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On the Mechanism of Carbon–Carbon Bond Formation in the CO Hydrogenation Reaction

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This paper examines the fundamental characteristics of carbon–carbon bond formation in the CO hydrogenation reaction. A mechanism is proposed in an attempt to account for these characteristics. This mechanism involves insertion of methylene into the carbon–carbon double bond of a surface vinylidene complex. The cyclopropylidene complex thus formed, then rearranges to the homologous vinylidene species. Equations which describe branched isomer distributions are derived from the theory and are used to fit observed distributions for a fused iron catalyst and a precipitated cobalt catalyst. The model has one adjustable parameter, and the fit includes the methyl and the ethyl branching characteristics of Fischer–Tropsch catalysis which were previously unaccounted for by methylene polymerization theories.

INTRODUCTION

The question of mechanism has been debated throughout the history of the Fischer–Tropsch reaction yet the method by which carbon–carbon bonds are made has eluded investigators and remains a controversial subject (*1–5*). Recent work suggests that a carbene mechanism is operating but details have been lacking and an explanation of the branching characteristics of the synthesis reaction is missing from methylene polymerization theories (*6, 7*).

The branching characteristics of the reaction products, which are manifested in relative isomer distributions, place severe restrictions on possible mechanisms. Consequently, we have proposed a detailed mechanism of carbon bond homologation which, in at least several cases, quantitatively accounts for the observed distributions. Three important characteristics seem to be shared by the branching distributions produced by most Fischer–Tropsch catalysts: first, the relative concentration of isomers rapidly decreases as the degree of branching increases; second, most of the branched molecules contain a single methyl branch but some contain an ethyl branch; and third, a quaternary carbon atom is never formed in the class of molecules which contain two or more branches. These characteristics are illustrated in Fig. 1 where reference is made to an iron catalyst (*8*).

In addition to explaining the branching characteristics of the reaction, the theory is also consistent with the widely held belief that 1-olefins are primary reaction products and offers a new explanation of how olefins can initiate chain growth.

THE PROPOSED MECHANISM

The proposed mechanism has its roots in both organometallic chemistry and in the organic chemistry of carbenes. We begin by turning to a current topic in organometallic chemistry which concerns itself with the formation of molecules having transition-metal-to-carbon multiple bonds. This young field of chemistry now provides numerous examples of molecules or ions which contain a vinylidene ligand coordinated to a transition metal or to a transition metal cluster. Examples include the cationic trinuclear cobalt cluster $(CO)_9Co_3(C{=}CH_2)^+$, the neutral binuclear iron cluster $(CO)_3(C_5H_5)_2Fe_2(C{=}CH_2)$, and the mononuclear cation $(CO)(C_5H_5)(PPh_3)Fe(C{=}CH_2)^+$ (*9–11*). We propose an anal-

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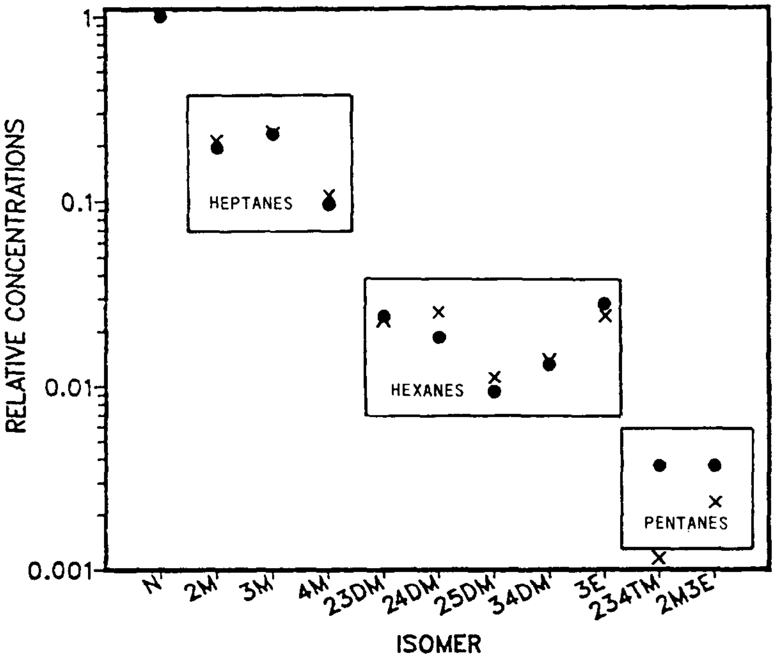

FIG. 1. Branched isomer distribution derived from data in Ref. (*8*) for the C_8 fraction of product formed over an entrained iron catalyst. N = normal, M = methyl, DM = dimethyl, TM = trimethyl, and E = ethyl. ●, Experimental; ×, calculated.

ogous vinylidene surface complex, $M{=}C{=}CH_2$, as a chain initiator in the synthesis reaction. This vinylidene complex might possibly be formed by the reaction of a "naked" surface carbon atom with a surface methylene complex.

For an explanation of chain propagation we turn to organic chemistry and the reactions of carbenes. It is well known that methylene, CH_2, readily reacts with carbon–carbon double bonds to form cyclopropanes (*12*). We propose that growing chains propagate by the insertion of methylene into the carbon–carbon double bond of a surface vinylidene complex to form a cyclopropylidene transition state (Fig. 2). The cyclic surface complex then rearranges to extend the carbon chain in a linear fashion (A loop), or, alternatively, rearranges to produce a branched molecule (B loop). In both cases the net result is a new alkylvinylidene complex which contains one new carbon atom and which can again react with another methylene to continue the process.

The domination of the linear isomer concentration over branched isomer concentrations is a result of the relative stabilities of the carbonium ion parts of the zwitterionic intermediate shown in the A and B cycles of Fig. 2. The nonbranching pathway generates a secondary carbonium ion while the branching route produces the relatively unstable primary carbonium ion. While the carbonium ion portion of the double ion produces a driving force for the migratory

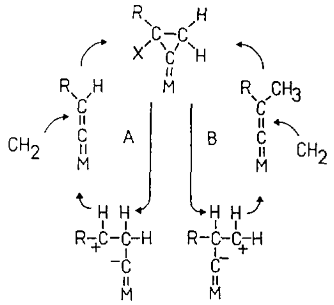

FIG. 2. Methylene insertion into the carbon–carbon double bond of vinylidene. The A loop shows the linear growth cycle while the B loop depicts the branched growth cycle.

part of the rearrangement, the anionic portion can be stabilized by delocalization of the negative charge density onto the catalyst surface.

The absence of quaternary carbon atoms in product molecules as well as the occurrence of ethyl branching can be understood in terms of two consecutive branching events (B loops) as propagation proceeds. A methyl branch is formed as the B loop is traversed the first time. Figure 3 shows that the second branching event initially creates a quaternary carbon atom, but as the cyclopropylidene intermediate rearranges, a 1,2-methyl migration breaks a carbon–carbon bond eliminating the quaternary carbon atom and simultaneously producing an ethyl-branched alkylvinylidene surface complex.

In a similar manner, the unlikely sequence of three consecutive branching events will produce a propyl-branched molecule. The effects of multiple branching events will be made quantitative in a later section of this paper.

As was mentioned earlier, the methylene/vinylidene theory is qualitatively consistent with the widely held belief that 1-olefins are primary reaction products (*5*). It is obvious that the simple sequential hydrogenation of a surface alkylvinylidene complex at the carbidic carbon atom will produce the desired olefin. Furthermore, the theory offers in addition to the reverse of the hydrogenation reaction, an alternative explanation for the reinitiation of chain growth by olefins (*13*). Let us consider the likely nature of a "naked" surface carbon atom of the kind which might be produced upon the dissociative adsorption of a CO molecule. Such a moiety is coordinatively unsaturated, extremely deficient in electrons, and likely to behave chemically as a strong electrophile (*14*). It is reasonable, then, for such a surface atom to comprise a site which can attack the carbon–carbon double bond of an olefin molecule which collides with it, leading to a surface cyclopropylidene complex. At this point the olefin molecule has entered the chain growth cycle of Fig. 2 and would be expected to grow in the normal manner.

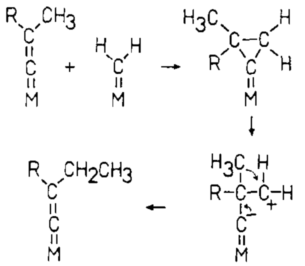

FIG. 3. Consecutive branching events account for ethyl branching and the absence of quaternary carbon atoms in the product distribution.

PRODUCT DISTRIBUTIONS

For the purpose of this analysis and for reasons explained below, all olefins are assumed to be hydrogenated to paraffins. We now develop the mathematical functions which predict the observed product distributions. Notice that chain propagation consists of a sequence of binary choices. At each point in the growth process either the A loop or the B loop is traversed. Thus all possible growth sequences for an arbitrary growing chain can be mapped onto a binary tree (see Fig. 4).

Let a be the probability of traversal of the A loop and let b be the probability of traversal of the B loop. Then it is easy to derive (via the steady state approximation) two recursion relations which relate C_{N+1}, the surface concentration of an isomer containing $N + 1$ carbon atoms, to C_N, the surface concentration of its precursor containing N carbon atoms. Two relations are found since C_{N+1} may have formed via a linear growth event or by a branching event.

$$C_{N+1}/C_N = x/(x + y + z) = a \qquad (1)$$

$$C_{N+1}/C_N = y/(x + y + z) = b \qquad (2)$$

Thus Eq. (1) obtains for an upward branch on the growth tree while Eq. (2) holds for a downward branch. Here, x and y

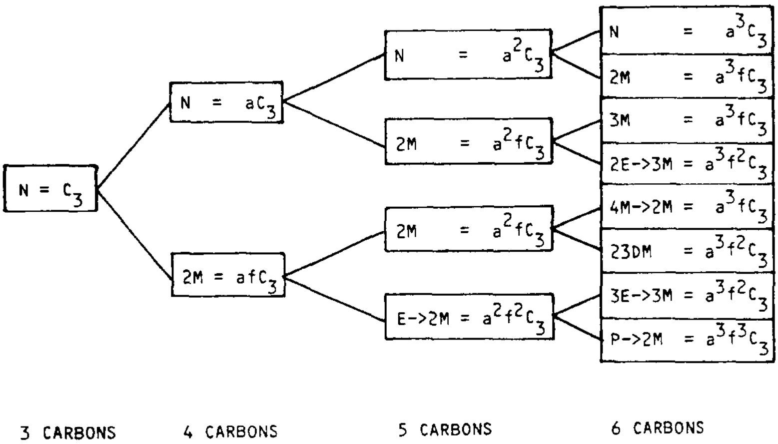

FIG. 4. Binary tree delineates all possible sequences of A and B events. N = normal, 2M = 2-methyl, 23DM = 2,3-dimethyl, E = ethyl, P = propyl, etc.

are pseudo rate constants for linear and branched growth while z is the pseudo rate constant for termination. We will also find it useful to define f as the ratio b/a. The reader should note that these equations are very simple approximations and do not allow for the possible variation of reaction rates with chain length. One might expect the propagation rate for small chains to differ from the rate for long chains for steric and electronic reasons. Nevertheless, the present approximation seems to be adequate for the purpose of this paper.

The two recursion relations are used to calculate the surface concentration of each isomer relative to the concentration of a given reference species (C_3 in Fig. 4). Summation over the "column" for N carbons yields the Carbon Number Distribution:

$$C_N/C_X = (a + b)^{N-X} = a^{N-X}(1 + f)^{N-X} \qquad N,X > 2 \quad (3)$$

where X is the carbon number of the reference species. This equation is isomorphic with the Flory equation when the Flory constant is identified with the sum $a + b$ (*15*). Thus the new theory partitions the Flory constant into a branching and nonbranching part. We also emphasize at this point that the theory explicitly draws a distinction between the formation of C_1 and C_2 molecules and the formation of molecules containing three or more carbon atoms. Methanation is viewed as competitive with the chain growing reaction while carbon–carbon bond formation for C_2 is viewed as fundamentally different than carbon–carbon bond formation in the higher hydrocarbons.

Branched Isomer Distributions are calculated relative to the concentration of the linear isomer for each carbon number, i.e., a separate calculation is performed for each "column" of the binary tree. The concentration at each node in a "column" of the tree is divided by the concentration for the linear isomer heading that "column." In this manner one obtains expressions for the concentrations of all branched isomers in terms of a single parameter, the ratio f. Also note that some molecules can be formed by two or more distinct pathways on the binary tree. 2-Methylbutane is an example. Here, two surface species (isopropylvinylidene and methylethylvinylidene) produce a single product upon desorption and hydrogenation. Similarly, the surface species formally designated as propyl-branched C_6 (methylpropylvinylidene) by virtue of the sequence of binary events which lead to its formation eventually contributes to the 2-methylpentane concentration. Through this effect, experimental evidence of multiple consecutive branching events is "hidden" in the concentrations of the monomethyl molecules. Multiple consecutive branching events produce distinct products only when the carbon number of the products exceeds six. These improbable molecules appear only as a small fraction of the molecules with higher carbon numbers and, since product concentration is falling exponentially as carbon number increases, they can only be detected by carefully applied analytical methods.

Experimentally, the branched isomer distributions can be obtained by high resolution capillary gas chromatography. Chromatograms of the total product (both olefins and paraffins) are very complex. Since we are primarily concerned with the connectivity of the carbon atoms in product molecules and not on the location of double bonds, the products can be hydrogenated prior to their separation. The simplified chromatographic data thus obtained allows the calculation of observed branched isomer distributions relative to their respective linear isomer concentrations.

Data sets of sufficiently high resolution to allow testing of theories which seek to explain branched isomer distributions are not generally available in the Fischer–Tropsch literature. One notable exception is the work of Pichler *et al.* (*8*) on iron and cobalt catalysts. We will use their data as a basis for testing our ideas. These same data have recently been used by Anderson and Chan (*16*) to test several one- and two-parameter models of chain growth. They compare their one- and two-parameter fits to the fit they obtain from the one parameter, Simple Chain Growth (SCG) model. A major deficiency of the SCG model is its inability to account for ethyl-branched molecules. Anderson and Chan found it necessary to introduce additional parameters to account for ethyl branching. In contrast, the methylene/vinylidene model retains a single adjustable parameter and still accounts for the observed ethyl-branched products. It is instructive to notice at this point that "Schulz–Flory polymerization" is a simplified form of the SCG model obtained by setting the branching parameter f equal to zero. In turn, the SCG model is the limiting form of the equations derived from the methylene/vinylidene mechanism when f is so small that terms in f^2 and higher powers can be ignored in the equations for monomethyl species, terms in f^3 and higher powers can be ignored in the equations for dimethyl species and so on. For the SCG model concentrations of ethyl-branched species are calculated as zero.

Pichler *et al.* (*8*) give chromatographic analyses of the products from iron and cobalt catalysts under several operating conditions and for several different catalyst preparations. Data are given for a precipitated iron catalyst, a fused iron catalyst, and a precipitated cobalt catalyst ($Co:ThO_2$: kieselguhr = 100 : 18 : 100). Product from the precipitated iron catalyst was obtained in large scale fixed-bed processes at Sasol (South African Coal, Oil, and Gas Corp.). Product from the fused iron catalyst was obtained at 22 atm and about 320°C in a large scale entrained bed reactor at Sasol. Finally, product from the cobalt catalyst was obtained at Karlsruhe by atmospheric pressure synthesis at 190°C.

RESULTS

In the data for the iron/fixed-bed process the normal isomer concentration remains a constant fraction of carbon number concentration with increasing carbon number. These data cannot be fit by the model presented in this paper, by the SCG model, or by any of Anderson and Chan's models (*16*). The data for the fused iron catalyst and cobalt catalyst are suitable bases for calculation and they yield reasonably straight lines on Schulz–Flory plots for data between C_7 and C_{17} (see Fig. 5). The results of one-parameter fits to the branched isomer data using both the methylene/vinylidene and SCG models are presented in Tables 1 and 2. The single parameter, f, of the models was adjusted to yield

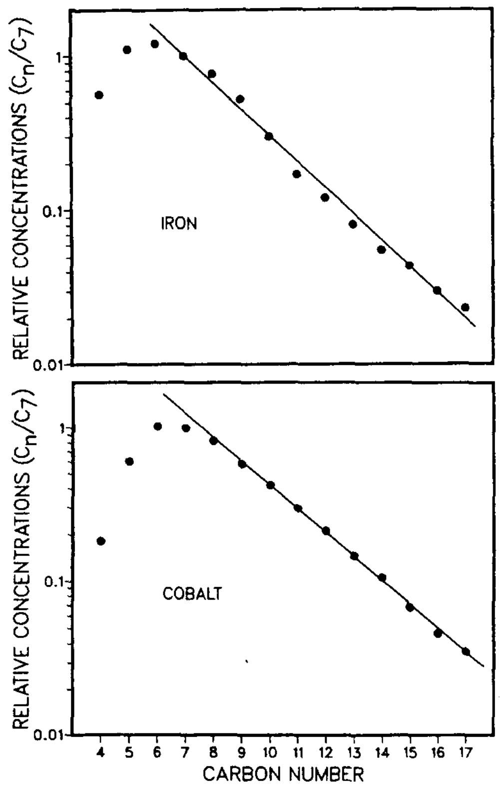

FIG. 5. Schulz–Flory plots for entrained iron and fixed-bed cobalt catalysts. Data points were derived from results reported in Ref. (*8*). Least-squares lines fitted to data between C_7 and C_{17} yielded alpha values of 0.675(9) for iron and 0.701(3) for cobalt.

its "best" value in the least-squares sense by minimizing the overall residual sum of squares for the branched-to-normal concentration ratios for each carbon number. The calculation was made for isomers in the C_6 to C_9 range for both catalysts. The two ratios in the C_4 and C_5 cases were omitted from the least-squares calculation because the C_4 and C_5 points on a Schulz–Flory plot fell substantially below the line defined by C_7 to C_{17} data. The ratios were calculated to one significant figure more than that reported for the original data to minimize rounding errors in the fitting process. We also note that while the cobalt catalyst produced products which were all aliphatic hydrocarbons, the fused iron catalyst produced some aromatics and naphthenes, probably due to secondary reactions which are enhanced by the high operating temperature of 320°C.

In general the fit of the calculated isomer ratios to the observed isomer ratios is quite satisfactory given the experimental uncertainties in separating, identifying, and quantifying the products in these complex mixtures. For the fused iron catalyst the calculated value of f is 0.10(2) where we have used a compact notation to mean $f = 0.10$ with a standard deviation of 0.02. A Schulz–Flory plot of the data for the fused iron catalyst yields an alpha value of 0.675(9). Since f is the ratio of b to a and alpha is their sum, we calculate the value of a, the probability of linear growth, to be 0.61(2) and the value of b, the probability of branched growth, to be 0.06(1). For comparison the corresponding values for the cobalt catalyst are:

	Iron	Cobalt
Alpha	0.675(9)	0.701(3)
f	0.10(2)	0.08(2)
a	0.61(2)	0.65(1)
b	0.06(1)	0.05(1)

These are the values obtained using the methylene/vinylidene model. The values obtained using the SCG model do not differ significantly. However, the quality of the methylene/vinylidene fit is superior as indicated by the residual sum of squares (RSS):

Model	Iron		Cobalt	
	Total RSS	Ethyl RSS	Total RSS	Ethyl RSS
Methylene/ vinylidene	0.00644	0.00008	0.00228	0.00017
Simple chain growth	0.01327	0.00166	0.00346	0.00082

It is clear that the differences between the two theories produce small effects in the linear-to-branched isomer ratios. Thus high precision data are required to adequately discriminate between the models. We feel that the "noise" in the data at hand is on the high side for this purpose but that a "signal" favoring the methylene/vinylidene theory is present. Perhaps it can be

TABLE 1

Predicted Isomer Distribution for Product from an Entrained Iron Catalyst[a]

Carbon number	Isomer	Observed ratio	Methylene/vinylidene	SCG
4	2-Methylpropane	0.0917	0.1008	0.1038
5	2-Methylbutane	0.2335	0.2118	0.2076
6	2-Methylpentane	0.2065	0.2026	0.2076
	3-Methylpentane	0.1429	0.1211	0.1038
	2,3-Dimethylbutane	0.0113	0.0102	0.0108
7	2-Methylhexane	0.1891	0.2017	0.2076
	3-Methylhexane	0.2845	0.2240	0.2076
	2,3-Dimethylpentane	0.0307	0.0224	0.0215
	2,4-Dimethylpentane	0.0068	0.0102	0.0108
	3-Ethylpentane	0.0136	0.0102	0.0000
8	2-Methylheptane	0.1940	0.2016	0.2076
	3-Methylheptane	0.2295	0.2221	0.2076
	4-Methylheptane	0.0970	0.1028	0.1038
	2,3-Dimethylhexane	0.0243	0.0205	0.0215
	2,4-Dimethylhexane	0.0187	0.0224	0.0215
	2,5-Dimethylhexane	0.0093	0.0102	0.0108
	3,4-Dimethylhexane	0.0131	0.0123	0.0108
	3-Ethylhexane	0.0280	0.0213	0.0000
	Trimethylpentane	0.0037	0.0010	0.0011
	Methylethylpentane	0.0037	0.0020	0.0000
9	2- and 4-Methyloctane	0.3659	0.4055	0.4152
	3-Methyloctane	0.2167	0.2219	0.2076
	2,3-Dimethylheptane	0.0219	0.0203	0.0215
	2,4-Dimethylheptane	0.0139	0.0205	0.0215
	2,5- and 3,5-Dimethylheptane	0.0378	0.0347	0.0323
	2,6-Dimethylheptane	0.0199	0.0102	0.0108
	3,4-Dimethyl and 4-ethylheptane	0.0417	0.0348	0.0215
	3-Ethylheptane	0.0239	0.0204	0.0000
	Trimethylhexane	0.0032	0.0043	0.0045
	f		0.1008	0.1038
	Sigma *f*		0.0229	0.0258
	RSS		0.006440	0.013273

[a] Observed data were derived from results obtained in Ref. (*8*).

detected best by comparing the results for pairs of compounds which are predicted to have equal linear-to-branched ratios by the SCG theory (e.g., 2-methylhexane and 3-methylhexane). It will be seen (Tables 1 and 2) that in the great majority of cases the methylene/vinylidene theory "perturbs" the SCG prediction so as to order the pairs in accord with the experimental results.

Finally, we note that these experiments cannot discriminate between the methylene/vinylidene theory and any other theory of branching which maps onto a binary tree in the same way. However, the methylene/vinylidene theory does have an aspect which is unique relative to other current methylene polymerization theories (e.g., migratory insertion of methylene into an alkyl chain). Namely, it predicts that the carbon atom which is attached to the surface in the initial vinylidene complex, remains attached to the surface throughout the chain

TABLE 2

Predicted Isomer Distribution for Product from a Fixed-Bed Cobalt Catalyst[a]

Carbon number	Isomer	Observed ratio	Methylene/vinylidene	SCG
4	2-Methylpropane	0.0482	0.0827	0.0852
5	2-Methylbutane	0.1390	0.1722	0.1704
6	2-Methylpentane	0.1551	0.1660	0.1704
	3-Methylpentane	0.0844	0.0964	0.0852
	2,3-Dimethylbutane	0.0012	0.0068	0.0073
7	2-Methylhexane	0.1535	0.1654	0.1704
	3-Methylhexane	0.1943	0.1802	0.1704
	2,3-Dimethylpentane	0.0041	0.0148	0.0145
	2,4-Dimethylpentane	0.0014	0.0068	0.0073
	3-Ethylpentane	0.0054	0.0068	0.0000
8	2-Methylheptane	0.1487	0.1654	0.1704
	3-Methylheptane	0.1811	0.1792	0.1704
	4-Methylheptane	0.1001	0.0838	0.0852
	2,3-Dimethylhexane	0.0044	0.0138	0.0145
	2,4-Dimethylhexane	0.0074	0.0148	0.0145
	2,5-Dimethylhexane	0.0059	0.0068	0.0073
	3,4-Dimethylhexane	0.0000	0.0080	0.0073
	3-Ethylhexane	0.0250	0.0142	0.0000
	Trimethylpentane	0.0000	0.0006	0.0006
	Methylethylpentane	0.0000	0.0011	0.0000
9	2- and 4-Methyloctane	0.3482	0.3320	0.3408
	3-Methyloctane	0.1785	0.1791	0.1704
	2,3-Dimethylheptane	0.0016	0.0137	0.0145
	2,4-Dimethylheptane	0.0095	0.0138	0.0145
	2,5- and 3,5-Dimethylheptane	0.0221	0.0228	0.0218
	2,6-Dimethylheptane	0.0032	0.0068	0.0073
	3,4-Dimethyl and 4-ethylheptane	0.0095	0.0229	0.0145
	3-Ethylheptane	0.0126	0.0137	0.0000
	Trimethylhexane	0.0000	0.0024	0.0025
	f		0.0827	0.0852
	Sigma f		0.0215	0.0216
	RSS		0.002280	0.003460

[a] Observed data were derived from results obtained in Ref. (*8*).

growth process. The new carbon atom is inserted between the first and second carbon atoms of the growing chain. On the other hand, during the migratory insertion reaction the metal–carbon bond is broken at each step in the chain growth process and methylene is inserted between the metal and the first carbon of the growing alkyl group. We are presently pursuing experiments to test this distinction.

We have presented in this paper a detailed theory of carbon–carbon bond formation (at the molecular level) which provides a convenient picture of chain propagation pathways in terms of a binary tree. The theory explains the exponential drop in product concentration with increasing product carbon number and partitions the Schulz–Flory constant, alpha, into nonbranching and branching components. This partitioning allows finer distinctions to be drawn among Fischer–Tropsch catalyst, thereby improving their characterization. The dominance of linear isomer concentration over branched isomer concentration is understood in terms of the relative stabilities of reaction intermediates. The theory also accounts for the absence of quaternary carbon atoms within product molecules in a straightforward and natural way. The theory quantitatively fits observed branched isomer distributions in terms of a single parameter *f*. The fit includes the methyl and the ethyl branching characteristics of Fischer–Tropsch catalysis which were previously lacking from methylene polymerization theories. Finally, the theory suggests a new mode (reaction with a "naked" surface carbon atom) by which olefins can be incorporated into the growth process.

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