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Reply to Comments by G. Henrici-Olivé and S. Olivé

In their comments, Henrici-Olivé and Olivé have tried to rationalize the validity of a mechanism for the heterogeneously catalyzed Fischer–Tropsch (FT) reaction not by presenting experimental proof using solid surfaces or catalysts but by arguments that mainly compare events in homogeneous catalysis. Furthermore, they state that the Schulz–Flory distribution equation was used by them as a tool for the mechanistic evaluation of the synthesis reaction. I believe that Henrici-Olivé and Olivé have missed the point of my note (*1*).

In my note (*1*), I refrained from entering the controversial area of Fischer–Tropsch mechanisms as I wished merely to point out that Herington (*2*) and Friedel and Anderson (*3*) were among the first to use concepts developed for polymer distributions to analyze FT data. It was further shown that the mathematical equation used by the U.S. Bureau of Mines' researchers (*3*, *4*) was the same as the Schulz–Flory equation used by Henrici-Olivé and Olivé (*5*) to analyze FT data about two decades later. Thus the concept of the FT process being akin to polymerization is not a novel one as Ref. (*5*), which does not reference previous such work in the field, would lead one to believe.

Furthermore, irrespective of the detailed mechanism, as long as chains grow by stepwise addition of identical single carbon units, the ratio of the termination to propagation rate remains independent of chain length, and one has simple termination as opposed to termination by chain combination, one can fit the experimental data as shown both in Refs. (*4*) and (*5*) by the Schulz–Flory distribution law. Hence, such a distribution cannot be used as "a tool," except in a very general way, to evaluate any detailed mechanism for the FT synthesis.

Comparing elementary steps for similar reactions in homogeneous and heterogeneous catalysis is often edifying and interesting. And though such comparisons can allow logical yet intuitive arguments to be made regarding viable mechanisms on solid catalysts, they may be used only as complementary clues and cannot replace experimental evidence. It is indeed enigmatic that on conventional heterogeneous FT catalysts ethylene, when added to the H_2/CO feed, is known to initiate and be incorporated in growing hydrocarbon chains (*6*) but does not participate in an oxo-type reaction to give aldehydes as primary products. The statement "the detection of a soluble catalyst system, providing Fischer–Tropsch growth on benzene molecules (*7*) appears to underline the obvious fact that there is only one chemistry, and that homogeneous and heterogeneous catalysis do have a common basis" is inappropriate.

There is growing evidence (*8–11*) that the synthesis reaction may be initiated on certain surfaces by the hydrogenation of an active carbon obtained by the dissociative chemisorption of CO. Growth may then take place by CO (*8*), CH_2 (*9*), or CH (*11*) insertion (alkyl migration reac-

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tion), and this too may depend on the type of surface. One can further postulate that CO insertion may lead to oxygenates, whereas CH or CH_2 insertion may give hydrocarbon chains.

Though modern experimental techniques and an increased knowledge of surface chemistry have allowed more sophisticated speculations regarding FT mechanisms, the basic ideas are quite old. For example, in 1926 Fischer and Tropsch (*12*) suggested that an active surface carbide, via which CH_2 groups were formed, played a key role in their synthesis. And in 1943, Eidus (*13*) postulated that the CH_2 groups, which were the links for growing hydrocarbon chains, were formed by the hydrogenation of undissociated chemisorbed CO and the elimination of water; still a viable alternative to the dissociative mechanism.

Finally, as long as one is concerned about "priorities," a few more comments may be made. In 1959, Sternberg and Wender (*14*) were among the first to formulate the CO insertion reaction. And in fact, in 1958, Wender *et al.* (*15*) stated that CO insertion between the metal and the growing hydrocarbon chain suggested an alternate mechanism for the production of straight chain molecules in FT synthesis. A more detailed FT mechanism, based on this previous proposal of CO insertion, was put forward in 1970 by Pichler *et al.* (*16*). This mechanism of Pichler *et al.* is extremely similar to the one proposed by Henrici-Olivé and Olivé 6 years later (*5*).

The mechanistic game is almost always fraught with debate and controversy, and often arguments are based as much upon analogies and intuition as they are upon experimental data. Advances in mechanistic understanding are often subtle and often basic ideas, as shown above for the FT reaction, can be traced to earlier workers in the field. It would help mitigate controversy if appropriate work was referenced and the differences, especially if they be subtle, between past and current ideas elucidated.

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