Stoichiometric and Catalytic Homologation of Olefins on the Fischer-Tropsch Catalysts Fe/SiO_2, Ru/SiO_2, Os/SiO_2, and Rh/SiO_2. Mechanistic Implication in the Mode of C-C Bond Formation

M. Leconte, A. Theolier, D. Rojas, and J. M. Basset*

Institut de Recherches sur la Catalyse—C.N.R.S.
69626 Villeurbanne Cêdex, France

Received June 21, 1983

Recently, Pettit and co-workers[1] have shown that diazomethane plus H_2 can be transformed to hydrocarbons on group 8 metal catalysts. With $CH_2N_2 + H_2$ these catalysts gave the same type of Schulz–Flory distribution as the equimolar mixture of CO + H_2. The results confirmed the fact that chain growth in Fischer–Tropsch synthesis does not involve undissociated CO but rather CH_x and most likely CH_2 surface fragments. We report here that with Fe/SiO_2 (**1**), Ru/SiO_2 (**2**), Os/SiO_2 (**3**), and Rh/SiO_2 (**4**), catalysts, C_nH_{2n} olefins can be stoichiometrically or catalytically (under H_2) homologated[2] to higher and lower olefins, and we bring evidence that the mode of C–C bond formation is the same in Fischer–Tropsch synthesis and in olefin homologation.

At 250–300 °C and under 1 atm of syn gas (CO/H_2 = 1/1), the catalysts **1–4**[3] give a typical Fischer–Tropsch distribution of hydrocarbons with a narrow range of carbon number (C_1–C_5). When used in the same range of temperature and in the absence of CO and H_2, the same catalysts are able to convert stoichiometrically any α or internal C_n olefin to a mixture of hydrocarbons ranging from C_1 to ca. C_{n+2}. Under H_2 (olefin/H_2 = 1/1), the reaction is catalytic and can last for several days. A typical product distribution obtained with propylene is given on Figure 1 in comparison with the product distribution obtained in syn gas reaction. No detectable homologation to higher carbon numbers was obtained with propane in similar experimental conditions (catalysts, temperature, partial pressure or reactants, and flow rate).

If one focuses on the properly so-called homologation, the reactions depicted on the Scheme I were observed independently. Interestingly, as indicated in the reactions of Scheme I (reactions 4 and 5), the carbon skeleton of the olefin is maintained after homologation. This result indicates that C_{n+1} olefin is formed by addition of a C_1 fragment to the C_n skeleton and not by a kind of random association of C_1 fragments.[5] (It is likely that the C_1 fragment comes from the hydrogenolysis of the C_n olefin).

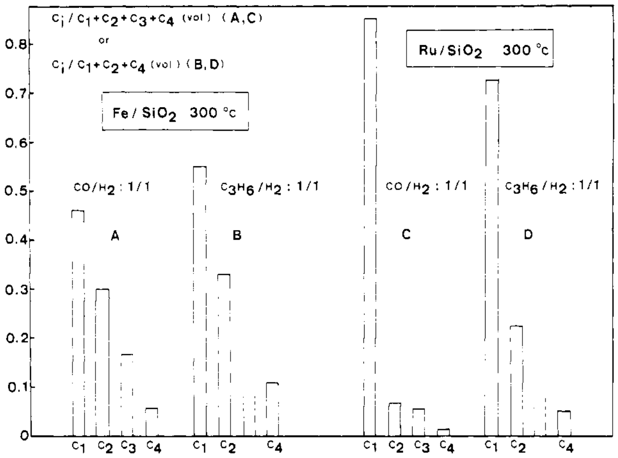


Figure 1. Product distribution (olefins + paraffins from C_1 to C_4) in CO + H_2 reaction ($p \approx 1$ atm) or $C_3H_6 + H_2$ reaction ($p = 1$ atm) with Fe/SiO_2 and Ru/SiO_2 catalysts.[4]

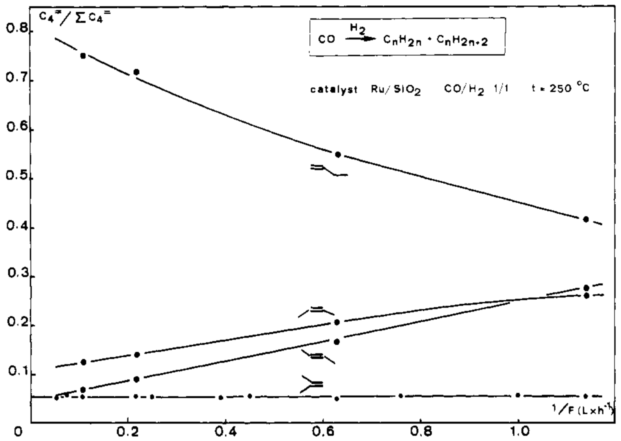
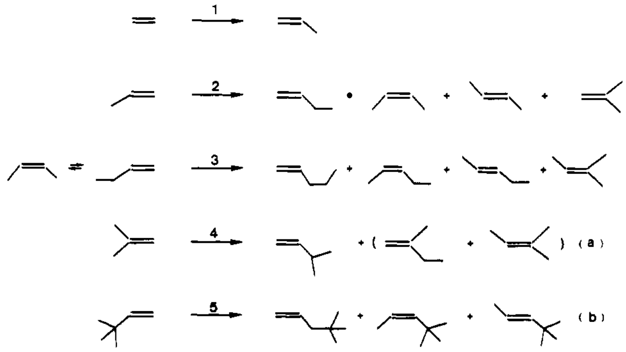


Figure 2. Product distribution in the C_4 olefinic compounds as a function of contact time (1/flow rate) in CO + H_2 reaction (p = 1 atm) (catalyst 150 mg).

Scheme I. Homologation Reactions Observed Catalytically under H_2 with Fe-, Ru-, and Os/SiO_2 Catalysts (Reactions 1–4) or Stoichiometrically (in a Sealed Tube) with Rh/SiO_2 Catalyst (Reactions 1–5)



[a] No linear C_5 olefins were detected; 2-methyl-1-butene and 2-methyl-2-butene were observed only at increasing contact time. [b] No linear C_7 olefins were detected.

The results of Figure 1 suggest a same mechanism for C–C bond formation in syn gas conversion and olefin homologation. In order to test this assumption we have considered the formation of C_4 olefinic hydrocarbons both in CO + H_2 reaction and C_3H_6 + H_2 reaction.

The yields of linear and branched olefins have been measured at various contact times and initial selectivies obtained by extrapolation to zero conversion. The isobutene/*n*-butene ratio remained constant with time, only double bond migration being

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[1] Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181; **1981**, *103*, 1287. Osterloh, W. T.; Cornell, M. E.; Pettit, R. Ibid **1982**, *104*, 3759. For a review of intermediates in Fischer–Tropsch synthesis, see, e.g.: Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

[2] Homologation of olefins is now a known reaction that occurs at the surface of metals or oxides; see e.g.: (a) O'Neill, P. P.; Rooney, J. J. *J. Am. Chem. Soc.* **1972**, *94*, 4383. (b) Hugues, F.; Besson, B.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 719. (c) Hugues, F.; Besson, B.; Bussiere, P.; Dalmon, J. A.; Basset, J. M.; Olivier, D. *Nouv. J. Chim.* **1981**, *5*, 207. (d) Strehlow, R. A.; Douglas, E. C.; *J. Chem. Soc., Chem. Commun.* **1983**, 259. (e) Yamaguchi, T.; Nakamura, S.; Tanabe, K. *Ibid.* **1982**, 621. (f) Dwyer, D. J.; Somorjai, G. A.; *J. Catal.* **1979**, *56*, 249. Homologation of alkanes also occurs on metallic surfaces, but it is suspected, that the alkanes are initially dehydrogenated to olefins; see e.g.: (g) O'Donohoe, C.; Clarke, J. K. A.; Rooney, J. J. *J. Chem. Soc., Faraday Trans 1* **1980**, *76*, 345. (h) Sarkany, A.; Tetenyi, P. *J. Chem. Soc., Chem. Commun.* **1980**, 525.

[3] The catalysts **1–3** were prepared by thermal decomposition of $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ supported on silica. The supports were pretreated at 500 °C under 10^{-4} torr for 16 h before adsorption of the cluster with a solution of hexane. The final metal contents were respectively 0.33%, 1.0%, and 1.3% for Fe, Ru, and Os. The clusters were then decomposed overnight under flowing H_2 at 300 °C. The average particle size, determined by electron microscopy were respectively 30, 14, and 16 Å for Fe, Ru, and Os. The amount of catalyst was in the range 100–400 mg depending on experimental conditions. The reactor was a dynamic microreactor working at atmospheric pressure. The catalyst **4** was prepared by reduction under flowing H_2 at 470 °C of $RhCl_3$ supported on silica. The average particle size was about 16 Å.

[4] This product distribution does not vary significantly with contact time (in a range of space velocity from 10^3 to 20×10^3 h^{-1}); the paraffin/olefin ratios increase with contact time in both the CO + H_2 reaction and C_3H_6 + H_2 reaction.

[5] Fischer, F.; Tropsch, H. *Brennst.-Chem.* **1926**, *7*, 97. Craxford, S. R.; Rideal, E. K. *J. Chem. Soc.* **1939**, *1*, 604.

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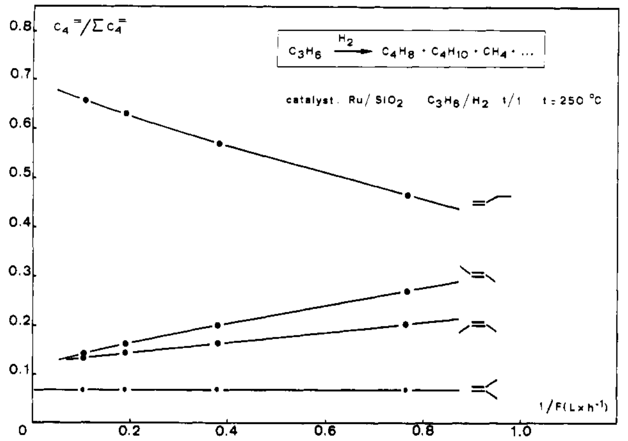

Figure 3. Product distribution in the C_4 olefinic compounds as a function of contact time (1/flow rate) in $C_3H_6 + H_2$ reaction (p = 1 atm) (catalyst 150 mg).

Table I. Isobutene/n-Butene Ratios (at 0% Conversion) in CO + H_2 Reaction and $C_3H_6 + H_2$ Reaction with Fe/SiO_2, Ru/SiO_2, and Os/SiO_2 Catalysts

		isobutene/n-butene ratios (1 atm)	
catalyst	temp, °C	CO/H_2 = 1/1	C_3H_6/H_2 = 1/1
Fe/SiO_2	250	0.10 ± 0.01	0.09 ± 0.01
	300	0.13 ± 0.01	0.15 ± 0.01
Ru/SiO_2	250	0.06 ± 0.01[a]	0.08 ± 0.01[b]
Os/SiO_2	250	0.05 ± 0.02	0.08 ± 0.01

[a] The same value has been obtained with the CO/H_2 ratios of 1.5/1, 1/1, and 1/2. [b] The same value has been obtained with the C_3H_6/H_2 ratios of 2/1, 1/1, and 1/2.

noted (1-butene → 2-butene) (Figures 2 and 3).

For a given catalyst and a given temperature, the iso/n ratios of C_4 olefinic hydrocarbons at zero conversion are the same for CO + H_2 reaction and $C_3H_6 + H_2$ reaction (within exprimental error) (Table I).

One should also notice that both reactions exhibit a high initial selectivity for α olefins. There are some differences in the cis–trans ratio of 2-butenes and in the initial selectivity for α olefins between Figures 2 and 3. These differences may be due to the presence of CO in the syn gas reaction that competes with the olefin for coordination to the surface and modifies the overall kinetics of double-bond migration and cis–trans isomerization. Apparently, the presence of CO does not modify significantly the kinetic parameters that govern the formation of branched olefin.

It appears from the above results (carbon number distribution and initial selectivity) that the mechanism of C–C bond formation is the same in syn gas reaction and olefin homologation on Fe-, Ru-, and Os/SiO_2 catalysts. The C–C bond formation does not require the presence of molecular CO in agreement with Pettit and co-workers,[1] Biloen,[6] Bell,[7] and others.[8] Our results, along with those of Pettit[1] indicate the same mechanism of C–C bond formation starting from CO + H_2, $CH_2N_2 + H_2$, or $C_nH_{2n} + H_2$. Besides we show here that this mode of C–C bond formation involves the addition of a C_1 fragment to a C_n fragment. These results do not demonstrate whether the mechanism for chain growth involves an insertion of a carbene to a metal alkyl or the coupling of a carbene to an olefin. It also does not enlighten on the mechanisms of formation of oxygenated compounds where the support may play an important role.

Acknowledgment. This work was supported by the GRECO Co. and CNRS.

Registry No. Ethene, 74-85-1; propene, 115-07-1; 1-butene, 106-98-9; 2-methyl-1-propene, 115-11-7; 3,3-dimethyl-1-butene, 558-37-2; (Z)-2-butene, 590-18-1; iron, 7439-89-6; ruthenium, 7440-18-8; osmium, 7440-04-2; rhodium, 7440-16-6; carbon monoxide, 630-08-0.

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(6) Biloen, P.; Helle, J. N.; Sachtler, W. M. H. *J. Catal.* **1979**, *58*, 95. Biloen, P. *Abstr. Pap.-Am. Chem. Soc.* **1981**, *182nd*, INDE, 39. Biloen, P.; Helle, J. N.; Vandenberg, F.; Sachtler, W. M. H. *J. Catal.*, in press.

(7) Bell, A. T. *Catal. Rev.-Sci. Eng.* **1981**, *23*, 203.

(8) Kobori, Y.; Yamasaki, H.; Naito, S.; Onishi, T.; Tamaru, K. *J. Chem. Soc., Faraday Trans.* **1982**, *78*, 1473.

Enzymatic Cyclization of [1-^{18}O]Geranyl Pyrophosphate to *l-endo*-Fenchol

Rodney Croteau* and John Shaskus

Institute of Biological Chemistry
and Biochemistry/Biophysics Program
Washington State University
Pullman, Washington 99164

David E. Cane,*[1] Akio Saito, and Conway Chang

Department of Chemistry, Brown University
Providence, Rhode Island 02912

Received September 22, 1983

The recent discovery that enzyme systems isolated from sage (*Salvia officinalis*) and from tansy (*Tanacetum vulgare*) will catalyze the conversion of geranyl pyrophosphate (**1**) to the *d* and *l* enantiomers, respectively, of 2-bornyl pyrophosphate (**2**)[2] has already led to several critical insights into the mechanism of terpenoid cyclization reactions.[3] The facts that neither enzyme requires redox cofactors and that, in the absence of competing phosphatases and pyrophosphatases, both geranyl pyrophosphate and its tertiary allylic isomer, linalyl pyrophosphate (**3**), are strongly preferred as substrates over the corresponding cis allylic pyrophosphate, neryl pyrophosphate, are fully consistent with the simple stereochemical model illustrated in Scheme I. The latter model, based on the generation of a series of ion-paired intermediates, is completely supported by the results of numerous model studies of terpenoid cyclizations.[4] On the basis of this model, we have recently investigated the role of the pyrophosphate moiety in the formation of bornyl pyrophosphate and have reported the unexpected observation that the original pyrophosphate ester oxygen of geranyl pyrophosphate is the exclusive source of the corresponding pyrophosphate ester oxygen of the *d*- or *l*-bornyl pyrophosphate product.[5] The lack of detectable positional isotope exchange implies a remarkably tight restriction on the motion of the transiently generated pyrophosphate anion during the cyclization process. We now report the extension of our studies to the enzymatic formation of *l-endo*-fenchol (**4**) and present results that further illustrate the generality of our proposed stereochemical model.

Cell-free extracts of fennel (*Foeniculum vulgare*) have previously been shown to contain a cyclase that catalyzes the conversion of geranyl pyrophosphate to *l-endo*-fenchol (**4**).[6] In spite of numerous efforts to obtain a phosphatase-free preparation of this cyclase, these and all other attempts to detect the corre-

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(3) For recent comprehensive reviews of monoterpene and sesquiterpene biosynthesis, respectively, see: (a) Croteau, R. In "Biosynthesis of Isoprenoid Compounds"; Porter, J. W., Spurgeon, S. L., Eds.; Wiley: New York, 1981; pp 225–282. (b) Cane, D. E. *Ibid.* pp 283–374.

(4) Gotfredsen, S.; Obrecht, J. P.; Arigoni, D. *Chimia* **1977**, *31* (2), 62. Winstein, S.; Valkanas, G.; Wilcox, C. F. *J. Am. Chem. Soc.* **1972**, *94*, 2286. Stephan, K. *J. Prakt. Chem.* **1898**, *58*, 109. Poulter, C. D.; King, C.-H. R. *J. Am. Chem. Soc.* **1982**, *104*, 1420, 1422.

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