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Mechanism of the Isomerization of 1-Alkene during Iron-Catalyzed Fischer–Tropsch Synthesis

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The deuterium/hydrogen exchange reaction was performed under iron-catalyzed Fischer–Tropsch reaction conditions using a mixture of deuterated octane, nonane, decane, tridecane, and pentadecane as the probes. The results indicated that deuterium/hydrogen exchange does not occur in alkanes under these conditions. Under the same reaction conditions, 1-octene-d_{16} was used as the probe to study the isomerization of 1-alkene. The 1-octene-d_{16} was reduced to deuterated octane, and isomerized to deuterated *trans*-2-octene and *cis*-2-octene with approximately equal amounts of the two isomers. No other internal deuterated octene and C_7 products were obtained. The deuterium/hydrogen exchange reaction occurred in deuterated 1-octene as well as in the products formed from it. The maximum number of deuterium atoms that can be replaced by hydrogen is 5. There is no C_8D_{16} isotopomer of 2-octenes. To account for these experimental facts, a mechanism was proposed for the isomerization of 1-alkene under iron-catalyzed Fischer–Tropsch reaction conditions. © 2001 Academic Press

Key Words: **deuterium; Fischer–Tropsch synthesis; iron catalyst; isotopic tracer; isomerization, alkene.**

INTRODUCTION

In studying the mechanism of Fischer–Tropsch (FT) synthesis, isotopic tracer techniques have been widely used and, based on the results, several very important conclusions have been reported (1–9). The most frequently used isotopes in FT reactions are carbon-14- and carbon-13-labeled compounds. Almost all of the possible carbon-14- and carbon-13-labeled compounds suitable for studying the mechanism of FT reactions, such as alcohols, alkenes, CO, CO_2, aldehyde, and many others, have been used as probes (10). Compared to the number of carbon-14 and carbon-13 tracer experiments, very few deuterium tracer experiments have been conducted to study the mechanism of FT reactions.

Kruykov and co-workers used ^{14}C- and deuterium-labeled aldehyde and ethanol to study the H/D exchange between these two compounds under FT reaction conditions (11, 12). They found that there was a H/D exchange between the aldehyde and ethanol, but they did not use those probes to further study the details of the mechanism of FT reactions. It has been reported (13–17) that when H_2 was replaced by D_2 to hydrogenate CO, an inverse kinetic isotope effect was obtained. Most of the deuterium tracer experiments conducted so far have not addressed the key mechanistic problems of the FT reactions, such as the readsorption of 1-alkene. Miller and Moskovits (18) used ethylene to study the mechanism of the FT reaction and found that the deuterium from the deuterated ethylene was incorporated into the alkanes and alkenes almost entirely as CD_2 units. The authors published their results in a note in 1989; however, further details of this study have not been published since that time.

Recently, we have reported that product hold-up has a very important impact on the data interpretation in isotopic tracer studies of FT reactions (19, 20). We reported that due to the nature of isotope tracer experiments in FT synthesis, this product accumulation factor could be minimized, but could not be removed completely in ^{14}C tracer studies. Because of this, the deuterium tracer technique becomes an attractive alternative.

The belief that H/D exchange might occur under FT reaction conditions (8) is the main reason why just a few deuterium tracer experiments have been conducted even though the deuterium tracer technique is one of the most frequently used methods in homogeneous organic reactions. It is surprising that no experiment has been performed to show whether there is a H/D exchange reaction among the major products under FT reaction conditions. If there is no H/D exchange in alkanes, it will be possible to study the chemical behavior of 1-alkene under FT reaction conditions using the deuterated 1-alkene as the probe.

There are many ways for double bond isomerization to take place including in photochemical reactions and on treatment with metal ions (21). In the presence of metal catalysts, the hydrogenation of 1-alkene is often accompanied by double bond migration and cis/trans isomerization. For the homogeneous catalyzed reaction, at least two mechanisms have been recognized for the isomerization of

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the alkene in the presence of a metal complex: the metal ion hydride addition–elimination mechanism and the π-allyl complex mechanism (21, 22). For metallic catalysts the bond breaking is usually considered to be homolytic so that the breaking of the hydrogen bond forms two hydrogen atoms with an electron that is utilized in bonding to the metal surface. Thus, metal-catalyzed hydrogenation and/or isomerization reactions are usually considered to be, or to resemble, a mechanism that involves a radical intermediate (23).

Since the pioneering work of the Farkas brothers, the addition and exchange of H/D has been widely utilized to study the mechanism of metal-catalyzed conversions of hydrocarbons (24). A vast literature has developed that describes conversions with most metal catalysts. However, Maitlis and co-workers (8) indicate that "deuterium is not suitable as a label since scrambling occurs on heating deuterio-organics, especially over metal under hydrogen." It is true that in most cases the H/D exchange reaction occurs over metals, but there are exceptions. Our work using platinum catalysts shows, however, that H/D exchange is not a simple process. Thus, at 482°C, we observe that an alumina support, either acidic or nonacidic, catalyzes H/D exchange in *n*-octane as rapidly as, or more than Pt at levels normally found in naphtha reforming catalysts. With Pt supported on silica, the exchange of D with *n*-octane was rapid at lower temperatures but exchange was much less at 482°C. There is little H/D exchange between octane-d_{18} and methylcyclohexane or between octane-d_0 and methylcyclohexane-d_{14} with Pt/SiO_2 at a temperature as high as 482°C (25). There is also little H/D exchange in octane and in methylcyclohexane over Pt/SiO2 at 482°C when D_2 gas was passing through the reaction zone, even though all of the products, such as ethylbenzene, xylenes, and toluene, contain deuterium in a statistic distribution (25). The lack of H/D exchange in the reagents defines the mechanism for dehydrocyclization (25–30). Richard and co-workers (31) reported that over a supported ruthenium catalyst at 150°C and 0.45 MPa (44.23 atm) total pressure (H_2), less than 5% of the deuterium in benzene-d_6 was exchanged after 75 min (88% conversion to products). These results clearly show that the H/D exchange reaction does not always occur under catalytic conditions at high temperature, at least not so rapidly that it masks the chemistry defined by kinetic-controlled reactions. Metal catalysts are noted for their ability to effect the hydrogenolysis of alkanes as well as to catalyze H/D exchange. Thus, Monnier *et al.* (32) found that, while an iron Fischer–Tropsch catalyst would catalyze the hydrogenolysis of *n*-hexadecane, the presence of a low partial pressure of CO would inhibit this reaction so that it was not detectable. As another example, Huang *et al.* (33) found that *n*-octacosane did not undergo measurable hydrogenolysis following more than 150 h of exposure to a doubly promoted iron catalyst under medium-pressure FT synthesis conditions. The results normally associated with metals may not apply here because (1) we are dealing with an iron carbide catalyst rather than a metal catalyst and (2) CO is present at reasonably high concentrations.

In the iron-catalyzed FT reactions, a mixture of alkane, 1-alkene, *cis*- and *trans*-2-alkenes, other internal alkenes, isoalkanes, and oxygenates of each carbon number may be formed. Alkenes can be reabsorbed to produce higher carbon number hydrocarbons (1–4, 6, 7, 10, 34–48). The fraction of the internal alkenes that are primary products remains an unanswered question. Many investigators consider 1-alkene to be the primary product and that internal alkenes arise from isomerization products.

In this study, we want to address the questions of whether there is H/D exchange in alkanes under the iron-catalyzed FT reaction conditions and the extent of isomerization of 1-alkens product.

EXPERIMENTAL

Deuterated octane-d_{18}, nonane-d_{20}, decane-d_{22}, tridecane-d_{28}, and pentadecane-d_{32} were purchased from Cambridge Isotope Laboratories, Inc. The deuterium contents (according to the manufacturer) are 99%, 98%, 99%, 98%, and 98%, respectively. Other chemicals were obtained from Aldrich and used without further purification.

The synthesis of 1-octene-d_{16} was conducted by a method modified from a previous report (49). To a mixture of 5 g of octanol-d_{17} and 3 g of pyridine in 150 ml of diethyl ether, 3 g of acetyl chloride in 50 ml of diethyl ether was added dropwise with excellent mechanical stirring. After the addition was completed, the reaction mixture was warmed to boiling and kept for an additional 30 min. When the reaction mixture was cooled, 100 ml of 10% HCl was added. The organic layer was separated, and the water layer was extracted with ether (50 ml × 3). The organic fractions were combined and washed with 10% HCl (10 ml × 2) and then with water (10 ml), and then dried over anhydrous $MgSO_4$. After evaporation of the solvent, 7.9 g of octyl-d_{17} acetate was obtained without further purification. The pyrolysis of octyl-d_{17} acetate was conducted at 480°C at a flow rate of 0.54 ml/h in a glass reactor. To the mixture of the products collected was added 2 ml of H_2O, and the organic fraction was separated. After distillation, 2.5 g of octene-d_{16} was obtained. The deuterium content of this compound was determined by GC/MS to be 98.5%.

The FT reaction was carried out in a 1-L continuously stirred autoclave reactor (CSTR) as described previously (37–46). The iron catalyst (100 Fe : 4.4 Si : 1.4 K atomic ratio) was activated using CO at 270°C and the synthesis was conducted at 0.12 MPa (11.9 atm) and 270°C using a 10 wt% catalyst slurry (50). Three traps follow the reactor and are held at 160°C, 60°C, and 0°C. For the run that included the addition of deuterated alkanes (referred to as the alkane addition run), a mixture of octane-d_{18}, nonane-d_{20}, decane-d_{22}, tridecane-d_{28}, pentadecane-d_{32}, and *o*-xylene (total 10 ml) was added to the H_2/CO feed to the 1-L autoclave during a 5-h period. Immediately prior to addition of the tracers, the three products traps were emptied. At the end of the addition of the deuterated alkanes, the product traps were again drained and the contents were analyzed using our normal procedure as well as the GC/MS analysis. In the run with 1-octene-d_{16} a similar procedure was followed. 1-Octene-d_{16} (2.5 g of 1-octene-d_{16} diluted with 5 g of *o*-xylene) was added to the reactor over 5 h. At the end of the addition of 1-octene-d_{16}, the product traps were drained and drained again after another 19 h. The carbon added in 1-octene is 10.3% of the total hydrocarbon products (FT hydrocarbons plus added 1-octene).

The deuterium content of the tracer compounds and its products was determined using GC/MS. The data were corrected for the ^{13}C content of the products. In the cases when quantitative analysis of the relative amount of isotopomer of a compound was not possible by GC, the GC/MS method was used. Because of the inverse isotope effect of the deuterated compound on gas chromatography (51–57), the relative amount of the total area of the molecular ion of each isotopomer was used to calculate the molar ratio (58). To compare the relative amount of different compounds using the total area of the molecular ion of each compound, the corrections were made using a known mixture as the standard.

RESULTS AND DISCUSSIONS

No H/D Exchange in Alkanes

Deuterated octane, nonane, decane, tridecane, and pentadecane were selected as the probes in studying the H/D exchange reaction under Fe-catalyzed FT reaction conditions. The deuterium content of each starting compound as well as the five deuterated probes recovered after 5 h run under these conditions was determined using GC/MS. As can be seen from the data in Table 1 and the representative data shown in Fig. 1, the D% and D/mol of the alkane probes after reaction are the same as those before reaction. These results clearly show that there is no measurable H/D exchange in alkanes under iron-catalyzed FT reaction conditions where CO conversion is not complete.

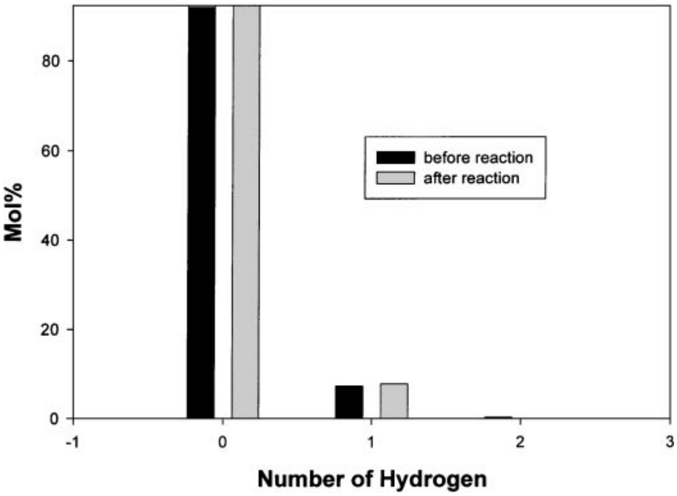


FIG. 1. Deuterium distribution in octane before and after the alkane addition run.

TABLE 1

Deuterium Contents in Deuterated Alkanes

Deuterated alkane	Before reaction		After reaction (5 h on stream)	
	D%	D/Mol	D%	D/Mol
Octane	99.6	18.0	99.6	18.0
Nonane	97.7	19.5	97.8	19.6
Decane	98.8	21.7	98.9	21.8
Tridecane	97.9	27.4	97.7	27.4
Pentadecane	96.7	30.8	96.3	30.8

As can be seen from the above results that there is no measurable H/D exchange in the deuterated alkanes. The deuterated alkane did not exchange its deuterium with its ordinary counterpart; it did not exchange its deuterium with alkene, which is one of the major products of the FT reaction; and it did not exchange its deuterium with H_2, which is a reactant for the FT reaction. The deuterium content of recovered tracer compound would decrease if exchange occurred, and it did not. Since there is no H/D exchange in the alkane, the opportunity to use deuterium tracer techniques to study the mechanism for FT reaction is appropriate.

It is reasonable to assume, as shown in the following, that for a given deuterated 1-alkene, the deuterium on carbon C_4 and higher carbon positions will not be subject to H/D exchange and its behavior will be similar to that of the paraffin under iron-catalyzed FT reaction conditions.

$$\overbrace{CD_3 — (CD_2)_n}^{\text{No D/H Exchange}} — \overbrace{CD_2 — CD = CD_2}^{\text{Subject to D/H Exchange}}$$

On the other hand, whether the deuteriums on carbon C_1 to C_3 positions will undergo H/D exchange if isomerization occurs depends upon the mechanism that applies. If the isomerization occurs through a π-allyl complex mechanism, there should be little or no H/D exchange; if it is through a metal ion hydride addition–elimination mechanism, H/D exchange should occur.

TABLE 2

Mole Percentage of Hydrogenation and Isomerization of Added 1-Octene-d_{16} under Iron-Catalyzed Hydrocarbon Synthesis Conditions

	Mol% (5 h on stream)	Mol% (24 h on stream)
1-Octene	85.9	66.5
Octane	8.0	20.8
trans-2-Octene	3.0	7.1
cis-2-Octene	3.1	5.6

The Mechanism of Isomerization of 1-Octene-d_{16} under Iron-Catalyzed FT Reaction Conditions.

a. The product distribution. The data in Table 2 provide the composition of the deuterium-containing C_8 products collected at the end of the 5-h addition of 1-octene-d_{16} and the sample collected 19 h later. 1-Octene-d_{16} was isomerized to deuterium-containing *cis*-plus *trans*-2-octenes and hydrogenated to deuterium-containing *n*-octane. The extent of conversion, as expected, was greater in the sample collected after 19 h than in the sample collected immediately after termination of 1-octene-d_{16} addition. The ratio of *cis*- to *trans*-2-octene is essentially 1, indicating no steric preference for the abstraction and addition of the H (D) that leads to the 2-octene products.

The cis : trans ratio of the isomerization product may depend upon the catalyst (59–61). The results and interpretations of the relative ratio of *trans-/cis*-2-isomers are often contradictory (22). The high ratio of *trans-/cis*-2-butene (62) and the high ratio of *cis-/trans*-2-isomers (63, 64) may results from a similar mechanism. Since the experimental ratio of *cis-/trans*-2-octene formed from the added 1-octene-d_{16} is close to 1, the trans : cis ratio of the 2-alkene product alone cannot define which mechanism is applicable.

Figure 2 shows the chromatogram of the C_8 products during the isomerization of 1-octene-d_{16} under iron-catalyzed FT reaction conditions. Peaks for only four significant compounds were obtained. Compared to these four peaks, there is no measurable amount of other internal octenes. This confirmed the assumption that only the deuterium on C_1 to C_3 carbons in 1-octene-d_{16} will be subjected to H/D exchange. If 3-octenes and 4-octenes were also produced, the deuterium on C_4 and C_5 carbons would also be subjected to H/D exchange and the H incorporation would exceed 5. The lack of 3-octene is believed to be the result of low adsorption rates of 2-octene as compared to 1-octane (65) and is in agreement with exchange up to only 5 H.

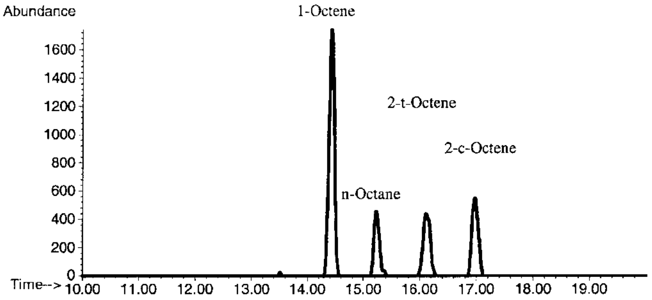


FIG. 2. Total ion chromatograph of deuterium-containing C_8 products that are in the reactor effluent product at the end of the addition of 1-C_8D_{16}.

In the double bond migration of 1-alkene under acidic or basic conditions, Zaitsev's rule applies and the double bond is located between the carbons with the fewest hydrogens. For example, in the case of base-promoted isomerization of 1-decene, the mixture of products contains not only 1-decene and *cis*- and *trans*-2-decene but also the *cis* and *trans* isomers of 3-, 4-, and 5-decene as well as branched alkene as a result of the rearrangement of carbocation (21). Since 3- or 4- or branched deuterated octenes were not obtained, the isomerization of 1-octene under iron-catalyzed FT reaction conditions through carbonium or carbocation intermediate is ruled out.

In the C_7 hydrocarbon region in gas chromatography, there is no indication of any deuterated compound. Thus, hydrogenolysis to produce C_7 isomers does not occur to a measurable extent. This result is in agreement with earlier studies (33, 66).

The deuterated compounds with molecular ion (M^+) 139 to 141 were found in the C_9 hydrocarbon region of the gas chromatograph. These compounds could be either C_9 alkanes or C_9 alkenes with up to 15 deuterium atoms. This result indicates that the added 1-octene can initiate chain growth under iron-catalyzed FT reaction conditions, in agreement with the results of carbon-14-labeled decene tracer studies under similar conditions (40, 42, 67). However, under these experimental conditions, the C_9 products containing deuterium were too low for the relative rates of hydrogenation to chain growth to be easily determined. The data show that the hydrogenation rate was greater than chain initiation rate.

b. Mechanism for deuterium distribution in octenes and octanes. For the isomerization of 1-alkene through a π-allyl complex, there should be several important characteristics: more *trans*-2-alkene than *cis*-2-alkne will be produced, the reaction will involve a 1,3-hydrogen shift, and no external hydrogen is required. A typical mechanism was demonstrated with $Fe_3(CO)_{12}$, which shows that double bond migration does not need external hydrogen and that the reaction takes place through a 1,3-hydrogen shift (68). For a mixture in which 1-octene-d_{16} and 1-octene-d_0 is present, as would be the case when we add 1-octene-d_{16} to the synthesis gas which produces 1-octene-d_0, the product exiting the reactor would contain 1-octene-d_{16} and 2-octene-d_{16} combined with 1-octene-d_0 and 2-octene-d_0 if the isomerization occurred only by internal D (or H) shift.

TABLE 3

Deuterium Distribution in Octenes

	1-Octene			*trans*-2-Octene		*cis*-2-Octene	
	Starting reagent	5 h on stream	24 h on stream	5 h on stream	24 h on stream	5 h on stream	24 h on stream
D%	98.5	92.7	87.1	88.6	83.5	88.5	85.1
D/Mol	15.8	14.8	13.9	14.2	13.4	14.2	13.6
C_8D_{16}	77.6	31.5	11.5	0	0	0	0
$C_8D_{15}H$	20.8	33.5	21.8	41.1	17.4	39.6	24.5
$C_8D_{14}H_2$	1.6	23.2	28.3	36.4	28.4	39.3	29.7
$C_8D_{13}H_3$	0	10.7	28.9	20.8	32.4	18.0	28.6
$C_8D_{12}H_4$	0	1.0	7.2	1.7	16.6	3.1	17.2
$C_8D_{11}H_5$	0	0	2.4	0	5.2	0	0

The data in Table 3 indicate that there is H/D exchange in the 1-octene recovered from the reaction mixture. The feed 1-octene-d_{16} contains 98.5% D (15.8 D/molecule) whereas the sample collected at the end of the 5-h period of addition contains 92.7% D (14.8D/molecule) and therefore shows an exchange of about 1 D/molecule. The sample collected 19 h after terminating the addition of 1-octene-d_{16} contained 87.1% D (exchange of ~2 D/molecule). The highest hydrogen-containing isotopomer is 1-octene-$d_{11}h_5$.

With respect to the mechanisms for the isomerization reaction, the most important finding in this study is that there is no detectable d_{16} isotopomer in 2-octene. The added 1-octene contained 78% of the d_{16} isotopomer and the 1-octene in the sample recovered after the 5-h period contained 32% of the d_{16} isotopomer. This makes the lack of any d_{16} isotopomer in the recovered 2-octenes significant since this requires that, for the formation of *cis*- and *trans*-2-octene, at least one D be replaced by H. If the isomerization was exclusively by the π-allyl complex, the amount of the 2-octene-d_{16} isotopomer must be between 32 and 78%. If even 1.5% of the d_{16} isotopomer was formed, it would have been observed in the GC/MS analysis that was utilized. This requires that the π-allyl complex pathway, if it contributes at all, must be less than about the 2% limitation.

The results are consistent with a mechanism that involves the metal ion hydride addition–elimination mechanism (Eq. [1]), in which the external hydrogen leads to H/D exchange in the 1-alkene through Eq. [1].

$$\begin{aligned} \mathrm{RCD_2CD{=}CD_2} &\overset{\mathrm{M-H}}{\rightleftharpoons} \mathrm{RCD_2C(M)D{-}CD_2H} \\ &\overset{\mathrm{M-D}}{\rightleftharpoons} \mathrm{RCD{=}CDCD_2H} \qquad [1] \end{aligned}$$

If the process shown in Eq. [1] reverses several times, the maximum number of deuteriums in the 1-alkene exiting the reactor that can be replaced by hydrogen is five, since only the deuteriums in the C_1, C_2, and C_3 positions can be exchanged. This mechanism would require heterolytic bond breaking during the chemisorption of hydrogen.

In heterogeneous catalysis, hydrogen is almost always considered to be adsorbed by homolytic bond cleavage; that is, hydrogen dissociates to form two hydrogen atoms that bond with the surface utilizing an electron associated with the metal (69). It is the exception when hydrogen is adsorbed by heterolytic bond cleavage; one rare example of this is adsorption on ZnO where H^+ is formed and adsorbs on a surface oxygen ion and the H^- that forms is bonded to the surface zinc ion (70). Likewise, the involvement of molecular hydrogen in hydrogenation is rare (71).

The exchange of H and D in 1-octene could also be explained by a mechanism that involves homolytic adsorption of H_2 with the formation of M–H, where M is an active site in iron carbide, and then follows a reaction pathway that is the same as that shown in Eq. [1]. The only difference between this reaction pathway and the hydride ion pathway is the step leading to the formation of M–H: in the hydride ion mechanism the vinyl D is abstracted by M as a D^- whereas in the homolytic bond-breaking mechanism the vinyl D is abstracted by M as $D\cdot$. The homolytic bond cleavage mechanism is considered to apply to the H/D exchange of *n*-octane with a Pt-silica catalyst (25–30). However, the exchange leads to a distribution of isotopomers that is statistically based on the H/D ratio in the feed so that, for the conversion of an equimolar mixture of *n*-octane-d_{18} and *n*-octane-d_0, the isotopomer present in the largest amount will be *n*-octane-d_9. For the homolytic bond cleavage to apply in the present case, there must be some reason for the exchange to be limited to 5 D and, considering the experimental error of the GC/MS analysis and the small amount of the H_5 isotopomer, the limit may be 4 D. A reasonable explanation is the relative adsorption of 1- and 2-octene. In competition with CO, 1-octene is expected to be preferentially adsorbed compared to 2-octene. Thus, it is reasonable to expect 1-octene-d_{16} to be adsorbed through reaction with M–H that is formed by homolytic bond cleavage of hydrogen to then undergo the reactions shown in Eq. [1]. If this is the case, desorption of 1- and 2-octene must compete favorably with the rate of hydrogenation and with the isomerization of 2-octene to 3-octene. The homolytic bond cleavage mechanism agrees with the data generated in this study and appears to be the most reasonable reaction mechanism.

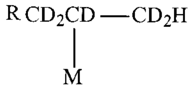
The deuterium distribution in octane (Table 4) is similar to that of 1-octene and higher than that of the 2-octenes. This result indicates that octane, once formed, does not continue to undergo H/D exchange. Since no d_{16} isomer of 2-octene was found, 44% of the $C_8D_{16}H_2$ isomer of *n*-octane was produced exclusively from the hydrogenation of 1-octene; the remaining isotopomers can be generated from both 1-octene and 2-octene. Similar to the octenes, d_{11} is the lowest deuterium-containing isotopomer of *n*-octane ($C_8D_{11}H_7$); i.e., the exchange of up to 5 D with H to produce octene isotopomers followed by the addition of 2 H to form *n*-octane.

TABLE 4

Deuterium Distribution in Octane

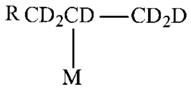
	5 h on stream	24 h on stream
D%	94.7	87.1
D/Mol	15.2	13.9
$C_8D_{16}H_2$	44.0	12.4
$C_8D_{15}H_3$	37.2	26.9
$C_8D_{14}H_4$	9.1	22.8
$C_8D_{13}H_5$	9.7	24.3
$C_8D_{12}H_6$	0	7.8
$C_8D_{11}H_7$	0	5.8

As indicated in Eq. [1], in the formation of 2-alkene from 1-alkene, the half-hydrogenated intermediate was formed. This half-hydrogenated intermediate, which is the common intermediate in both isomerization and hydrogen addition, may revert to the starting 1-alkene, yield 2-alkene, or be hydrogenated to alkane. In the case of 1-octene-d_{16}, whether the half-hydrogenated intermediate is structure A or a mixture of structure A and structure B depends upon the relative ratio of the surface pool of H/D.



$$\mathrm{R\,CD_2\underset{\displaystyle M}{\underset{|}{CD}}{-}CD_2H}$$

Structure A



$$\mathrm{R\,CD_2\underset{\displaystyle M}{\underset{|}{CD}}{-}CD_2D}$$

Structure B

If the amount of H is much greater than that of D, the intermediate will be structure A only. The further hydrogenation of A will give $C_8D_{16}H_2$ while β-elimination will produce either 1-octene with a 33% possibility for the d_{16} isotopomer; or 2-octene with the possibility of a d_{16} isotopomer being zero. In this tracer experiment, the ratio of H atoms (from H_2) to D atoms (from 1-octene-d_{16}) is more than 80 : 1, even assuming all D can equilibrate during the 5-h addition period. For the 24-h sample, the ratio is close to 900 to 1. This ensures that M–H will dominate in the isomerization and hydrogenation reactions. If the ratio of the surface pool of H/D was small, a significant amount of structure B would be produced, which could generate the d_{16} isotopomer of 2-octene.

CONCLUSIONS

Under iron-catalyzed FT synthesis conditions, the 1-octene was hydrogenated to octane, isomerized to *trans*- and *cis*-2-octenes with the formation of approximately equal amounts of these isomers, and was also incorporated into higher carbon number hydrocarbons. Products from cracking and isomerization to internal octenes other than the 2-octene isomers did not occur to a measurable extent. When 1-octene-d_{16} was used as the probe, there is H/D exchange in octenes and octane; the lowest deuterium-containing isomer products are the d_{11} isotopomers, and there are no d_{16} isomers in the 2-octenes. To account for all of these experimental facts, the mechanism for isomerization of 1-alkene in an Fe-catalyzed FT reaction is proposed to be the metal ion hydride or metal–hydrogen atom addition–elimination mechanism, with the latter considered to be most likely.

For the metal-catalyzed FT synthesis, several mechanisms have been proposed. These mechanisms differ in the details of initiation, propagation, and termination steps. However, despite these differences, most of these mechanisms agree on the starting hydrogen-containing species as M–H or H_{ads}. It is reasonable to assume that the metal-adsorbed hydrogen species that plays a very important role in FT reactions is also the one that promotes the isomerization of 1-alkene.

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