JOURNAL OF CATALYSIS 92, 232–239 (1985)

Alkyl and π-Allyl Intermediates in n-C_4 Hydrocarbon Reactions over Ruthenium

KUEI-WU HUANG AND JOHN G. EKERDT

Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712

Received July 11, 1984; revised November 14, 1984

The reactions of n-butane and n-butenes were investigated over Ru/SiO_2 at 150°C using a reactive scavenging technique to test for the presence of alkyl species. Pyridine suppressed hydrogenation and hydrocracking reactions to an extent that double-bond isomerization was observable at a H_2/butene ratio of 11. 2-n-Butylpyridine and 2-sec-butylpyridine formed between pyridine and the n-butyl and sec-butyl species, respectively, revealing that these alkyl species form and can be scavenged. The distribution of the butylpyridines and the distribution of the hydrocarbon products are used to propose elementary steps in hydrogenolysis, homologation, hydrogenation, and double-bond isomerization over ruthenium. © 1985 Academic Press, Inc.

I. INTRODUCTION

The role of alkyl species in Fischer–Tropsch synthesis has been discussed in review articles (*1, 2*). Fischer–Tropsch product selectivity and molecular weight distribution are controlled by the relative rates of postulated reactions involving alkyl chain growth and alkyl termination to alkanes and olefins. This study was undertaken to investigate alkyl reactions over a group VIII metal as a means of understanding these Fischer–Tropsch termination reactions.

Osterloh *et al.* (*3*) have proposed that alkyl species are the intermediates undergoing C–C bond scission during the hydrogenolysis of linear hydrocarbons over Ni, Co, and Ru. Normal butenes and butane are used as the reactants in studies reported herein. Ruthenium was selected as the catalyst for our study because it does not form bulk carbides and because Fischer–Tropsch synthesis over Ru has been explained using alkyl intermediates in chain growth and termination (*4*).

Multiple intermediates should be expected when reacting hydrocarbons over transition metals. Horiuti and Polanyi investigated ethylene hydrogenation over Ni 50 years ago and proposed that an alkyl species was the key intermediate (*5*). Their mechanism has been used extensively to describe the reaction of other olefins over transition metal catalysts. Gault and coworkers (*6–10*) studied olefin reactions over Ni, Pd, and Fe and demonstrated that the same intermediates, alkyl, π-allyl, σ-vinyl, and π-bonded olefin, may not be present over different transition metals. It has been suggested that the intermediates over a given metal may also change with temperature (*11, 12*). The role of some of these intermediates in homologation, hydrogenation, and isomerization over Ru is discussed later.

A chemical scavenging technique was used to test for the presence of alkyl species and to determine their role in C_4 reactions over Ru. This technique has been used to scavenge alkyl species during Fischer–Tropsch synthesis over silica-supported iron by introducing pyridine to the CO/H_2 reactant mixture and forming 2-alkylpyridines (*13*). Mechanisms for alkylating pyridine over transition metal surfaces are not reported. Moyes and Wells (*14*) have proposed a mechanism for H/D exchange at the 2-position over Ni which involves interaction of pyridine with the sur-

0021-9517/85 $3.00

face through nitrogen, loss of hydrogen from the 2-position with subsequent bonding to the surface through the α-carbon, and finally deuteration of this species to form 2-d_1-pyridine. Alkylation of pyridine at the α-carbon may proceed by an analogous process. Rates of alkylation are expected to depend on the concentration of alkyl species as well as the size of the alkyl species.

II. METHODS

System description. The system schematic is shown in Fig. 1. A gas metering panel with digital flow rate monitors was used to blend the gases. A 10-mm-i.d. quartz tube reactor, fitted with a fritted disk upon which the catalyst was loaded, was used. The quartz tube reactor had a 20-cm preheating zone. The temperature of the catalyst was controlled by an oven surrounding the quartz tube reactor and was monitored by contacting a stainless-steel-sheathed thermocouple with the catalyst bed.

The gas-tight pyridine saturator was kept at 0°C. A pear-shaped flask, used for sample collection, was immersed in liquid nitrogen and could be disconnected for analysis after trapping the pyridine derivatives and other nitrogen-containing compounds in the product stream. A multiport gas-sampling valve was used to take samples for on-line analysis of C_1 to C_6 hydrocarbons.

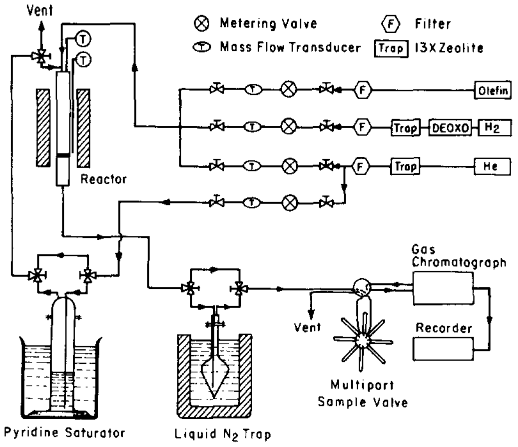


FIG. 1. Schematic representation of the experimental apparatus.

Procedures. A fresh loading of 50 mg of catalyst was used for each run. The catalyst was reduced *in situ* under 40 cm^3/min hydrogen flow at 430°C for 3 h. The temperature of the catalyst was then lowered to the reaction temperature, 150°C, under hydrogen. After switching off the hydrogen, helium (106 cm^3/min) was introduced to the system to purge hydrogen before a run.

One at a time, the hydrocarbon gas (n-butane or n-butene) at 2 cm^3/min and hydrogen at 22 cm^3/min were sent through the reactor. The total pressure of the system was 1 atm and the total flow rate was 130 cm^3/min, the balance being He. One hour run-in time was found, by experience, to be the most appropriate period before taking gas samples.

A gas sample was taken by actuating the multiport gas-sampling valve. Pyridine was then brought to the system by flowing 20 cm^3/min helium, which was part of the balancing gas, through the pyridine saturator. The period of trapping the pyridine derivatives and other nitrogen-containing compounds in the pear-shaped flask lasted 20 min.

The condensate in the pear-shaped flask was rinsed out using 0.2 cm^3 of diethylether. The solution was pipetted to a 6 × 50-mm culture tube and was concentrated to a 0.02-cm^3 droplet by allowing the ether to evaporate at room temperature. About 0.8 μl was injected into the capillary column.

After trapping, the pear-shaped flask was bypassed and another gas sample along with the pyridine derivatives was taken for hydrocarbon analysis, which should reflect the effect of pyridine on the reactions over Ru/SiO_2. (It was determined experimentally that the catalyst did not deactivate with time-on-stream for at least 1 h following the introduction of pyridine to the system.)

Analysis. A Varian 2440 gas chromatograph (GC) equipped with a flame ionization detector was used to analyze C_1 to C_6

hydrocarbons. The hydrocarbons were separated on a 9.10-m × 3.2-mm-o.d. stainless-steel column packed with 23% SP-1700 on 80/100 Chromosorb P-AW. The oven temperature was 70°C. A Hewlett–Packard 5880 GC fitted with a nitrogen-phosphorus detector (NPD) was used to analyze pyridine, the alkyl-substituted pyridines, and other nitrogen-containing compounds. A 30-m × 0.25-mm-i.d. fused silica capillary column loaded with Carbowax was used. The oven temperature was kept at 40°C for 10 min and then ramped to 180 at 10°C/min. The standards for 2-n-butylpyridine and 2-sec-butylpyridine were synthesized by reacting pyridine with the corresponding alkyl lithiums. GC–MS was used to help identify 2-sec-butylpyridine, which has exactly the same retention time as 4-ethylpyridine.

Catalyst. The catalyst was made by wet-impregnating ruthenium chloride solution onto fumed silica powder (Cab-O-Sil, HS-5 grade); it was found to contain 3.78 wt% Ru. The paste was dried in a rotary vacuum evaporator. Next the catalyst was reduced under flowing hydrogen at 400°C for 2 h. The reduced catalyst was sieved to 325 mesh or less and was stored in a desiccator.

Materials. Hydrogen (99.999%) was treated in a Deoxo (Matheson) unit followed by a 13× molecular sieve trap. Helium (99.995%) was passed through a 13× molecular sieve trap. 1-Butene (99.9% minimum) and n-butane (99.9% minimum) were both research grade from Matheson. *trans*-2-Butene (99.4%, with 0.4% n-butane and 0.2% *cis*-2-butene) and *cis*-2-butene (96.0%, with 4.0% *trans*-2-butene) were both CP grade from Union Carbide. Hydrocarbon reactants were used without further purification.

III. RESULTS

Table 1 lists the hydrocarbon products over Ru/SiO$_2$ at 150°C. This temperature

TABLE 1

Hydrocarbon Product Distributions at 150°C

Product	Reactant[a]								
	1-C_4H_8		*trans*-2-C_4H_8		*cis*-2-C_4H_8		n-C_4H_{10}		Control[b]
	Before[c]	After[c]	Before	After	Before	After	Before	After	After
CH_4	9.56[d]	0.12	16.59	0.13	17.40	0.10	33.34	0.35	4.40
C_2H_4 + C_2H_6[e]	4.80	0.03	8.60	0.07	8.46	0.06	24.65	0.26	2.00
C_3H_8	2.90	0.15	3.57	0.10	3.57	0.07	6.53	0.27	0.80
C_3H_6	0.0	0.09	0.0	0.03	0.0	Trace	0.0	0.0	0.0
iso-C_4H_{10}	0.20	0.0	0.46	0.0	0.06	0.0	0.09	0.13	0.0
n-C_4H_{10}	81.27 (7997)[f]	39.10 (3848)	70.09 (8357)	22.70 (3324)	69.51 (8127)	22.40 (3970)	35.38 (3015)	97.67 (8324)	55.81 (58)
1-C_4H_8	0.0	34.11	0.0	3.40	0.0	4.58	0.0	—[g]	5.45
trans-2-C_4H_8	0.0	15.30	0.0	57.60	0.0	24.57	0.0	0.83	19.13
cis-2-C_4H_8	0.0	10.52	0.0	16.00	0.0	48.20	0.0	0.49	12.43
n-C_5H_{12}	1.09	0.08	0.70	0.0	0.87	0.0	0.0	0.0	0.0
n-C_6H_{14}	0.17	0.0	Trace	0.0	0.14	0.0	0.0	0.0	0.0

[a] The feed also contained H_2 at a ratio of H_2/hydrocarbon = 11.

[b] Hydrocarbon was absent only H_2, He and pyridine flowed into the reactor.

[c] Before/after adding pyridine to the feed mixture.

[d] Mole percentage.

[e] These were not separated on the GC.

[f] n-C_4H_{10} concentration in ppm.

[g] The large n-C_4H_{10} signal tailed into the region where 1-C_4H_8 elutes; 1-C_4H_8 was detected.

was selected to enhance the probability of eluting butylpyridines from the reactor (bp 2-sec-butylpyridine: ~180°C; 2-n-butylpyridine: 193°C) and to minimize the effects of pyridine decomposition which increased with increasing temperatures. For 1-butene, no unsaturated C_4's were found in the product stream before the addition of pyridine. Most of the reactant was hydrogenated to n-butane; methane, ethane and propane were formed through C–C bond scission. It is interesting that in addition to hydrogenation and C–C bond scission, homologation to n-pentane and n-hexane also occurred. The addition of pyridine suppressed significantly C–C bond scission, hydrogenation, and homologation. Internal butenes and a small amount of propylene were observed in the presence of pyridine.

The internal butenes displayed results similar to those for 1-butene. Both internal butenes underwent the homologation reaction. In all cases only linear products were detected.

Hydrogenolysis was the only reaction detected for n-butane; no homologation was found, in contrast to the results for the n-butenes. The addition of pyridine suppressed hydrogenolysis and at the same time it facilitated the formation of a very low yield of C_4 butenes.

Pyridine underwent ring opening over Ru/SiO_2 in the presence of H_2 at 150°C, as shown in Table 1. The amount of hydrocarbons formed was relatively small compared to the C_4-reactants. However, the reaction of pyridine with H_2 alone over Ru/SiO_2 resulted in the formation of alkyl-substituted pyridines (Table 2), and was not negligible.

Table 2 lists the alkyl-substituted pyridines formed. These numbers represent the NPD area fraction of the indicated compounds; the major component was unreacted pyridine. Increases in the area fractions of C_4-pyridines above those displayed in the control experiment were of order 10 or less. The scavenging yields and distributions were reproducible and increases in the area fraction by a factor of ca. 4 reflect the contribution of the hydrocarbon reactant.

All the alkyl-substituted pyridine products were α-substituted on the pyridine ring. The control experiment with pyridine and H_2 revealed that C_1- to C_4-alkylpyridines formed in the absence of added hydrocarbon; this alkylpyridine formation is referred to as the background level. For 1-butene, a significant amount of sec-butylpyridine (about 4 times above the background level) and a high level of n-butylpyridine were formed during the scavenging process. On the other hand, for internal butenes the n-butyl fragment scavenged to a lesser extent. Interestingly, sec-butylpyridine was equivalent to the background level

TABLE 2

Alkylpyridine Distributions

Product	Reactant				
	$1\text{-}C_4H_8$	*trans*-$2\text{-}C_4H_8$	*cis*-$2\text{-}C_4H_8$	$n\text{-}C_4H_{10}$	Control[a]
2-Methylpyridine	0.01290[b](3.4)[c]	0.01000(2.6)	0.01410(3.7)	0.01480(3.9)	0.00382(1.0)
2-Ethylpyridine	0.00080(7.3)	0.00062(5.6)	0.00082(7.5)	0.00087(7.9)	0.00011(1.0)
2-Propylpyridine	0.00039(19.5)	0.00014(7.0)	0.00017(8.5)	0.00019(9.5)	0.00002(1.0)
2-sec-Butylpyridine	0.00140(3.8)	0.00037(1.0)	0.00040(1.1)	0.00174(4.7)	0.00037(1.0)
2-n-Butylpyridine	0.00380(21.1)	0.00073(4.1)	0.00065(3.6)	0.00071(3.9)	0.00018(1.0)

[a] Hydrocarbon was absent; only H_2, He, and pyridine flowed into the reactor.

[b] Area fraction of the total NPD signal area.

[c] Area fraction normalized by the control area fraction.

for both internal butenes. The alkylpyridine distribution for n-butane shows that the concentration of sec-butylpyridine was present above the background level by a significant amount. More sec-butylpyridine was formed than n-butylpyridine from n-butane.

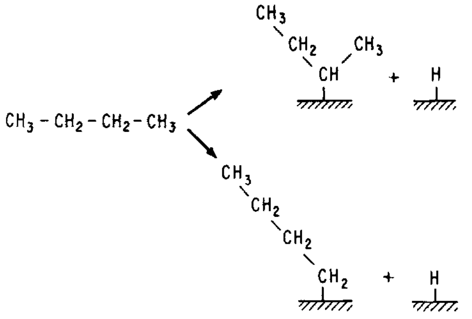
Blank tests for SiO_2 showed some inherent activity for hydrogenation and isomerization for the n-butenes, and no activity for n-butane hydrogenolysis and n-butene C–C bond scission. The addition of pyridine completely inhibited the SiO_2 blank activity altogether, and no alkyl-substituted pyridines were detected. No homologation was detected over SiO_2.

IV. DISCUSSION

The hydrocarbon distributions in Table 1 reveal that C–C bond scission, homologation, hydrogenation, and isomerization reactions occurred at 150°C. 2-n-Butylpyridine and 2-sec-butylpyridine formation establish that n-butyl and sec-butyl species can be scavenged from the Ru surface under reaction conditions. The distributions of C_4-substituted pyridines and the hydrocarbon product distributions are used to propose intermediates and mechanistic details over a ruthenium catalyst for the reactions listed above.

It is obvious from Table 1 that pyridine inhibited the C–C scission reaction which is well known to be sensitive to many kinds of perturbations to the catalyst (e.g., partial pressure of H_2 and particle size distribution) (*15–17*). The evidence here is insufficient to say whether pyridine poisoned or blocked surface sites for hydrogen adsorption or surface sites for hydrocarbon adsorption. It could be both.

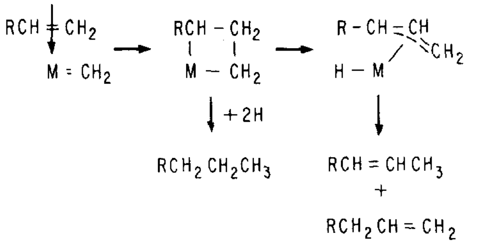
The data for n-butane in Table 1 show that butene isomers were formed after the addition of pyridine. Table 2 shows that for n-butane, both n-butyl and sec-butyl fragments exist on the surface in addition to the lower carbon number alkyl fragments. The C_4 alkyl fragments from n-butane are explained by Scheme 1 which represents the first step of n-butane hydrogenolysis over Ru. Osterloh *et al.* (*3*) have reasoned that both n-alkyl and branched alkyl species are formed via random C–H bond cleavage during n-octane hydrogenolysis over Ru/SiO_2 at 125°C. The scavenging results confirm the existence of the n-alkyl and branched alkyl species on the surface. (Our data do not reveal the subsequent reactions involved in the hydrogenolysis reaction.) 2-sec-Butylpyridine was detected at a higher concentration than 2-n-butylpyridine. One would expect n-butyl species to be scavenged more efficiently than sec-butyl species for steric reasons. The butylpyridine distribution seems to indicate that a higher concentration sec-butyl fragments formed on the surface than n-butyl fragments when n-butane reacted over Ru/SiO_2.



SCHEME 1

The results in Table 1 show that no homologation was observed for n-butane, whereas for n-butenes chain growth always occurred in the absence of pyridine and led to the formation of n-alkanes. Under some reaction conditions not reported here (e.g., at 300°C and H_2/n-butene of 5–6), n-alkenes were also formed. Similar results for 1-octene and n-octane were reported by Osterloh *et al.* (*3*), although no detailed analysis was given. The addition of pyridine to the system essentially stopped the homologation reactions; only 1-butene was found to produce a small amount of n-pentane.

The appearance of methane during the C_4 olefin reactions suggests that methylene was also present (*18*). Olefin homologation and C–C bond scission were both inhibited



SCHEME 2

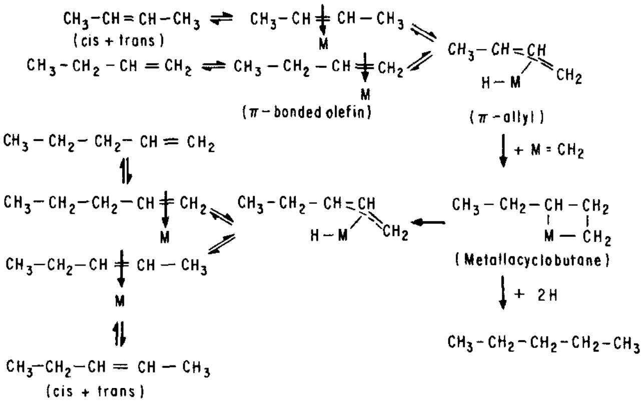
by the addition of pyridine. We propose that homologation may have decreased because methylene is needed in the homologation reaction and its concentration is reduced in the presence of pyridine.

O'Donohoe *et al.* (*18*) have proposed a mechanism for olefin homologation which is shown in Scheme 2. The reaction involves coupling an olefin with a surface methylene to form a metallacyclobutane which subsequently rearranges to the next higher olefin or is hydrogenated to the next higher alkane. They did not present details for the rearrangement or hydrogenation on a metal surface. Variations of this scheme have been presented. Hugues *et al.* (*19*) proposed a similar process leading to the metallacyclobutane with α-olefin formation proceeding via β-hydrogen transfer within the metallacycle.

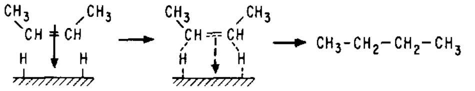
It is interesting to note the internal butenes did not react to any detectable amount of branched C_5 or C_6 products, in agreement with the results reported by Osterloh *et al.* (*3*). It has been proposed that the preferential formation of n-butenes versus isobutene during the coupling of surface methylene and propylene was due to the electrophilic character of surface methylene (*19*). This carbocationic character of surface methylene alone seems to be not enough to explain the preference of nonbranched homologous products from the internal butenes here. As an alternative to Scheme 2, we suggest that the butenes adsorb and transform into a common intermediate, perhaps a π-allyl. Scheme 3 summarizes the alternate homologation mechanism in which the π-allyl intermediate reacts with surface methylene to the next higher nonbranched alkane via a metallacyclobutane. In Scheme 3, M could be a single metallic atom or an ensemble of atoms.

The route to alkanes from the metallacyclobutane is unknown. It could involve stepwise hydrogenation of the metallacyclobutane or may proceed via a C_5 π-allyl which ultimately forms a C_5 π-bonded olefin. The π-bonded olefin being the species which undergoes hydrogenation. At 300°C we did observe *cis*- and *trans*-2-pentene from 1-butene, which is consistent with the metallacycle rearranging to a π-bonded olefin.

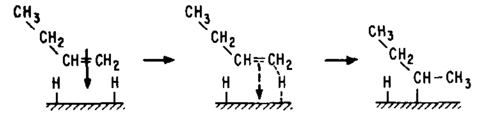
The hydrogenation of ethylene on nickel was explained in the Horiuti–Polanyi (*5*) mechanism to occur via an alkyl species.



SCHEME 3



SCHEME 4



SCHEME 6

This concept has been extended to explain hydrogenation of n-olefins of higher molecular weight. The data in Table 2 for 1-butene strongly suggest that there were n-butyl and sec-butyl species on the surface. On the other hand, the data for the internal butenes are quite different; no sec-butyl above the background level was found. It is very possible then that the hydrogenation of the internal butenes occurred by way of a reaction that does not involve the intermediate formation of sec-butyl species.

A possible explanation (Scheme 4), is that, for internal butenes, the electron density of the π-bonded olefin on the surface is evenly distributed at the two internal carbons such that the chemisorbed species would acquire two surface hydrogen atoms simultaneously. This type of reaction is similar to that proposed by Osborn *et al.* (*20*) for homogeneous hydrogenation (Scheme 5). π-Bonded ethylene has been reported over silica-supported Pt and Pd (*21*); the π-bonded ethylene was removed by hydrogen exposure.

In the case of 1-butene, the π-bonded olefin may undergo stepwise hydrogenation (Schemes 6 and 7), as a result of the asymmetric configuration of the π-complex. It is not possible to determine if the α-carbon reacted with surface hydrogen faster than the β-carbon. The higher concentration of n-butylpyridine than sec-butylpyridine in Table 2 could have been due to possible steric effects in which alkylation of pyridine is faster with n-alkyl species.

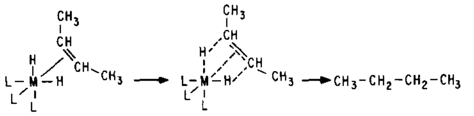
The origin of n-butylpyridine during the reaction of internal butenes is uncertain. 1-Butene was formed from the internal butenes. Some of the n-butyl species may have resulted during the hydrogenation of this 1-butene.

For the double-bond isomerization reaction, we favor the π-allyl intermediate mechanism of Chang *et al.* (*22*). They proposed that five surface species form from n-butenes, three π-bonded olefins, and *syn*- and *anti*-π-allyls. The interconversion is summarized in Scheme 8. We do not have direct evidence for the existence of π-allyl species in our system. Chang *et al.*'s study was over ZnO; scavenging experiments were performed over ZnO at 300°C in the absence of H_2 where butene isomerization is rapid. No scavenged products were detected over ZnO which could mean that pyridine can not be alkylated over ZnO at 300°C and/or that pyridine is not alkylated by π-allyls. Furthermore, sec-butyl species are never detected when reacting the internal butenes suggesting that isomerization does not proceed via sec-butyl species.

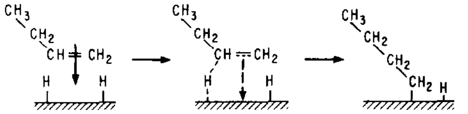
V. CONCLUSIONS

Pyridine inhibits overwhelmingly hydrogenolysis and C–C bond scission allowing one to observe both hydrogenation and isomerization of n-butenes over Ru/SiO_2 at relatively high temperatures.

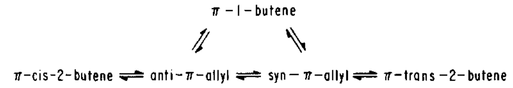
The pyridine scavenging data for n-butane hydrogenolysis indicate that sec-butyl fragments formed more preferentially than n-butyl fragments on the surface. This supports the model for hydrogenolysis sug-



SCHEME 5



SCHEME 7



SCHEME 8

gested by Osterloh *et al.* (*3*) who concluded, using statistical distribution arguments, that n-alkyl and branched alkyl species formed via random C–H bond cleavage.

Both an unsaturated carbon–carbon bond in the hydrocarbon reactant and methylene are required for homologation to occur. π-Allyls on the surface were proposed as a common intermediate formed from the n-butenes which react with methylene. The resulting metallacyclobutane was suggested to be responsible for the formation of nonbranched homologation products.

The Horiuti–Polanyi mechanism involving an intermediate alkyl species was proposed for the hydrogenation of 1-butene due to the asymmetric configuration of the olefin. A multicentered intermediate was suggested for the hydrogenation of the internal butenes. This arises from the fact that no sec-butyl fragments were scavenged by pyridine when reacting *cis*- and *trans*-2-butene and the fact that a similar kind of multicentered intermediate forms in the case of homogeneous hydrogenation of olefins.

The three π-bonded olefins of the n-butenes and the two π-allylic intermediates, proposed by Chang *et al.* (*22*), were used to explain the isomerization reaction. The two π-allylic intermediates are not distinguishable when reacting with methylene during the course of homologation.

ACKNOWLEDGMENTS

The authors acknowledge the helpful comments of Dr. E. P. Kyba of the University of Texas. Clyde N. Clubb synthesized the butylpridine standards. This work was supported by a grant from the Dow Chemical Company Foundation and funds from the University Research Institute of the University of Texas.

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