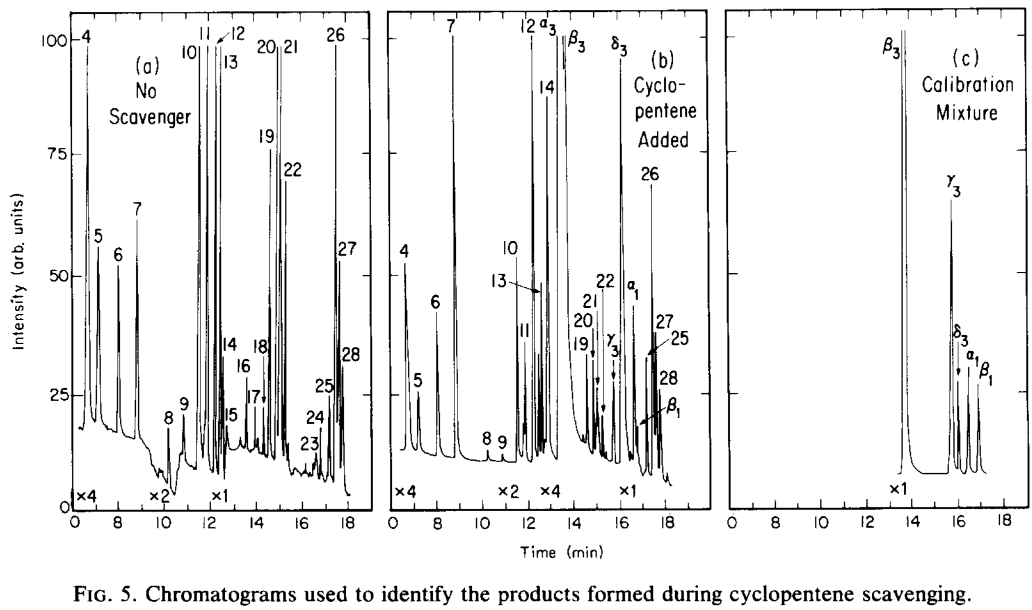

FIG. 5. Chromatograms used to identify the products formed during cyclopentene scavenging.

TABLE 6

Identification of Chromatographic Peaks for Cyclopentene and Cyclopentene Derivatives

Peak[a]	Compound	Forward fit	Reverse fit	Ratio relative retention indices (sample/calibration mixture)[b]
α_3	Cyclopentane	964	917	1.00
β_3	Cyclopentene	994	907	1.00
γ_3	Methylcyclopentane	991	902	0.99
δ_3	1-Methylcyclopentene	989	715	0.99
α_1	Cyclohexane	992	898	1.02
β_1	Cyclohexene	995	971	0.96

[a] Peaks appearing in Fig. 5.

[b] See text for definition of relative retention index.

tane, cyclopentene, methylcyclopentane, 1-methylcyclopentene, cyclohexene, and cyclohexane on the basis of GC/MS analyses and a comparison of the relative retention index of each peak with those of pure components (see chromatogram c in Fig. 5).

Table 7 shows the effects of reaction conditions on the conversion of cyclopentene to products and the conversion of CO to C_1 through C_{14} products. As can be seen, the addition of 1.3 to 1.7% of cyclopentene to the feed had little if any influence on the conversion of CO, relative to that observed in the absence of scavenger addition. Between 15 and 32% of the cyclopentene is hydrogenated to cyclopentane, the conversion to this product increasing with either an increase in the H_2/CO ratio or a decrease in the gas flow rate. With the exception of the run in which $H_2/CO = 3$ and $Q = 403$ STP cm^3/min, the principal C_6 product obtained from cyclopentene is methylcyclopentane. The conversion to this product decreases monotonically with increasing H_2/CO ratio. The conversion of cyclopentene to methylcyclopentene is about an order of magnitude smaller than that of methylcyclopentane and decreases as the H_2/CO ratio is increased. The conversions of cyclopentene to 1-methylcyclopentene and methylcyclopentane are strong functions of the flow rate. At low flow rates

TABLE 7

Effects of Reaction Conditions on the Concentration of Products Formed from Cyclopentene

T (K)	498	498	498	498	498	498
H_2/CO	3	6	9	3	3	3
Q (STP cm^3/min)	122	122	122	37	122	403
Mole fraction C_5H_8	1.4×10^{-2}	1.4×10^{-2}	1.5×10^{-2}	1.7×10^{-2}	1.4×10^{-2}	1.3×10^{-2}
X_{CO} with C_5H_8 added	4.5×10^{-2}	5.1×10^{-2}	6.3×10^{-2}	2.1×10^{-1}	4.5×10^{-2}	2.1×10^{-2}
X_{CO} without C_5H_8 added	5.0×10^{-2}	5.8×10^{-2}	7.4×10^{-2}	2.3×10^{-1}	5.0×10^{-2}	2.4×10^{-2}
$[P]/[C_5H_8]$						
Cyclopentane	1.9×10^{-1}	2.3×10^{-1}	3.2×10^{-1}	2.7×10^{-1}	1.9×10^{-1}	1.5×10^{-1}
1-Methylcyclopentene	2.8×10^{-4}	9.7×10^{-5}	5.6×10^{-5}	8.1×10^{-5}	2.8×10^{-4}	3.3×10^{-4}
Methylcyclopentane	2.7×10^{-3}	5.8×10^{-4}	4.9×10^{-4}	3.6×10^{-4}	2.7×10^{-4}	8.7×10^{-5}
Cyclohexene	1.3×10^{-5}	—	—	—	1.3×10^{-5}	2.9×10^{-5}
Cyclohexane	2.3×10^{-5}	9.8×10^{-5}	2.1×10^{-4}	8.8×10^{-5}	2.3×10^{-5}	1.9×10^{-5}

the methylcyclopentane concentration is higher. At high flow rates the opposite is true. The conversion to cyclohexane is of the same order of magnitude as that to methylcyclopentene, but the response of the cyclohexane conversion to changes in reaction conditions is different. In this case, the conversion increases with increasing H_2/CO ratio and decreasing flow rate. Since cyclohexene could be detected in only three of the six experiments, the trends in cyclohexene conversion with changes in reaction conditions cannot be unambiguously defined.

The mechanisms for the formation of methylcyclopentene and methylcyclopentane are very likely the same as those proposed in Fig. 3 to explain the formation of methylcyclohexene and methylcyclohexane. The appearance of cyclohexene and cyclohexane among the products of cyclopentene scavenging may be due to the isomerization of methylcyclopentene and/or methylcyclopentane. Alternatively, isomerization may occur during the initial stages of interaction between cyclopentene and either a surface methylene or methyl group.

Scavenging by cis-2-Butene

Portions of the chromatograms obtained in the absence and presence of *cis*-2-butene are shown in Fig. 6. The addition of the scavenger leads to a significant increase in the *cis*-2-butene peak, a small increase in the 2-pentene peak, and the appearance of three new peaks. Table 8 shows that these latter peaks can be identified as 2-methyl-2-butene, *cis*-dimethylcyclopropane, and *trans*-dimethylcyclopropane. The GC/MS analyses of the products obtained in the presence of *cis*-2-butene also show evidence for a small amount of ethylcyclopropane.

The effects of reaction conditions on the conversion of *cis*-2-butene to products and the conversion of CO to C_1 through C_{14} products is given in Table 9. All but one of these experiments were carried out using a *cis*-2-butene concentration of 3.0%. Here again, it is observed that the presence of the scavenger has no significant effect on the conversion of CO.

Table 9 shows that the major products obtained from *cis*-2-butene are 1-butene and normal butane. The conversion to each

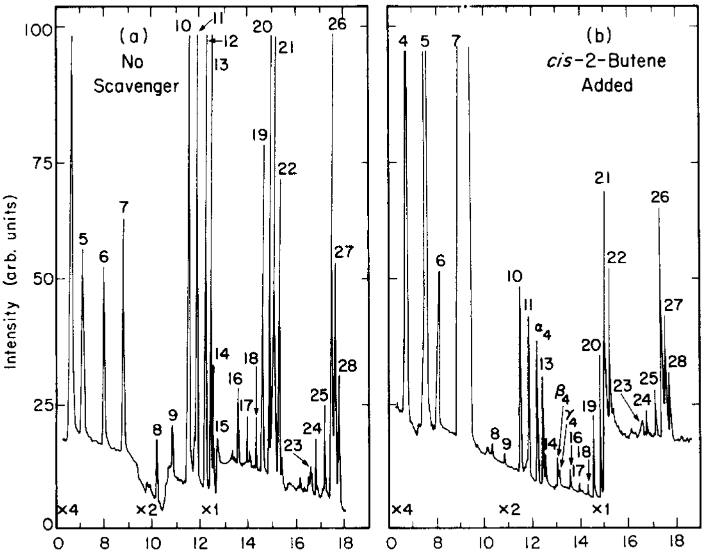

FIG. 6. Chromatograms used to identify the products formed during *cis*-2-butene scavenging.

TABLE 8

Identification of Chromatographic Peaks for *cis*-2-Butene and *cis*-2-Butene Derivatives

Peak[a]	Compound	Forward fit	Reverse fit	Ratio relative retention indices (sample/calibration mixture)[b]
7	*cis*-2-Butene (with *trans*-)	993	943	0.97
α_4	2-Methyl-2-butene	930	783	0.99
β_4	*cis*-Dimethylcyclopropane[c]	997	991	—
γ_4	*trans*-Dimethylcyclopropane[c]	864	909	—
—	Ethylcyclopropane[c]	864	909	—

[a] Peaks appearing in Fig. 6.

[b] See text for definition of relative retention index.

[c] Identification based solely on GC/MS analysis.

of these compounds increases with increasing H_2/CO ratio and decreasing gas flow rate. For all of the conditions examined, the conversion of *cis*-2-butene to the *trans* isomer of 1,2-dimethylcyclopropane greatly exceeds the conversion to the *cis* isomer of this product. It is interesting to note that while the conversion to the *trans* isomer passes through a sharp maximum with increasing H_2/CO ratio, the conversion to the *cis* isomer goes through a minimum. However, the conversion to both products increases with increasing flow rate. Very small amounts of ethylcyclopropane are formed. The responses of the conversion to this product to changes in H_2/CO ratio and flow rate are similar to those for the conversion to 1-butene, which suggests that 1-butene may be a precursor to ethylcyclopropane.

The mechanism by which the derivatives of cyclopropane are produced from *cis*-2-butene is probably similar to that shown in Fig. 3. It is quite possible that the formation of *trans*-1,2-dimethylcyclopropane involves a preliminary isomerization of *cis*-2-

TABLE 9

Effects of Reaction Conditions on the Concentrations of Products Formed from *cis*-2-Butene

T (K)	498	498	498	498	498	498
H_2/CO	3	6	9	3	3	3
Q (STP cm^3/min)	122	122	122	37	122	403
Mole fraction C_4H_8	3.0×10^{-2}	3.0×10^{-2}	3.0×10^{-2}	1.0×10^{-2}	3.0×10^{-2}	3.0×10^{-2}
X_{CO} with C_4H_8 added	4.5×10^{-2}	5.5×10^{-2}	7.2×10^{-2}	2.4×10^{-2}	4.9×10^{-2}	2.9×10^{-2}
X_{CO} without C_4H_8 added	5.0×10^{-2}	5.8×10^{-2}	7.4×10^{-2}	2.3×10^{-2}	5.0×10^{-2}	2.4×10^{-2}
$[P]/[C_4H_8]$						
Butane[a]	1.6×10^{-1}	2.3×10^{-1}	3.1×10^{-1}	3.0×10^{-1}	1.6×10^{-1}	1.1×10^{-1}
1-Butene[a]	8.0×10^{-2}	1.7×10^{-1}	2.2×10^{-1}	1.5×10^{-1}	8.0×10^{-2}	6.0×10^{-2}
cis-Dimethyl cyclopropane	3.2×10^{-5}	1.9×10^{-5}	5.1×10^{-5}	7.9×10^{-6}	3.2×10^{-5}	4.9×10^{-5}
trans-Dimethylcyclopropane	7.4×10^{-4}	7.5×10^{-3}	9.6×10^{-4}	2.3×10^{-4}	7.4×10^{-4}	7.0×10^{-3}
2-Methyl-2-butene	1.8×10^{-5}	5.8×10^{-6}	1.3×10^{-4}	6.4×10^{-5}	1.8×10^{-5}	8.3×10^{-6}
Ethylcyclopropane	2.6×10^{-6}	9.3×10^{-6}	1.2×10^{-5}	7.1×10^{-6}	2.6×10^{-6}	—

[a] Based on excess over that formed via CO hydrogenation.

butene to *trans*-2-butene. Alternatively, isomerization may occur at some intermediate stage during the addition of the methylene group across the double bond. As noted above, it seems likely that ethylcyclopropane is formed by the reaction of 1-butene with a methylene group. If this is so, the results presented in Table 9 suggest that 1-butene is substantially less reactive than *cis*-2-butene with regard to the addition of a methylene group.

Effect of Scavenger on Product Distribution

In each of the experiments in which a scavenger was used, the scavenger concentration was maintained sufficiently low to preclude significant changes in the nature of the synthesis products. Nevertheless, it was observed that even at scavenger concentrations on the order of 0.9 to 3.0%, changes in the carbon number distribution of the products could be detected. The extent of this effect is shown in Fig. 7 for each of the scavengers. It is immediately apparent that all four scavengers cause a suppression in the formation of higher-molecular-weight products relative to the amounts observed in the absence of any scavenger. Moreover, the degree of deviation increases in the order: $C_6H_{10} \approx C_6H_6 < C_5H_8 < C_4H_8$.

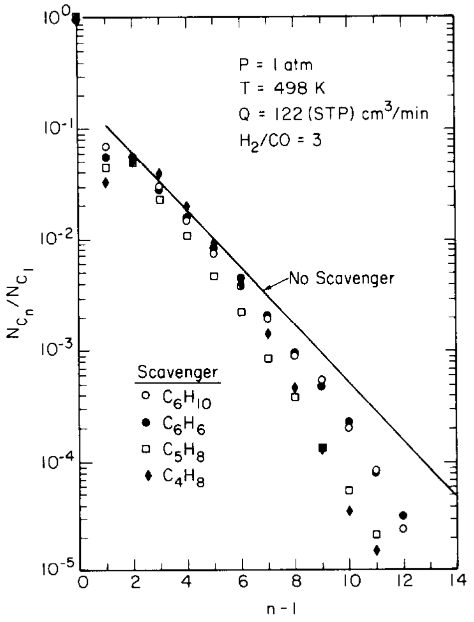

FIG. 7. Plot of log (N_{C_n}/N_{C_1}) versus (n-1) in the presence and absence of scavenger addition.

The influence of a scavenger on the product distribution can be interpreted by considering the effect of the scavenger on the probability of chain growth, α. This parameter is defined by

$$\alpha = \frac{r_p}{r_p + \sum_i r_{t_i}}, \tag{1}$$

where r_p is the rate of chain growth and r_{t_i} is the rate of chain termination via the ith process. Kellner and Bell (*10*) have shown that α can be represented by

$$\alpha = \frac{k_p\theta_n\theta_{CH_2}}{k_p\theta_n\theta_{CH_2} + k_{to}\theta_n\theta_v + k_{tp}\theta_n\theta_H}, \tag{2}$$

where k_p is the rate coefficient for propagation, k_{to} is the rate coefficient for termination via olefin formation, k_{tp} is the rate coefficient for termination via paraffin formation, θ_n is the surface coverage by alkyl groups of chain length n, θ_{CH_2} is the surface coverage by CH_2 groups, θ_H is the surface coverage by H atoms, and θ_v is the surface coverage by vacancies. If all three rate coefficients are independent of n, then α will be independent of n.

The value of α associated with a given product distribution can be determined from the slope of a straight line drawn on a plot of log N_{C_n}/N_{C_1} versus n-1 (*10*). Values of α determined in this fashion are presented in Table 10. It is apparent that the magnitude of α is reduced upon introduction of a scavenger and is most strongly affected by *cis*-2-butene.

Two explanations can be given for the observed effect of scavengers on α. Reaction of the scavenger with CH_2 groups will reduce the steady-state value of θ_{CH_2} relative to its magnitude in the absence of the scavenger. Equation (2) shows that this effect will cause a decrease in α. A further

TABLE 10

Effect of Scavenger Addition on α^a

Scavenger	α
None	0.56
Cyclohexene	0.48
Benzene	0.48
Cyclopentene	0.42
cis-2-Butene	0.40

[a] Reaction conditions: T = 498 K; H_2/CO = 3; P = 1 atm; Q = 122 STP cm^3/min.

decrease in α can be caused by the reaction of the scavenger with alkyl groups. The effect here will be to add an additional termination term to the denominator of Eq. (2).

CONCLUSIONS

It has been shown that cyclohexene, benzene, cyclopentene, and *cis*-2-butene added in low concentration to a mixture of CO and H_2 can be used to scavenge hydrocarbon species produced on the surface of Ru during CO hydrogenation. The presence of CH_2 groups is strongly supported by the formation of norcarane and 1,2-dimethylcyclopropane from cyclohexene and *cis*-2-butene, respectively, and by the formation of ethylcyclopropane from 1-butene produced by the isomerization of *cis*-2-butene. Evidence has also been obtained for the presence of methyl and higher-molecular-weight alkyl groups. The principal support for this conclusion is the observation of alkyl derivatives of cyclohexene and benzene when cyclohexene or benzene, respectively, is used as a scavenger. Finally, it has been observed that each of the scavengers causes a reduction in the probability of hydrocarbon chain growth, α, suggesting that the species removed by the scavenger participate in the process of hydrocarbon chain growth.

ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC03-76SF00098.

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