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LETTERS TO THE EDITORS

In Re: Fischer–Tropsch

Comments to Notes by R. B. Anderson (1) and R. J. Madon (2)

In a recent communication, R. B. Anderson (*1*) stated that the reaction mechanism suggested by us in 1976 (*3*) for the Fischer–Tropsch synthesis was the same as that described by himself and other workers a quarter of a century ago. This statement is incorrect.

Our mechanism is explicitly based on individual steps well established during the past two decades in homogeneous catalysis with transition metal complexes, such as coordination of CO, insertion of CO into metal–carbon bonds, oxidative addition, reductive elimination, β-hydrogen abstraction, etc., at monometallic catalyst centers (*4*). A metal hydride formed during β-hydrogen abstraction is assumed to be the carrier of the kinetic chain. Evidently this mechanism represents a new approach to the elucidation of the Fischer–Tropsch synthesis, as it has been acknowledged by several authors (*5–10*). During the past 2 years the mechanism suggested by us has received substantial support by the work of Casey and Neumann (*6*, *11*) and of Gladysz *et al.* (*7*, *12*) on the preparation and chemistry of formyl-complexes of transition metal compounds, the determination of the crystal structure of a π-bonded formaldehyde-transition metal complex by Roper *et al.* (*10*), and of a compound containing an acyl group π-bonded to a transition metal species by Floriani and co-workers (*13*), the theoretical calculations of Goddard *et al.* (*14*), as well as our own work on modifications of the Fischer–Tropsch synthesis (*15a–d*) and on the comparison of this synthesis to hydroformylation (*15e*). In particular, the detection of a soluble catalyst system, providing Fischer–Tropsch growth on benzene molecules (*15c*), appears to underline the obvious fact that there is only one chemistry, and that homogeneous and heterogeneous catalysis do have a common basis.

On the other hand, the mechanism assumed by the earlier workers (*1*, *16*) involved one-carbon additions at the end as well as at the penultimate carbons, the latter to account for methyl branches in the product. Evidently, such a mechanism would predict methyl branching being independent of conversion. However, Pichler *et al.* (*17*) have clearly and elegantly demonstrated that the primary products are linear α-olefins and alcohols, and that branching increases with the conversion. Schulz *et al.* (*18*), using ^{14}C-labeled α-olefins, have conclusively shown that these molecules are incorporated under Fischer–Tropsch conditions, leading to branching. As it is well known (*19*), the ability of α-olefins to coordinate to a transition metal center decreases strongly with the carbon number. Incorporation of ethylene results in linear growth; incorporation of propylene gives methyl branches, whereas the relatively small amount of ethyl branches stems from occasional incorporation of butene-1. (Internal olefins can safely be

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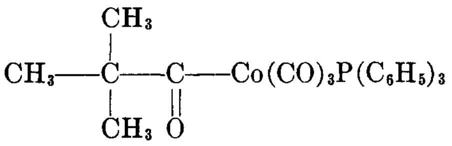
assumed not to coordinate under the conditions of Fischer–Tropsch synthesis.)

In order to explain the absence of product molecules containing two methyl branches at the same carbon, the early workers (*16*) postulated that addition does not occur at tertiary carbons. However, during hydroformylation of isobutylene, Heck and Breslow (*20*) isolated the compound



$$\mathrm{CH_3}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{Co(CO)_3P(C_6H_5)_3}$$

which shows that the reaction of tertiary carbon atoms with CO is feasible. On the other hand, the absence of two methyl branches at the same carbon atom follows naturally, if incorporation of α-olefins (primary products) is assumed as the cause of branching. Evidently this branching mechanism leads to similar statistics concerning isomer distribution, as those used by Anderson (just substitute f (*1*, *16*) by the probability of incorporation of propylene into the growing chain). This explains why Anderson was able to fit the experimental data into his mathematical framework.

A further discrepancy lies in the assumption of a common precursor for olefins, alcohols, and aldehydes (*16*), whereas our mechanism, based on the evidence of Pichler's School, considers only linear α-olefins and alcohols as primary products; alkanes, branched products, and aldehydes are formed in secondary reactions.

We wish to add some clearing comments concerning our use of the Schulz–Flory distribution ("normal" or "most probable" distribution) of molecular weights in our mechanistic study, which evidently arose some controversy with respect to "priority" (*1*, *2*).

G. V. Schulz (*21*) in 1935 derived his equation for the case of radical polymerization of vinyl monomers (addition polymerization); P. J. Flory (*22*) in 1936 published his equation for the case of linear polycondensation polymers and stated that both equations are essentially equivalent although based on entirely different sets of conditions. Obviously the same kind of statistics are involved in either case.

Some 15 years later, Friedel and Anderson (*23*), based on earlier work of Herington (*24*), developed an equation for the products of the Fischer–Tropsch synthesis. Since again the same statistics are involved (as long as branching can be neglected), the resulting equation is equivalent to the former two (although apparently the authors were not aware of the work of Schulz and of Flory).

For the particular case of branched products, a correction factor with an adjustable parameter was introduced by Anderson *et al.* (*25*), resulting in an equation which—as Madon (*2*) puts it—"helps to organize much experimental data." Since in our 1976 article we were not concerned with isomer distributions, but with the distribution of the primary products, we did not explicitly describe these efforts, although we duly referenced the early work.

We want to emphasize that we applied the Schulz–Flory distribution[1] as a tool in our mechanistic evaluation of the Fischer–Tropsch synthesis. We preferred to use it in the form given by Schulz, in view of the evident mechanistic parallelism between addition polymerization and the primary reactions in Fischer–Tropsch, and because of the direct relationship between distribution and mechanism in this formulation.

Finally we have some comments to Madon's interesting finding that the molecular weight distribution of hydrocarbons produced with a ruthenium catalyst is considerably narrower than the "normal" distribution (*2*). It is known from work of Pichler and his School (*26*, *27*) that

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[1] The expression "Schulz-Flory polymerization" used by Anderson (*1*) is confusing.

alkyl-ruthenium species (as intermediates of the Fischer–Tropsch synthesis with ruthenium) tend to resist β-hydrogen abstraction. Unless quenched with alkali or H_2, the growing chains remain "living." According to Flory (*28*), the molecular weight distribution of a polymer grown in the absence of chain termination and chain transfer is very narrow, and is represented in the ideal case by a Poisson function (i.e., the ratio of weight average to number average of the molecular weight, M_w/M_n, approaches unity). Experimental distributions are generally somewhat broader, for a number of reasons (*29*), and values of M_w/M_n of 1.1 to 1.2 are quite usual. [From Fig. 2 of (*2*), $M_w/M_n \simeq 1.1$ can be calculated.] Without knowing the detailed experimental set-up and work-up, we can only suggest checking into this possibility, taking into account that certain ruthenium carbonyls are volatile at high temperatures (*26*, *27*), and that the chain growth rate at a Ru center is of the order of about one CH_2 group per minute (*30*).

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