A Quantitative Theoretical Treatment of the Fischer Tropsch Synthesis

P. D. TAYLOR[1] and B. W. WOJCIECHOWSKI

Department of Chemical Engineering, Queens' University, Kingston, Ontario K7L 3N6

A generalized scheme for product distribution in Fischer Tropsch synthesis in the absence of non-kinetic effects due to diffusion, shape selectivity, catalyst bifunctionality (e.g. synthesis-cracking catalysts), etc. is presented. The derivations reproduce the Schulz-Flory distribution in one limit and go on to generalize the work of Anderson in predicting the distribution of methylated species in the synthesis product. Formulae for molar distributions, weight distributions and weight distribution modes are presented. It is shown that special cases of the generalized distributions lead to methanol production or methanation as well as predicting other, as yet unreported, product compositions.

On présente un modèle généralisé pour la distribution des produits dans la synthèse Fisher-Tropsch en l'absence d'effets non-cinétiques dus à la diffusion, à la sélectivité de forme ou à la bifonctionalité des catalyseurs (par exemple, craquage-synthèse). Les calculs reproduisent la distribution de Schulz-Flory avec une certaine limite et permettant de généraliser le travail d'Anderson dans la prédiction de la distribution des composés méthylés dans les produits de synthèse. On présente des formules pour les distributions molaires, les distributions en poids et les modes de la distribution en poids. On a constaté que des cas particuliers de distributions généralisées conduisent à la production de méthanol ou à la méthanation et permettent de prévoir des produits qu'on n'a pas rapportés jusqu'ici.

In the following we will consider the addition of one carbon at a time to the growing product chain. We will use the notation proposed by Anderson and Chan (1979). B:R will denote an undetermined chain fragment; 1, a primary or secondary carbon; and 2, a tertiary carbon in the chain. Thus isobutane is represented as 121 while 2,3 dimethyl hexane is 122111 or 111221. We adopt the convention that the growing end of the molecule is on the right. Thus 122111 and 111221 are physically indistinguishable in the product, but have arisen by a different sequence of steps and may have different frequency. We use n to denote carbon number, k to denote the number of methyl side chains and i to denote methyl position. Thus for both above examples of 2,3 dimethyl hexane we have $n = 8$, $k = 2$ and $(i_1, i_2) = (2,3)$. We use $M_n^k (i_1, i_2, \ldots i_k)$ to denote the number of moles of product with the indicated parameter values. Thus $M_8^2(2,3)$ gives moles of 2,3 dimethyl hexane. Also, M_n^k denotes the sum of all $M_n^k (i_1, i_2, \ldots i_k)$ over all meaningful values of the i-parameters. Thus

$$M_8^2 = M_8^2(2,3) + M_8^2(2,4) + M_8^2(2,5) + M_8^2(3,4)$$

gives the total moles of dimethyl hexane. Finally M_n denotes the sum of all M_n^k over all meaningful values of k, and gives the total number of moles of all product with carbon number n. Similarly M^k is the sum of M_n^k over all meaningful n. For example, M^2 denotes the total number of moles of dimethyl over the range $n = 6$ to infinity.

In the above, when we substitute W for M, we denote the total weight of that species. In our calculations we will assume the reasonable approximation that for alkanes and olefins $W = 14nM$.

We let α, β, δ, and γ denote the specific rates of addition

to the straight chain, of branching, of addition to a branched chain, and of termination respectively. These reaction rates are diagrammed as follows:
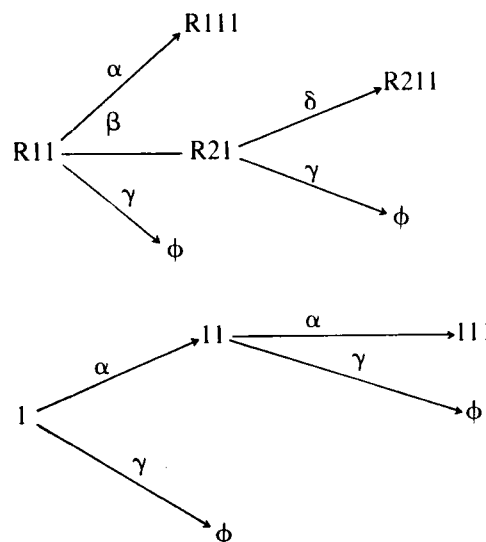
where R represents the inactive part of the chain while 1 and 2 are carbons as defined above. θ denotes desorption and hence the formation of a product. We assume all specific rates are independent of chain length. The case $\delta = \alpha$ is scheme A of Anderson, Friedel and Storch (1951) while $\delta = 2\alpha$ is their scheme B.

It is mathematically convenient to work with the following "distribution parameters":

$$a = \frac{\alpha}{\alpha + \beta + \gamma} \qquad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

[1] Department of Mathematics.

$$b = \frac{\beta}{\delta + \gamma} \quad \dots \quad (2)$$

$$d = \frac{\delta}{\alpha + \beta + \gamma} \quad \dots \quad (3)$$

$$c = \frac{\gamma}{\alpha + \gamma} = \frac{1 - a - bd}{1 + ab - bd} \quad \dots \quad (4)$$

These parameters will lead to simplified formulae for the M_n^k. The four parameters are not independent, and c has been expressed in terms of a, b and d.

The reaction rates α, β, δ and γ cannot be derived from product concentrations, but the *relative* reaction rates $\alpha' = \alpha/\gamma$, $\beta' = \beta/\gamma$ and $\delta' = \delta/\gamma$ can, and form a set of three independent parameters which determine product distributions. Using Equations (1), (2) and (3) we can easily express a, b and d in terms of α' β' and δ'. The reverse transformations are:

$$\alpha' = \frac{a(1 + b)}{1 - a - bd}, \qquad \beta' = \frac{b(1 - a + d)}{1 - a - bd},$$

$$\delta' = \frac{d(1 + b)}{1 - a - bd} \quad \dots \quad (5)$$

which yield specific rates relative to the rate of desorption. Another useful transformation involves rates relative to the rate of linear propagation, $\beta'' = \beta/\alpha$, etc.,

$$\beta'' = \frac{b(1 - a + d)}{a(1 + b)}, \qquad \delta'' = \frac{d}{a},$$

$$\gamma'' = \frac{1 - a - bd}{a(1 + b)} \quad \dots \quad (6)$$

In any case, it is a, b and d which are obtained directly from experiment, while the other quantities are calculated using Equation (5) or (6).

Calculation of product concentrations

For the purpose of calculating the relative amounts of the various products formed, we note the probabilities of the different reactions possible at any stage: in general
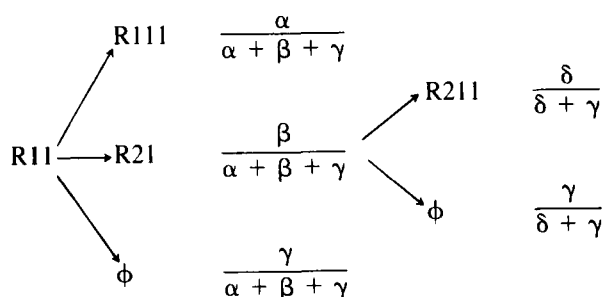
while in the first two steps
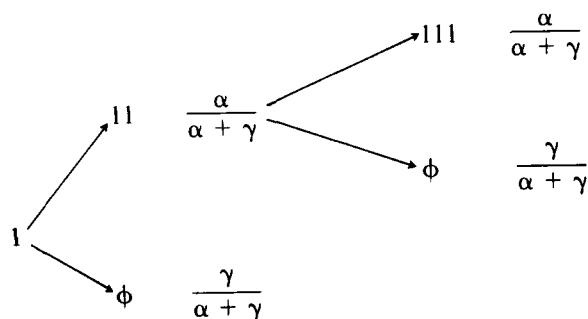
The total probability that a given product species will be formed from a starting C_2 (the chain 11) can be calculated as follows:

$$\text{Prob}(112121) = \left(\frac{\alpha}{\alpha + \gamma}\right)\left(\frac{\alpha}{\alpha + \beta + \gamma}\right)\left(\frac{\beta}{\alpha + \beta + \gamma}\right)$$

$$\times \left(\frac{\delta}{\delta + \gamma}\right)\left(\frac{\alpha}{\alpha + \beta + \gamma}\right)\left(\frac{\beta}{\alpha + \beta + \gamma}\right)\left(\frac{\gamma}{\delta + \gamma}\right)$$

$$= \frac{\alpha^3 \beta^2 \delta \gamma}{(\alpha + \beta + \gamma)^4 (\delta + \gamma)^2 (\alpha + \gamma)}$$

$$= a^3 b^2 dc \quad \dots \quad (7)$$

Although the distribution parameters are not themselves probabilities, it turns out that the probabilities of different products being formed always have a simple expression in terms of these parameters. Essentially, this is because the number of αs and δs in the numerator is always the same as the number of $(\alpha + \beta + \gamma)$s in the denominator, and the number of βs in the numerator always matches the number of $(\delta + \gamma)$s in the denominator.

Another point to note is that, although 121211 is physically indistinguishable from 112121, it has a different probability: $\text{Prob}(121211) = a^2 b^2 d^2 c$. This example illustrates that the "counting" is different for molecules which terminate with 11 and 21. This leads us to define A_n^k to be the number of moles of product of the form R11 with carbon number n and methyl number k, and B_n^k as the number of moles of such product of the form R21. Then $M_n^k = A_n^k + B_n^k$ with the convention $B_n^0 = 0$.

We normalize our count with $M_2^0 = 1$. Then a counting process similar to Equation (7) leads by induction, to the general forms:

$$A_n^k = \binom{n - k - 3}{k} a^{n - 2k - 2} b^k d^k, \qquad \begin{array}{l} k \geq 0 \\ n \geq 2k + 3 \end{array} \quad \dots \quad (8)$$

$$B_n^k = b A_{n-1}^{k-1}, \qquad \begin{array}{l} k \geq 1 \\ n \geq 2k + 2 \end{array} \quad \dots \quad (9)$$

where the combinatorial coefficient $\binom{n}{k} = \frac{n!}{k!(n - k)!}$. Adding these and doing some algebra we get

$$M_n^k = \binom{n - k - 2}{k} a^{n - 2k - 2} b^k d^{k - 1}$$

$$\left(\frac{(n - 2k - 2)d + ka}{n - k - 2}\right), \qquad \begin{array}{l} k \geq 0 \\ n \geq 2k + 2 \end{array} \quad \dots \quad (10)$$

all relative to $M_2^0 = 1$.

The special case $n = 1$ must be worked out directly from the probabilities. Starting from a one-carbon-atom species on the surface, the probability that it will produce a C_1 product is $\gamma/\alpha + \gamma$. The probability that the C_1 surface species will add one more carbon and then desorb as a C_2 product is $[\alpha/(\alpha + \gamma)] \cdot [\gamma/(\alpha + \gamma)]$. Hence we have

$$M_1^0 = \left(\frac{\gamma}{\alpha + \gamma}\right) \Big/ \left(\frac{\alpha}{\alpha + \gamma}\right)\left(\frac{\gamma}{\alpha + \gamma}\right)$$

$$= \frac{\alpha + \gamma}{\alpha} = \frac{1 + b(a - d)}{a(1 + b)} \quad \dots \quad (11)$$

as the product concentration of C_1 relative to that of C_2.

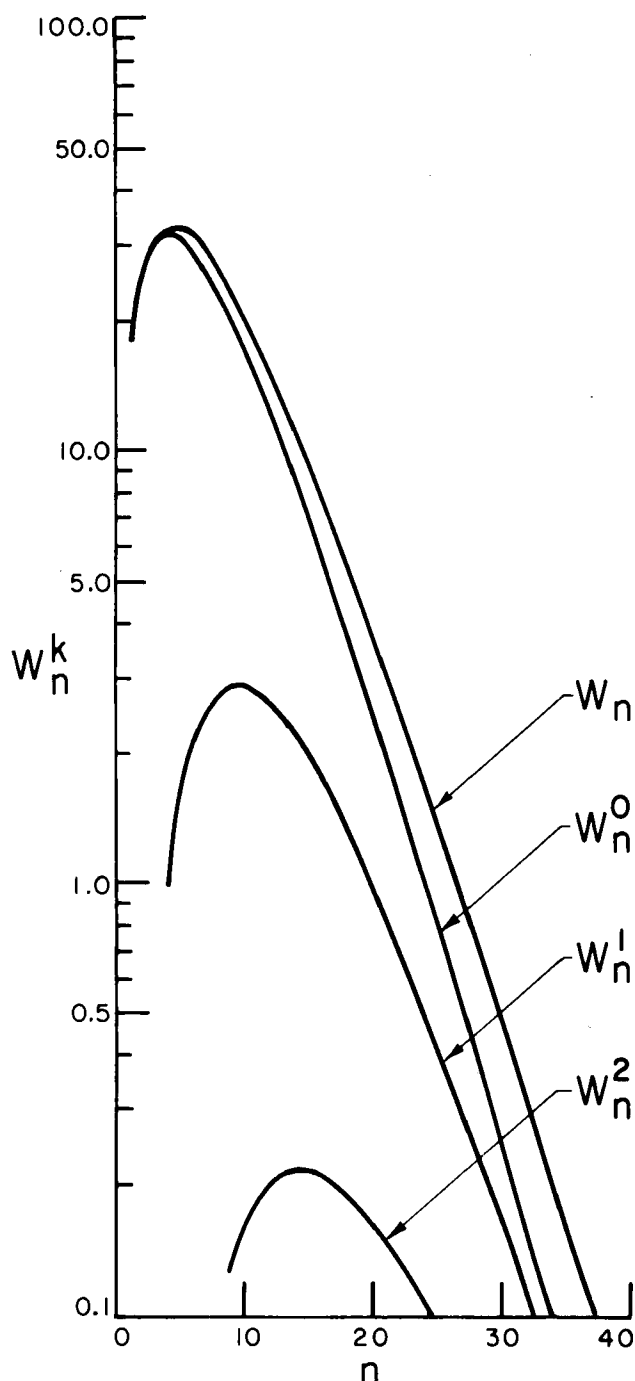Returning to the general equations we see that, when $\delta = \alpha$, (10) becomes

Figure 1 — Plots of total weight of products n-alkane, monomethyl, and dimethyl against carbon number n. Parameter values used are $a = 0.766$, $b = 0.0225$ and $d = 0.627$.

$$M_n^k = \binom{n-k-2}{k} a^{n-k-2} b^k, \qquad \begin{array}{l} \delta = \alpha \\ d = a \end{array} \qquad \ldots\ldots\ldots (12)$$

yielding a general formula for Anderson's type A distribution (Anderson R. B. et al., 1951).

Similarly for $\delta = 2\alpha$ (10) becomes

$$M_n^k = \binom{n-k-2}{k} 2^{k-1} a^{n-k-2} b^k \frac{(2n-3k-4)}{n-k-2},$$

$$\begin{array}{l} \delta = 2\alpha \\ d = 2a \end{array} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

and gives the general expression for Anderson's B type distribution.

We next single out the cases $k = 0$ (straight chains), $k = 1$ (monomethyls) and $k = 2$ (dimethyls):

$$M_n^0 = a^{n-2}, \qquad n \geq 2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

$$M_n^1 = a^{n-4} b((n-4)d + a), \qquad n \geq 4 \ldots\ldots\ldots (15)$$

$$M_n^2 = (n-5) a^{n-6} b^2 d((n-6)d + 2a)/2,$$

$$n \geq 6 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

The above formula for M_n^0 is widely known as the Schulz-Flory distribution.

Counting the monomethyls and dimethyls by type we have

$$M_n^1(i) = \begin{cases} ab & , & i = 2, n = 4 \\ a^{n-4} b(d+a), & i = 2, n \geq 5 \\ & & \ldots\ldots\ldots\ldots (17) \\ a^{n-4} bd , & i > 2, n = 2i \\ 2a^{n-4} bd, & i > 2, n > 2i \end{cases}$$

$$M_n^2(i,j) = \begin{cases} a^{n-6} b^2 da & , & i = 2, i + j = n - 1 \\ a^{n-6} b^2 d(a+d), & i = 2, i + j < n - 1 \\ & & \ldots\ldots\ldots (18) \\ a^{n-6} b^2 d^2 , & i > 2, i + j = n - 1 \\ 2a^{n-6} b^2 d^2, & i > 2, i + j < n - 1 \end{cases}$$

The variations in the above formulae are due to two factors: the case $i = 2$ is special because of the previously discussed termination probability, while symmetric molecules are special because they have only one (and not two) ways to form. A monomethyl is symmetric when $n = 2i$ and a dimethyl is symmetric when $i + j = n - 1$.

Weight distributions

The weights W_n^k are defined as $14nM_n^k$ where M_n^k is given in Equation (10). For each fixed k, W_n^k gives us the weight of all products with k methyls and carbon number n.

In Figure 1, these distributions are plotted for $k = 0$, 1 and 2 using a set of parameter values obtained by experiment (Taylor and Wojciechowski, to be published). As expected, the modes of these distributions increase with k. For the case $k = 0$ (straight chains) the mode is obtained from Equation (14) by maximizing na^n, and is

$$\hat{n}_0 = -1/\ln(a) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (19)$$

For $k = 1$ (monomethyls), the mode is obtained from Equation (15) by maximizing $a^n(n^2d - n(4d - a))$, and is

$$\hat{n}_1 = \hat{n}_0 - \frac{a}{2d} + 2\sqrt{\hat{n}_0^2 + \left(2 - \frac{a}{2d}\right)^2} \ldots\ldots\ldots (20)$$

for $k > 2$, explicit formulae for the mode cannot be obtained. In practice the distribution of $W_n^0 + W_n^1$ will usually approximate the distribution of total product $\sum_k W_n^k$, since b is normally small. This approximation has mode

$$\hat{n} = \hat{n}_0 - \frac{a(a+b)}{2bd} + 2$$

$$+ \sqrt{\hat{n}_0^2 + \left(2 - \frac{a(a+b)}{2bd}\right)^2} \ldots\ldots\ldots\ldots (21)$$

In Figure 1 the graph of W_n^k for $k = 0$ is above the graph for $k = 1$ which in turn is above $k = 2$ graph. For values of n larger than those displayed in the figure this is not the case. At $n_1 = 45$ the graph of W_n^1 crosses and remains higher than the graph of W_n^0 for all $n > 45$. This type of behavior continues with W_n^2 becoming dominant above $n = 89$ with the result that for large n the dominant product will be k-methyl, where $k \approx bdn/a^2$.

Using Equation (10) and some combinatorial results we can obtain a formula for the total weight of all product with any fixed k.

$$W^k = \sum_{n = 2k + 2}^{\infty} W_n^k = 14 \sum_{n = 2k + 2}^{\infty} n M_n^k$$

$$= \frac{14ab^k d^{k-1}}{(1 - a)^{k+2}} [(k + 2)a^2 - (3k + 4)a$$

$$+ (2k + 2) - (k + 2)da + (2k + 3)d] \quad \ldots \quad (22)$$

valid for $k > 1$. For $k = 0$ our method fails and we calculate directly

$$W^0 = \sum_{n = 1}^{\infty} W_n^0 = \frac{14(2 - a)}{(1 - a)^2}$$

$$+ 14 \frac{(1 + b(a - d))}{a(1 + b)} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (23)$$

This is the total weight of all straight chain products including C_1. The total weight, W, of all products can be calculated by summing the W^k in Equation (22) over all k and adding Equation (23):

$$W = W^0 + \sum_{n-1}^{\infty} W^k = \frac{14(2 - a)}{(1 - a)^2} + \frac{14(1 + b(a - d))}{a(1 + b)}$$

$$+ \frac{14ab}{1 - a} \left[\frac{(2 - a)(1 - a + d)}{(1 - a - bd)^2} + \frac{2(1 - a)}{(1 - a - bd)} \right.$$

$$+ \left. \frac{d(3 - 2a)}{(1 - a)(1 - a - bd)} \right] \quad \ldots \ldots \ldots \ldots \ldots \ldots (24)$$

Recall that this is all relative to 1 mole (a weight of 28 units) of C_2 and includes the theoretical yield of C_1.

For any fixed k formulae can be obtained for the total weight of all product with carbon number $\geq m$. For $k = 0$, the weight of all straight chain product of carbon number $\geq m$ is

$$\sum_{n = m}^{\infty} W_n^0 = \frac{14a^{(m-2)}(a(1 - m) + m)}{(1 - a)^2}, \quad m \geq 2 \quad \ldots \quad (25)$$

For $k = 1$, the weight of all monomethyl of carbon number $\geq m$ is

$$\sum_{n = m}^{\infty} W_n^1 = \frac{14a^{m-4}}{(1 - a)^3} [a^3(m - 1) + a^2(1 - 2m)$$

$$+ am + a^2 d(m^2 - 6m + 5) + ad(-2m^2$$

$$+ 10m - 3) + d(m^2 - 4m)], \quad m \geq 4 \quad \ldots \ldots \ldots (26)$$

As k increases the formulae become increasingly complex and numerical results are best obtained from the difference formulae

$$\sum_{n = m}^{\infty} W_n^k = W^k - \sum_{n - 2k + 2}^{m - 1} W_n^k \quad \ldots \ldots \ldots \ldots \ldots \ldots (27)$$

with W^k given by (22) and $\sum_{n = 2k + 2}^{m = 1} W_n^k$ calculated using numerical procedures.

It would be nice to have analytical formulae for W_n, the total weight of all products of molecular weight n:

$$W_n = \sum_{k = 0}^{[n/2] - 1} W_n^k \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (28)$$

but we have been unable to develop these. Although the sum is finite it may not have a closed-form expression. In any specific application it can, of course, simply be calculated, at least where n is not too large. Even for large n, if b is small, the terms in Equation (28) corresponding to large values of k will be small (since W_n^k is of order b^k), and the sum can be approximated by the first few terms. In Figure 1 we have plotted the sum $W_n^0 + W_n^1 + W_n^2$ against n for a value of $b = 0.0225$.

Extreme values

Certain special types of product distributions are predicted for extreme values of the reaction rates α, β, δ, and γ.

For $\beta = 0$ we obtain no methyls; all product is straight chain.

For $\delta = 0$, desorption occurs as soon as a side chain is added. Thus the product consists entirely of straight chains and 2-methyls.

If $\alpha \approx 0$, $\beta \neq 0$ and $\delta \neq 0$ any product of large carbon number that is formed will tend to be completely methylated (i.e. of the form $122 \ldots 221$).

If we accept that γ is a sum of γ_i, each γ_i corresponding to a specific form of termination, we obtain other special cases.

Assuming that γ_i produces alkanes, γ_2 olefins and γ_3 alcohols, then, if γ_2 and γ_3 approach zero while γ_1 is real, we obtain a highly saturated product. For the other two cases we obtain olefinic or alcoholic products.

If we let γ_2, γ_3, and α simultaneously approach zero the product will be mainly C_1 (a methanation catalyst). Similarly as γ_1, γ_2, and α approach zero a methanol-producing catalyst will in principle result.

Distribution anomalies of small molecules

It has generally been observed that Fischer Tropsch catalysts produce an anomalous yield of methane, and it may well be that carbon chains of length one and two behave differently on the catalyst surface than longer chains. In this section we work out the effects of altered reaction rates in the first two growth steps. Let us introduce altered rates α_1, γ_1, α_2 and γ_2 as follows
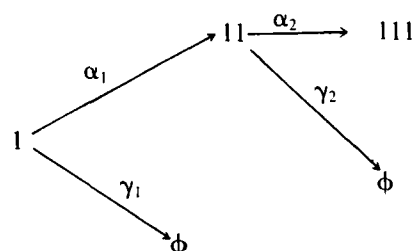
giving the following altered probabilities of product formation:
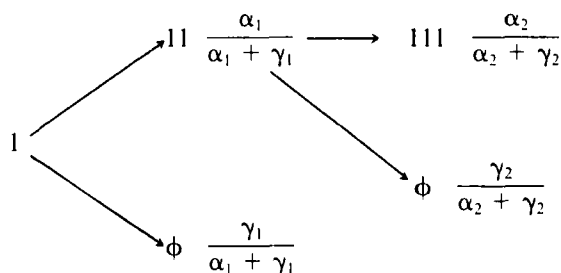
These alterations affect our product concentration formulae. Formula (10) for M_n^k must be multiplied by the factor $R = \alpha_2'/\alpha'$, where we use the relative reaction rates $\alpha' = \alpha/\gamma$ defined previously. All formulae are still relative to $M_2^0 = 1$.

The formula for M_1^0 becomes

$$M_1^0 = (\alpha_2' + 1)/\alpha_1' \qquad \qquad (29)$$

Formulae (12)–(18) should all be multiplied by R. Equation (14) for example becomes

$$M_n^0 = Ra^{n-2} \qquad n \geq 3 \qquad \qquad (30)$$

The mode formulae (19)–(21) remain unchanged. Of the weight formulae, Equation (22) is multiplied by R since it involves values of n only ≥ 4; Equation (23) becomes

$$W^0 = \sum_{n=1}^{x} W_n^0 = 14 \left[\frac{\alpha_2' + 1}{\alpha_1'} + 2 \right.$$

$$\left. + \frac{Ra(3 - 2a)}{(1 - a)^2} \right] \qquad \qquad (31)$$

and Equation (24) is modified accordingly.

With these altered parameters, the Schulz-Flory line, obtained by plotting $\log M_n^0$ against n using Equation (27), will move up by $\log R$, and the points at $n = 1$ and $n = 2$ may not lie on the line. The equation of the line in more general terms is therefore:

$$\log (M_n^0) = \log R + (n - 2) \log (a) \qquad \qquad (32)$$

and the line contains only the points with $n \geq 3$.

If we let Δ_i be the amount by which the points $(i, \log M_i^0)$ lie above the line, for $i = 1,2$, then since $M_2^0 = 1$,

$$\Delta_2 = - \log R = \log (\alpha'/\alpha_2') \qquad \qquad (33)$$

and from (29)

$$\Delta_1 = \log \left[\frac{\alpha'}{\alpha_1'} \cdot \frac{\alpha_2' + 1}{\alpha_2'} \cdot \frac{\alpha'}{\alpha' + \beta' + 1} \right]$$

$$\approx \log \left[\frac{\alpha'}{\alpha_1'} \cdot \frac{\alpha_2' + 1}{\alpha_2'} \cdot \frac{\alpha'}{\alpha' + 1} \right] - \frac{\beta'}{\alpha' + 1} \qquad \dots (34)$$

where the approximation is valid for small β'.

In general, Equations (33) and (34) can be solved for α_1'

and α_2' if values of Δ_i are available from experimental data. For example, if the M_2^0 point lies on the line, then $R = 1$ and $\alpha_2' = \alpha'$.

Conversely any model which proposes theoretical values of the α_i' will lead to predictions of the Δ_i which can be tested. For example, if we assume the reaction $II \rightarrow III$ is the sum of an α-type reaction on one carbon and β-type reaction on the other carbon, so that $\alpha_2 = \alpha + \beta$ while $\gamma_2 = \gamma_1 = \gamma$ then

$$\Delta_2 = - \log (1 + \beta/\alpha) \approx - \beta/\alpha \qquad \qquad (35)$$

the approximation being valid for small β. Notice that in general if $\alpha_2' > \alpha'$ the C_2 point will lie below the line.

For Δ_1 we have

$$\Delta_1 = \log (\alpha^2/\alpha_1 \alpha_2) - \beta/\alpha \qquad \qquad (36)$$

for small β and $\alpha_2 = \alpha + \beta$. In order for C_1 to lie above the line the product $\alpha_1 \alpha_2 > \alpha^2$.

Other modifications to the base case will be left until their presentation is justified by experimental evidence.

Conclusions

The above systematic treatment of chain growth represents an approach which can be extended and elaborated in a variety of ways. Furthermore the development need not be confined to synthesis reactions but can be applied wherever the postulated growth rules may apply.

Using the formulae presented here one can extract estimates of the various distribution parameters from experimental data as described previously (Taylor and Wojciechowski, to be published). At the same time the formulae facilitate the study of hypothetical synthesis catalysts and the identification of the parameters which yield desirable product compositions.

The next problem is to identify the factors which govern the values of the distribution parameters.

Acknowledgements

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