JOURNAL OF CATALYSIS 12, 72–83 (1968)

Formation of Dimeric Products during the Steady State Hydrogenation of Ethylene over Nickel

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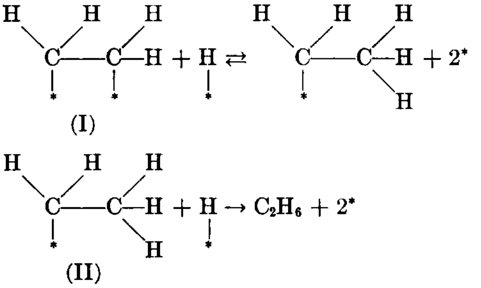
Received May 28, 1968; revised July 2, 1968

Analysis of products of the steady state ethylene hydrogenation over reduced nickel oxide reveals a steady state production of C_4 hydrocarbons. Such C_4 products are not formed from ethylene alone. The relative yield of dimers is enhanced by the presence of chemisorbed hydrogen. The distribution of C_4 products is a sensitive function of the H_2/C_2H_4 ratio in the reactant stream. As this ratio approaches zero, the ratio of *cis*- to *trans*-2-butene exceeds 10. These results, coupled with a parallel study of 1-butene isomerization, suggest that a species CH_3CH bound to either a single surface site by a double bond or to two sites by single bonds is a reactive species present during ethylene hydrogenation.

Introduction

Catalytic hydrogenation of ethylene (and *mutatis mutandis* other olefins) over metals apparently involves the following sequence of reactions (*1–4*):



In the reaction scheme the * stands for a surface atom. Although other steps may also be involved (*5*) the 1,2-disadsorbed ethylene (or π-complex) (I) and the adsorbed ethyl radical (II) are sufficient to explain results obtained both for the reaction of ethylene with hydrogen or deuterium and for exchange processes with ethane.

Infrared studies of adsorbed species on supported metallic catalysts provide support for the existence of the above species (*6, 7, 8*). In addition, however, these studies suggest that species containing trisubstituted CH groups (A) as well as C_4 hydrocarbons (B) are also present on the surface. [Such conclusions are not unequivocal (*8*).] Supporting evidence for the existence of such species is supplied by the observations that adsorption of ethylene on a bare metal surface is accompanied by self-hydrogenation (*9, 10*) and reduction with hydrogen of the residues formed thereby can give rise to C_4 hydrocarbons (*11*). It should be emphasized, however, that the occurrence of such reactions on adsorption and the existence of A and B on the surface need have no direct bearing on the reactions occurring during steady state hydrogenation over metallic catalysts: published evidence (*1, 4*) indicates A and B function as essentially inert residues and (I) and (II) are the true intermediates in hydrogenation reactions. In particular, this writer knows of no reports of C_4 hydrocarbons (formed from B) among the products of the steady state hydrogenation of ethylene over metals.

Despite the lack of evidence there is reason to suppose that if (II) exists under steady state conditions, some C_4 and perhaps C_6 products should be produced. In general, reactions of ethyl radicals include dimerization, even for radicals formed in solid olefins (*12*) or in the adsorbed state (*13*). It is true that under some conditions (*14*) the adsorbed radical may add hydrogen in preference to dimerization, but the formation of dimers is always observed. Of course, the formation of the metal bond to (II) may curtail the dimerization reaction, but recent studies (*15*) with homogeneous catalysts show that when (I) and (II) are both bonded to a metal in a complex, dimerization can occur. Such dimerization has been observed with complexes of rhodium (*15*), nickel (*16*), and palladium (*17*). These reactions have been explained on the basis of species similar to (I) and (II) reacting via an insertion reaction (*15*). [Studies of butene isomerization, however, indicate that compounds of rhodium may follow a different reaction path than that for nickel and palladium compounds (*18*, *19*, *20*).]

In this paper we report on the production of dimeric products during hydrogenation of ethylene over nickel catalysts. We chose nickel catalysts for this study because of the volume of data available for this catalyst on catalytic hydrogenation of ethylene,* chemisorption of ethylene (*9*, *10*), and its infrared spectra (*6*). We chose an unpromoted catalyst because the unreduced supported catalyst on silica-alumina (*21*, *22*) or silica (*23*, *24*) can bring about polymerization due to acid-type reactions. Although yields of dimer during catalytic hydrogenation are small compared to that of ethane, they are produced in the steady state competitively with ethane. Accordingly, from the nature of these dimeric products, we can deduce something about the intermediates from which they stem.

EXPERIMENTAL

Four catalysts were used in this study: IA, IB, IIA, IIB. All were nickel oxide samples prepared by the procedure of Best and Russell (*25*). Samples I and II refer to different preparations of nickel oxide; the letters A and B refer to different samples of the indicated batch. Adsorptive properties of this catalyst have been described. (*26*).

All four catalyst samples weighed 2 to 3 g. In a typical reduction procedure, a stream of hydrogen dried by passage through a liquid nitrogen trap (except for IIB) at a flow of about 100 cc/min was passed through the catalyst at room temperature. The temperature of the catalyst was then raised slowly until water appeared in the cool portion of the exit tube (usually between 150° and 200°C). The hydrogen flow was increased and when water was no longer evident in the exit tube, the temperature was raised in further stages to about 250°C. Except for the first part of this initial stage, water was not observed in the exit tube. After the initial stage, samples IA and IB were reduced an additional 16 hr at 360°C and then for 1 hr at 500°C. After the initial stage, samples IIA and IIB were reduced for 4 hr at 300°C followed by an additional 2 hr at 360°C. All catalysts were rereduced at the completion of a series of runs at about 350–375°C for 2 hr and either evacuated for 1 hr at reduction temperature or cooled in the hydrogen stream.

Both 1-butene and ethylene were C. P. grade hydrocarbons used without further purification.

Activity runs, mostly at 25°C, were made at a flow of hydrocarbon reactant of 6 to 7 cc STP/min. The flow of reactant hydrogen was varied to give hydrogen to olefin ratios (H_2/ol) from roughly 0 to 3. It is believed that the molar ratio, H_2/ol, was accurate to about 0.02. Under these conditions the hydrogenation reaction was complete within experimental error. This resulted in an excess of unreacted olefin in the effluent when H_2/ol was less than 1 and an excess of hydrogen when H_2/ol was greater than 1.

A steady state for ethylene hydrogenation was assumed to be established when samples of effluent, taken at intervals of 25 ± 5 min, agreed within experimental error. With a freshly reduced catalyst several hours were required to establish a steady state; with a "lined-out" catalyst the steady state was established within 30 min (except near $H_2/\text{ol} = 1$). Accordingly, only occasional duplicates were run and the validity of the assumed steady state was established by agreement of results for both decreasing and increasing H_2/ol over a 12-hr period. In a few cases runs for as long as 50 hr yielded

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* See refs. (*2*), (*5*), and (*28*) for leading references.

comparable results (±10%) for initial and final points. Poisoning was not encountered when the catalyst was exposed to pure ethylene.

With 1-butene hydrogenation a procedure paralleling that used for ethylene hydrogenation was used. Isomerization activity showed a dramatic change as the steady state was being established and a period of 4 to 6 hr was required for a freshly reduced catalyst to line out. For a fresh catalyst the ratio of isomerized butenes to butanes was greater than unity at H_2/ol ≈ 0.1, but for a "lined-out" catalyst this dropped to about 0.25 even though the catalyst still gave complete hydrogenation. Once the catalyst stabilized, the selectivity stayed steady for days. Prolonged exposure to pure 1-butene did poison the hydrogenation activity for a short period of time, but both this activity and the "lined-out" selectivity were restored by exposure to a pure hydrogen stream at room temperature.

Under conditions of maximum reaction, the peak temperature of the catalyst bed was about 10°C above the ambient temperature. In both ethylene and 1-butene runs no reaction was observed in the absence of hydrogen. For the ethylene hydrogenation experiments a series of runs on an empty reactor carried through the same pretreatment as the catalyst revealed no reaction.

Analyses were carried out on an 8-cc sample of effluent (~1 cc for 1-butene runs) using either a dimethyl sulfolane or isoquinoline column for C_4's and alumina for ethane-ethylene. A few check runs on the identity of the C_4's were made on a silver-glycol column. Normally, a thermal conductivity cell with an amplified output was used as a detector, but a few check runs were made with a flame-ionization detector.

RESULTS

Figures 1 and 2 show the amounts of C_4 product in 8 cc of effluent from the hydrogenation of ethylene over the catalyst IIB cooled in hydrogen after the initial reduction. Open symbols refer to values obtained for decreasing H_2/C_2H_4 after the catalyst "lined-out"; solid symbols refer to points obtained on increasing H_2/C_2H_4 after the runs with pure ethylene. The total time required to decrease the ratio to 0 and increase it to 0.85 was about 12 hr. At this point ($H_2/C_2H_4 = 0.85$) the catalyst was kept on stream overnight; hence, solid points at 0.85 or above represent data taken after 24 hr on stream. The drift in 12 hr is noticeable for the *cis* and *trans* isomers (Fig. 2: note arrows) but not for 1-butene and butane.

Qualitatively, the yields of C_4 products for all four catalysts are similar regardless of pretreatment. For H_2/C_2H_4 greater than unity only butane is found. As the ratio H_2/C_2H_4 is decreased butane goes through a sharp maximum at unity; below unity the yield of butenes exceeds the yield of butane. At the highest H_2/C_2H_4 ratios for which butenes are observed the more stable thermodynamic *trans* isomer is the major butene; for lower ratios *cis*-butene is the dominant product.

Results similar to those in Fig. 1 and 2 are shown in Fig. 3 for catalyst IB pretreated in a different manner: catalyst IB was reduced about 140°C higher and was evacuated at 350°C rather than cooled in hydrogen. Qualitatively, the shapes of these curves are much the same as those for catalyst IIB. (Note that butane and 1-butene were combined in the plot.) It is noteworthy, however, that yield of C_4 products from catalyst IB is nearly an order of magnitude less than that for catalyst IIB. In part, this may be due to changes in the specific nature of the adsorbed layer with crystallite size similar to that observed for nitrogen on nickel (*26*, *27*), but the largest part of the change is due to the promoting effect of high temperature-chemisorbed hydrogen (*28*, *29*). Table 1 presents a summary of results illustrating this effect. In order to show the precision of the data, we have given error limits for those runs done in duplicate. In general, re-reduction and the consequent sintering (*26*) causes a progressive decrease in the yield of C_4 products for samples pretreated in the same way: compare first and third or second and fourth rows for each H_2/C_2H_4 ratio. The effect of sintering, however, is small compared to the effect of pretreatment: compare rows 1 and 2 or 3 and 4

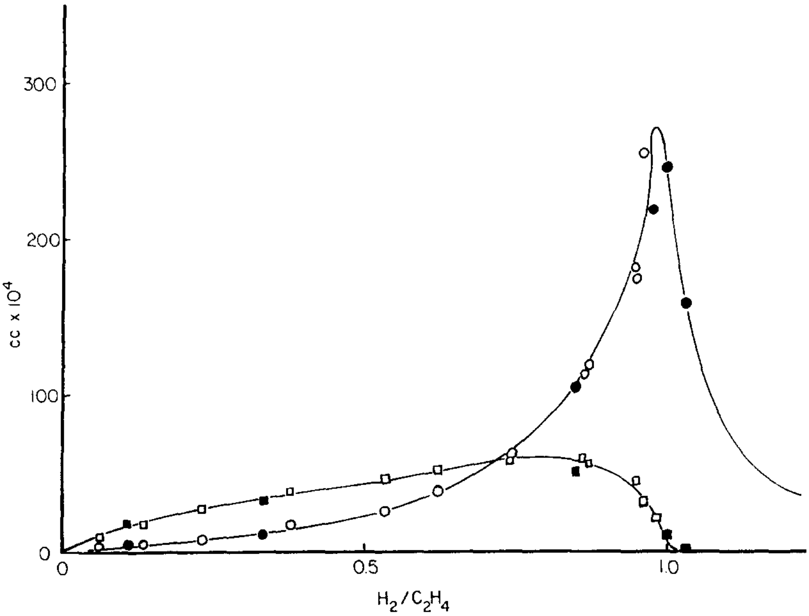

FIG. 1. Butane (circles) and 1-butene (squares) in 8 cc of effluent from hydrogenation of ethylene over catalyst IIB cooled in hydrogen as a function of H_2/C_2H_4.

for each H_2/C_2H_4 ratio. It appears that reduction of IIB and the accompanying sintering produce a catalyst that (if evacuated at high temperature) yields C_4 products only 50% greater than that from IB. By way of summary, the average of all the dimer yields was 0.91 ± 0.07% of the product for IIB (hydrogen-cooled) versus 0.23 ± 0.05% for IIB (evacuated). For sample IB (evacuated) the yield was 0.13 ± 0.01%.

Both reactions leading to dimers and to ethane require the presence of hydrogen and in this sense, they are competitive reactions.

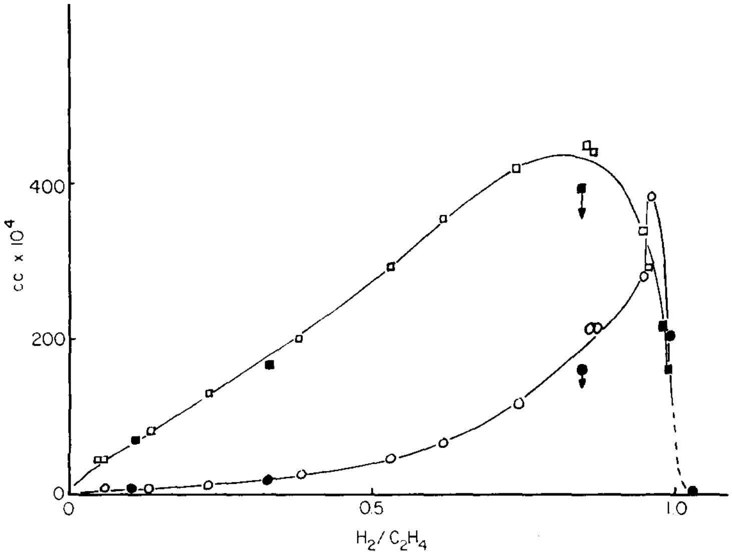

FIG. 2. *cis*-Butene (squares) and *trans*-butene in 8 cc of effluent from hydrogenation of ethylene over catalyst IIB cooled in hydrogen as a function of H_2/C_2H_4.

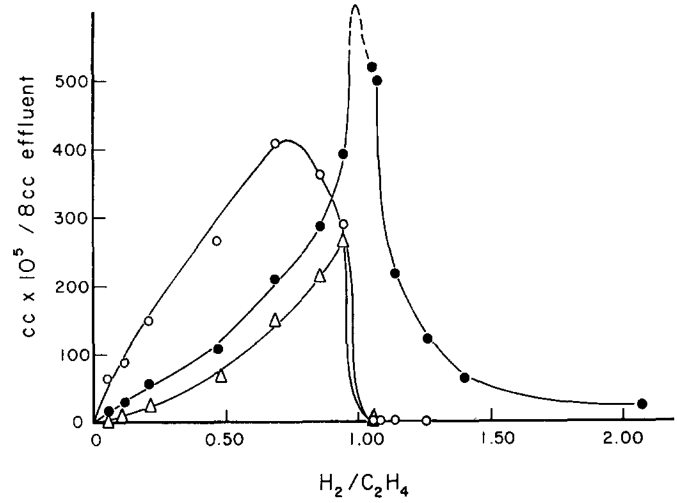

FIG. 3. Butane plus 1-butene (solid circles), *cis*-butene (open circles), and *trans*-butene (triangles) in 8 cc of effluent from the hydrogenation of ethylene over catalyst IB evacuated at the reduction temperature as a function of H_2/C_2H_4.

Figure 4 shows a plot of the ratio of dimeric products to the ethane produced. Open and filled symbols have the same significance as before. Roughly speaking, the relative yield of butane and *trans*-butene approach zero as the H_2/C_2H_4 ratio goes to zero whereas *cis*-butene and 1-butene approach nonzero values. In other words, reaction paths leading to butane and *trans*-butene do not compete (successfully) for hydrogen with paths leading to ethane, whereas paths leading to 1-butene and *cis*-butene do compete successfully.

In a few cases the effluent gas was checked

TABLE 1

EFFECT OF PRETREATMENT ON YIELD[a]

H_2/C_2	Pretreat.	Total C_4	C_4H_{10}	$1\text{-}C_4H_8$	*trans*	*cis*	*cis/trans*
0.91	r + H[b]	775	150	45	240	340	1.41
0.91	r + e[b]	213	61 ± 3	12 ± 1	65 ± 2	75 ± 1	1.15
0.91	r + H[b]	627	128 ± 2	38 ± 1	200 ± 1	261 ± 3	1.30
0.91	r + e[b]	136	44 ± 2	7 ± 1	39 ± 1	46 ± 1	1.18
0.91	r + e[c]	91	35		24	32	1.32
0.50	r + H[b]	377	22	45	40	270	6.8
0.50	r + e[b]	122	13 ± 1	21 ± 1	21 ± 2	67 ± 5	3.2
0.50	r + H[b]	310	25 ± 1	45 ± 1	35 ± 1	205 ± 3	5.9
0.50	r + e[b]	75	9.0 ± 1	14 ± 1	12 ± 1	40 ± 1	3.3
0.50	r + e[c]	49	12		8	29	3.6
0.23	r + H[b]	172	6	29	9.5	127	13.4
0.23	r + e[b]	—[d]	—[d]	—[d]	—[d]	—[d]	—[d]
0.23	r + H[b]	160	5.0 ± 1	29 ± 1	10 ± 1	116 ± 5	11.6
0.23	r + e[b]	35	4.0 ± 1	10 ± 1	3.4 ± 0.3	17.6 ± 2	5.2
0.23	r + e[c]	26	6.5		3	17	5.7

[a] Yield expressed as 10^4 × cc STP/8 cc of effluent.

[b] Sample IIB: reduced and evacuated at 375°C (r + e) or reduced at 375°C and cooled in the hydrogen stream (r + H).

[c] Sample IB: reduced at 500°C and evacuated at 360°C.

[d] Not run.

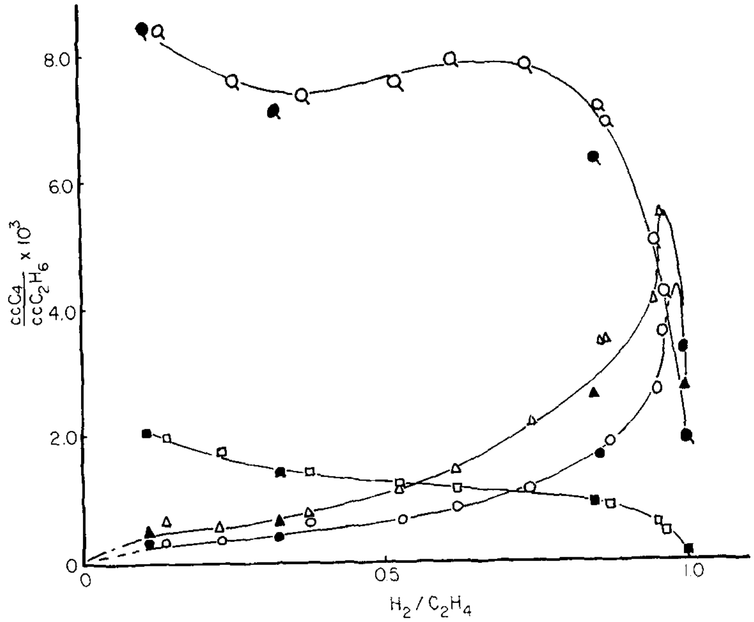

FIG. 4. Ratio of C_4 to ethane products in ethylene hydrogenation as a function of H_2/C_2H_4 over catalyst IIB cooled in H_2: ᑫ, *cis*-butene; △, *trans*-butene; ○, butane; □, 1-butene.

for C_6 hydrocarbons. They were detected but were generally only 2% to 3% of the C_4 products. No detailed analysis of C_6 hydrocarbons was carried out.

Formation of *cis*- rather than *trans*-butene is remarkably selective. Data for the ratio of *cis* to *trans* versus H_2/C_2H_4 is shown in Figs. 5 and 6. It can be seen that for hydrogen-cooled catalysts this ratio approaches 15 to 20 as the hydrogen in the reactant

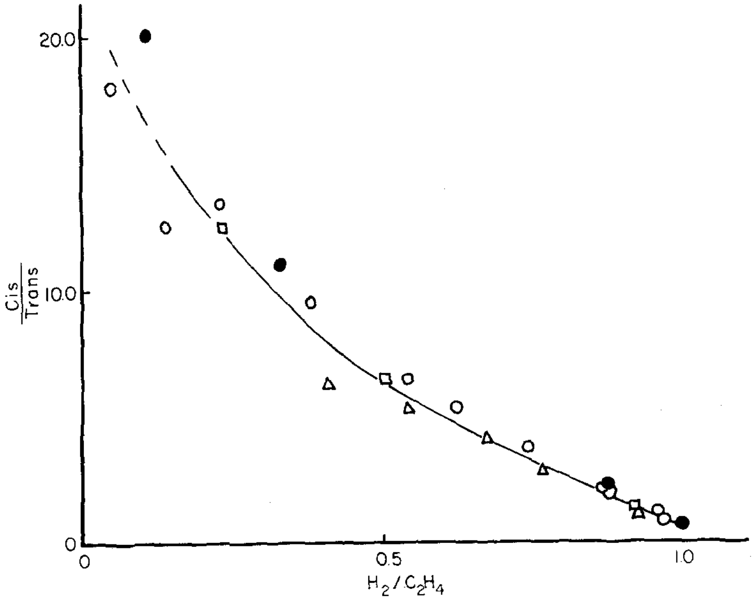

FIG. 5. Ratio of *cis*- to *trans*-butene formed during ethylene hydrogenation for catalysts cooled in hydrogen as a function of H_2/C_2H_4: △, catalyst IIA, rereduced 4×; ○, catalyst IIB after first reduction; □, catalyst IIB, rereduced 2×.

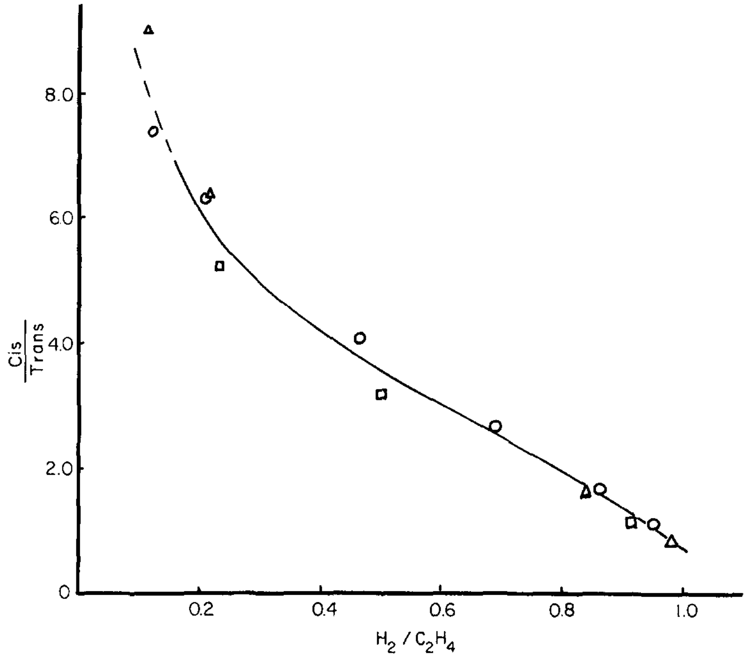

FIG. 6. Ratio of *cis*- to *trans*-butene during ethylene hydrogenation over catalysts evacuated at reduction temperature as a function of H_2/C_2H_4: △, catalyst IA, rereduced 4×; ○, catalyst IB, freshly reduced; ☐, catalyst IIB, freshly reduced.

approaches zero. For catalysts without chemisorbed hydrogen, i.e., evacuated at reduction temperatures, the ratio is somewhat lower but still remarkably high, i.e., about 10 as H_2/C_2H_4 approaches 0. It is noteworthy that this ratio depends almost exclusively on the presence or absence of chemisorbed hydrogen rather than the degree of sintering of the catalyst. For example, data in Table 1 showed the overall yield of dimer decreased when the catalyst was subjected to several re-reductions. By way of contrast the *cis–trans* ratio remains relatively constant for all catalysts cooled in hydrogen irrespective of the severity of reduction. This observation receives further support from the data in Fig. 6 insofar as the *cis–trans* ratio for catalysts IIB and IB are essentially the same, whereas the dimer yields differ by about 50% (Table 1).

Figure 7 shows the effect of temperature on dimer yield. Over the range studied the yield increases by about an order of magnitude. This may be related to the observation [based on infrared studies (*30*)] that the adsorbed phase in the presence of hydrogen contains a higher concentration of dimeric species at higher temperatures.

It is conceivable that these high *cis–trans* ratios could be characteristic of butene isomerization in a hydrogen-poor system. Results of a brief study of the isomerization

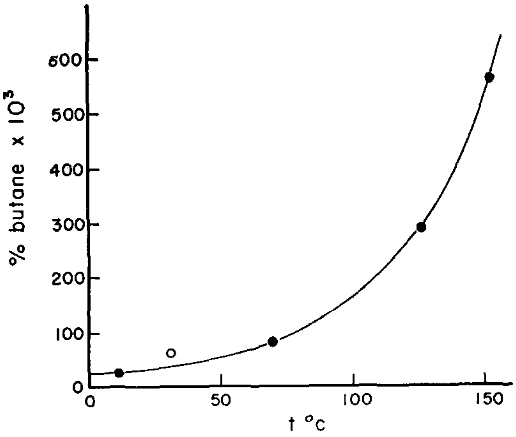

FIG. 7. Effect of temperature on yield of butane during ethylene hydrogenation over catalyst IB evacuated at reduction temperature for H_2/C_2H_4 = 1.04.

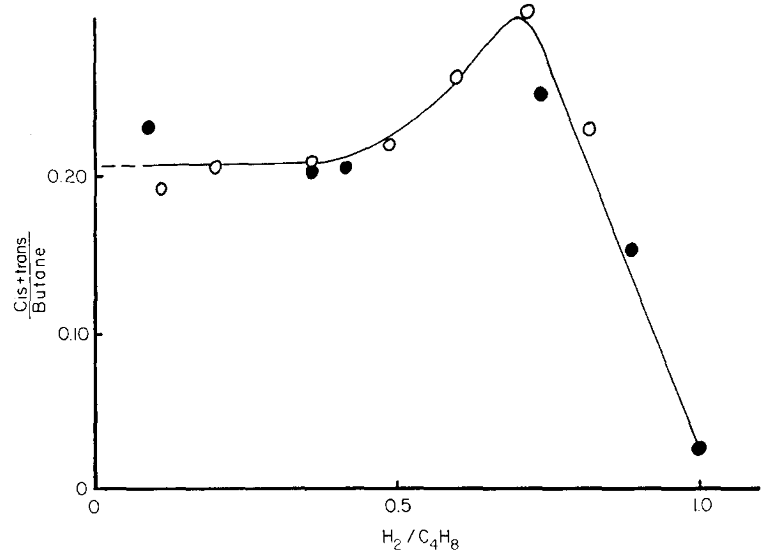

FIG. 8. Ratio of *cis*- + *trans*-butenes to butane during hydrogenation of 1-butene over catalyst IIA (rereduced 2×, cooled in hydrogen) as a function of H_2/C_4H_8.

of 1-butene as a function of $H_2/1\text{-}C_4H_8$ are summarized in Figs. 8 and 9. Data symbolized by open circles were obtained in one 10 hr period; data symbolized by closed points were obtained the next day after the catalyst had been purged at room temperature in a stream of hydrogen overnight. Figure 8 illustrates the competition between butene isomerization and hydrogenation. Clearly, the isomerization competes successfully with the hydrogenation reaction and goes to zero as H_2/C_4H_8 goes to zero. (We estimate that the isomerization rate at a H_2/C_4H_8 ratio of 0.5 is at least 500 times as fast as in the absence of hydrogen.)

The *cis–trans* ratio versus H_2/C_4H_8 is plotted in Fig. 9. This ratio does increase in favor of *cis* in the olefin-rich region and is in fact somewhat higher than values reported for the initial products from hydrogenation

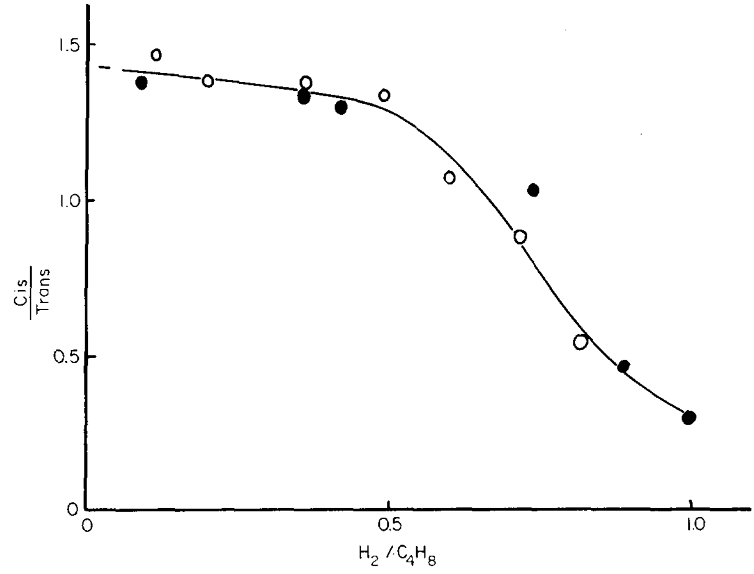

FIG. 9. Ratio *cis* to *trans* during hydrogenation of 1-butene from Fig. 8 as a function of H_2/C_4H_8.

of 1-butene with excess hydrogen (*1*). Nevertheless, this ratio is still an order of magnitude less than that found in the dimeric product from ethylene.

The effect of excess ethylene on the isomerization of butene may be different from the effect of excess butene. Some evidence that this difference is not great is supplied by the following experiment. First, a catalyst was "lined-out" with a H_2/C_2H_4 flow of 0.5. This run yielded a *cis–trans* ratio of 3.3 for the dimer product. Then a small amount of 1-butene was bled into the reactant flow. (This small amount was about 30 times the yield of C_4 dimer.) The effluent then yielded much more *cis-* and *trans*-2-butene, but the *cis–trans* ratio was slightly greater than 1.0. Thus, even in the presence of excess ethylene, isomerization of 1-butene yields a *cis–trans* ratio comparable to that found in the absence of ethylene and does not give the high ratios characteristic of the dimers formed during ethylene hydrogenation.

DISCUSSION

Dimer formation is so selective that it puts severe restrictions on the nature of the reactive species which give rise to dimers. The following seem clear:

(a) *cis*-2-Butene does not arise from isomerization of 1-butene. If it did, more of the *trans* isomer would be formed.

(b) If, as is usually supposed, isomerization of 1-butene in the presence of hydrogen involves a secondary butyl radical as an intermediate, the selective *cis*-butene formation cannot arise from a pathway which has a secondary butyl radical as an intermediate.

(c) Since *cis–trans* isomerization is faster than double-bond migration over nickel and the *cis–trans* ratio is far from equilibrium, 1-butene is not formed from the *cis*-butene or via a secondary butyl radical. It must arise from an independent pathway.

(d) Butane and *trans*-butene are formed by pathways that involve hydrogen but are *not* competitive with ethane formation as the hydrogen concentration goes to zero.

(e) *cis*-Butene and 1-butene are formed by pathways that involve hydrogen but are competitive with ethane formation as the hydrogen goes to zero.

Several possibilities that do or can yield high *cis* to *trans* ratios were considered. [It can be argued that perhaps the dimers are formed by unreduced catalyst. If this were so, one would expect *cis–trans* ratios less than unity (*23*, *24*).] Polymerization of acetylenes can yield *cis–trans* ratios as high as 10 over iridium.* We rule this out because 1-butene is the major C_4 olefin formed whereas we find it is a minor component of the dimeric olefins. Hydrogenation of 1,2-butadiene can give rise to large *cis–trans* ratios (*31*) over palladium, but the yield of 1-butene is again high so formation of 1,2-butadiene as an intermediate is regarded as unlikely. Dimethyl acetylene (*31*) yields *cis*-2-butene quite selectively, but pathways directly to *cis*-butene seem more likely than pathways via adsorbed dimethyl acetylene. Mechanisms related to the π-complex insertion mechanism proposed for homogeneous catalysts are attractive. The *cis*-π complex is more stable (*1*), and this can lead to a preference for formation of the *cis* isomer (*18*), but the preference does not seem great enough to account for the observed ratios. Mechanisms based on π-type complexes (over acidic oxides) yield maximum *cis–trans* ratios of 5 (*32*, *33*) for 1-butene isomerization.

Recently, π-allyl complexes have been proposed as intermediates for butene isomerization (*34*) in the absence of hydrogen. This would be an attractive possible intermediate for preferential *cis*-butene formation provided the anti-isomer were the more stable. Unfortunately, it is not the stable form in inorganic complexes and isomerizes readily to the *syn* form; hence, even a 50:50 mixture of the *syn* and *anti* form decomposes to yield *cis–trans* ratios of about 1:18 (*35*, *36*).

We believe the results can be explained by the following sequence of surface reactions and reasonably fast adsorption–desorption steps:

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* Reference (*5*), p. 289.

$CH_2{\cdot}CH_2 + H \rightleftarrows CH_3CH_2 + 2^*$ fast (1)

$CH_3CH_2 + H \rightarrow C_2H_6 + 2^*$ slow (2)

$^* + C_2H_5 \rightarrow CH_3{\cdot}CH + H$ slow (3)

$^* + CH_3{\cdot}CH \rightarrow CH_2{\cdot}CH_2$ fast (4)

$2CH_3CH \rightarrow cis\text{-}CH_3{\cdot}CH{\cdot}CH{\cdot}CH_3$ slow (5)

$cis\text{-}CH_3{\cdot}CH{\cdot}CH{\cdot}CH_3 + H \rightarrow CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_3 + 2^*$ fast (6)

$2^* + CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_3 \rightarrow$ *cis*, *trans*, 1-butene $+ H$ fast (7)

$H + CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_3 \rightarrow C_4H_{10} + 2^*$ slow (8)

$CH_3{\cdot}CH_2 + CH_2{\cdot}CH_2 \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2 + 2^*$ slow (9)

$2^* + CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2 \rightarrow CH_3{\cdot}CH_2{\cdot}CH{\cdot}CH_2$ (1-butene) $+ H$ fast (10)

In the above sequence of reactions, all unsaturated carbon atoms are bound to a single site by σ-bonds. We write CH_3CH as bound to a single site by a double bond. We also make the assumption that the steady state concentration of C_2H_5 is determined by (1) and that the steady state concentration of CH_3CH is determined by (3) and (4). With the additional assumptions that the concentration of empty sites is either fixed or determined primarily by the ethylene adsorption, it can be shown that the above sequence of reactions is consistent with experiment insofar as it predicts:

(a) Yields of butane and *trans*-butene relative to ethane should go to zero as the hydrogen concentration goes to zero.

(b) Relative yields of *cis*-butene to ethane should approach a constant value as the hydrogen concentration goes to zero.

(c) Relative yields of 1-butene to ethane should increase as the hydrogen concentration goes to zero.

In other words, if we assume the existence of the species, CH_3CH, which will react selectively to form adsorbed *cis*-butene, a consistent description of the results can be made on the basis of reasonable assumptions. This consistency does not require that olefins are bound as a 1,2-diadsorbed species or that $CH_3{\cdot}CH$ occupy only one site. Admittedly, the analysis is oversimplified, but the consistency is encouraging.

The species CH_3CH (III) is assumed to have the structure shown in Fig. 10a. We assume that normally the C–CH_3 bond is nearly perpendicular to the surface and the hydrogen atom approaches the surface quite closely. This view is in line with the observation that *cis*-2-butene is favored over *trans*-2-butene in the hydrogenation of 1,2-butadiene (*31*). Such species have been suggested before (*4*, *33*, *37*) in connection with exchange reactions of cyclic hydrocarbons. Eley (*4*) suggested it may be the dominant species at high coverages since it may require only one surface site, doubly bonded. Little (*8*) has offered an interpretation of the infrared spectra of adsorbed hydrocarbons in which this species also plays a role.

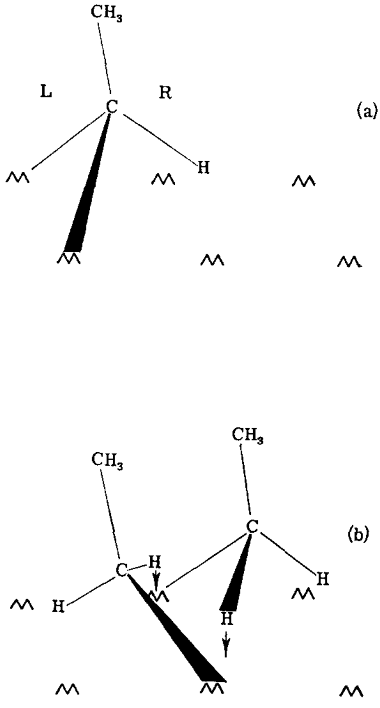

FIG. 10. Possible intermediates.

Recently, it has been suggested by Chatt (*19*a) that such a species may be an intermediate bound to palladium in the homogeneous isomerization of olefins. Such a species also provides an explanation (*38*) of the fact that in ethylene oxidation in solution catalyzed by $PdCl_2$, all the hydrogens in the resultant acetaldehyde are those originally present in the ethylene.

Dimerization of species (III) would result in a 2-butene. The approach can be L to L, L to R, or R to R. Of these, the first seems most likely since this would involve the minimum amount of motion to form a double bond and would rotate hydrogen atoms rather than methyl groups toward the surface. Presumably, during the formation, as the double bond formed there would be a rotation around it of the molecule as a whole to yield an olefin π-complexed to the surface. This olefin would have the *cis*-2-butene configuration. The same argument holds if CH_3CH is double-bonded to a single site.

It is also conceivable that dimerization could proceed by a step in which all four bonds to the surface were in the same plane. Provided the specified orientation was kept, formation of a *vic*-diadsorbed alkane in this configuration would yield *cis*-butene on reversion to the olefin.

Other schemes could, of course, accomplish this same result. For example, it is possible that there could be a concerted reaction of two adsorbed ethyl radicals, as shown in Fig. 10b. This also would be consistent with data in Fig. 4. We believe the reaction involving species (III) is the more likely, however, since this concerted mode of attack on ethyl radicals, if it occurred on only one bond, could lead to a secondary butyl radical which should yield *trans*-butene.

Among the proposed reactions, a path to butane via dimerization of ethyl radicals was not included. This reaction was excluded because on the basis of our rough analysis of such a kinetic sequence, this would lead to a path for butane which would compete successfully for hydrogen with ethane. Since the experimental data did not yield this result, we suggest that the principal source of butane was the path which would not compete successfully with ethane.

Studies of the composition of the adsorbed layer on nickel with and without chemisorbed hydrogen led Hall and Hassell (*28*) to the conclusion that on nickel *without* chemisorbed hydrogen: ". . . larger quantities of ethylene are held less tenaciously by the more active surface." In line with this it appears that self-hydrogenation may be promoted by the presence of chemisorbed hydrogen, which leads to more tenaciously held ethylene, even though its presence decreases the activity for ethylene hydrogenation. Thus, the promoting effect of chemisorbed hydrogen probably arises from two effects. First, chemisorption of hydrogen suppresses the slow step in ethane formation, addition of hydrogen to (II), and allows dimer-producing paths to compute more effectively with ethane formation. Second, the chemisorption of hydrogen enhances strong interaction of ethylene with the surface, and increases the rate of step (3); this leads to a higher steady state concentration of (III) and a faster rate of dimer formation.

In conclusion, we would like to note that we recognize the speculative nature of the analysis of the results of these experiments. This is especially true of arguments based on kinetic analysis of the data for such a complex experimental procedure. Nevertheless, the selective formation of dimers during the steady state hydrogenation of ethylene provides a probe to explore the nature of reactive species on the surface. To dismiss the dimers because they are a minor product is to dismiss information on a system about which we know relatively little.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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