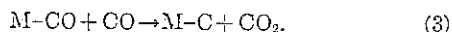
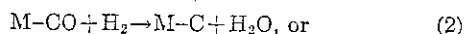


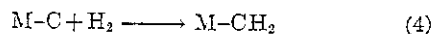
MECHANISM OF THE FISCHER-TROPSCH SYNTHESIS

The two principal hypotheses regarding the mechanism of the synthesis were proposed in 1926. Metal carbide was considered to be an intermediate product by Fischer and Tropsch,⁴⁶ and organic oxygenates were postulated to be intermediates by Elvins and Nash.⁴⁷ Detailed data on the composition of synthesis products later made possible formulation of mechanisms of chain growth, as the products are not in thermodynamic equilibrium with respect to isomers or ratios of alcohols to olefins and olefins to paraffins.

The carbide hypothesis, in its simplest form, postulates that adsorbed carbon monoxide is reduced to surface carbide according to



Equation (2) was believed to occur principally on cobalt and nickel surfaces and equation (3) on iron. The water-gas-shift reaction was incorrectly eliminated as a source of carbon dioxide on the basis of experimental evidence. The surface carbide is then hydrogenated according to



and the adsorbed methylene groups polymerize and desorb as olefinic and paraffinic hydrocarbons. Craxford and Rideal⁴⁸ gave a more detailed version of the carbide hypothesis, especially with respect to chain growth, for which a polymerization-depolymerization mechanism was proposed.

The carbide hypothesis was originally based on, and at many subsequent stages supported by, the observation that the chief Fischer-Tropsch catalysts—iron, cobalt, and nickel—react with carbon monoxide to form bulk carbides and that these carbides can react with hydrogen to form hydrocarbons. Little or no

direct evidence exists to substantiate the existence of surface carbide, although the hypothesis of surface carbide is convenient in many ways. Subsequently, bulk carbides of cobalt and nickel were shown to be virtually inactive in synthesis.⁴⁹⁻⁵¹

Kummer, DeWitt, and Emmett⁵² studied the synthesis at atmospheric pressure on cobalt and iron catalysts that had been carburized with C¹⁴O. Suitable preliminary studies were made to exclude exchange reactions as a source of carbon-14 in synthesis products. To avoid possible effects of surface heterogeneity, synthesis tests of short duration were made, so that only 1 percent of the surface carbide would be removed even if all products resulted from carbide hydrogenation. For experiments short enough to involve a maximum of 1 to 50 percent of surface carbide, only 10 to 15 percent of the product could possibly have been derived from carbide reduction at 260° to 300° C. These data do not preclude the possibility that carbon atoms may exist momentarily on the catalyst surface during some step in the synthesis.

Since 1947 evidence has accumulated indicating that several aspects of the carbide theory are incorrect: (a) The primary reaction produces chiefly water, and carbon dioxide is largely formed in a subsequent reaction; and (b) the observed distribution of hydrocarbon isomers is not consistent with postulates of Craxford and Rideal.

Eidus⁵³ proposed a more acceptable mechanism in which methylene radicals are intermediates in the synthesis. In his scheme two adjacent methylene radicals react to form adsorbed ethylene attached at two sites, and this group adds CH₂ radicals one unit at a time to form a long straight carbon chain. In this

⁴⁶ Weller, S., Hofer, L. J. E., and Anderson, R. B., The Role of Bulk Cobalt Carbide in the Fischer-Tropsch Synthesis: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 799-801.

⁴⁷ See footnote 38, p. 16.

⁴⁸ Perrin, M., [The Synthesis of Aliphatic Hydrocarbons]: Doctoral dissertation, University of Lyon, Lyon, France, 1948, 85 pp.

⁴⁹ Kummer, J. T., DeWitt, T. W., and Emmett, P. H., Some Mechanism Studies on the Fischer-Tropsch Synthesis Using C¹⁴: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 3632-3643.

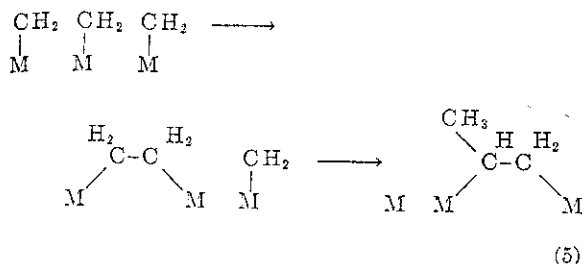
⁵⁰ Eidus, Y. T., [Mechanism of the Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen]: Uspekhi Khim., vol. 20, No. 1, 1951, pp. 54-70; trans. into English in Bureau of Mines Inf. Circ. 7821, 1958, pp. 7-10.

⁴⁶ Fischer, F., and Tropsch, H., [Synthesis of Petroleum at Atmospheric Pressures from Gasification Products of Coal]: Brennstoff-Chem., vol. 7, 1926, pp. 97-104.

⁴⁷ Elvins, O. C., and Nash, A. W., Reduction of Carbon Monoxide: Nature, vol. 118, 1926, p. 154.

⁴⁸ Craxford, S. R., and Rideal, E. K., Mechanism of the Synthesis of Hydrocarbons From Water Gas: Jour. Chem. Soc., 1939, pp. 1604-1614.

process the growing chain at the surface is an adsorbed α -olefin as equation (5) shows.



The mechanisms for chain termination and formation of branched hydrocarbons were not given; however, Bureau of Mines workers^{54 55} showed that observed isomer distribution could be explained with an α -olefinic intermediate, if one-carbon additions were permitted, but at different rates, on the two carbons of the olefinic bond, as will be described subsequently in this paper.

A serious shortcoming of this methylene polymerization hypothesis is its failure to explain the formation of alcohols—important primary products with iron and under some conditions cobalt catalysts. The Eidus hypothesis does explain the incorporation of ethylene and higher olefins into synthesis products when olefin is added to synthesis gas. Experiments involving the incorporation of tagged ethylene will be described later.

Herington⁵⁶ proposed that carbon chains grow one carbon atom at a time and assigned a probability that a given intermediate will grow at the surface rather than desorb. Friedel and Anderson⁵⁷ showed that, for any range of carbon numbers for which this probability is constant, the moles of product of carbon number n , ϕ_n may be related to moles in carbon number x , ϕ_x by

$$\phi_n = \phi_x \exp. [-\alpha(n-x)] \quad (6)$$

where α is the probability that a chain will grow. Although equation (6) is seldom accurate over the entire range of carbon numbers, it is a useful approximation.

To explain isomer and carbon number distributions, Bureau of Mines workers^{58 59} consid-

ered schemes of stepwise growth of the carbon chain. In one scheme stepwise chain growth is assumed to occur at the first or second carbon from one end of a growing chain, with the restriction that growth does not occur at adjacent-to-end carbons already attached to three carbon atoms. First-order reactions of growing intermediates with respect to concentration at the catalyst surface were assumed. Rate constants, independent of chain length and structure, were assumed for addition to end and adjacent-to-end carbons for desorption from the catalyst surface.

The rate of appearance, in moles, of products formed by addition to an end carbon is then $R_{n+1}/R_n = a$ and for addition to adjacent-to-end carbons $R'_{n+1}/R_n = af$, where R_n is the rate of appearance of hydrocarbons of carbon number n in moles per unit time, a is a constant largely determining the carbon-number distribution, and f is a constant principally determining isomer distribution. Then, starting with C_2 and accounting for all possible reaction steps, the relative isomer and carbon-number distributions, in terms of a and f , may be developed to C_6 , as shown in table 6. The carbon number distributions are in the form

$$\phi_n = 2\phi_2 F_n a^{n-2}, \quad (7)$$

where F_n is the quantity in parentheses in the last column of table 6. This development assumes that both carbon atoms in the C_2 intermediate act as end carbons.

TABLE 6.—Isomer and carbon-number distribution in terms of a and f

Carbon chain	Relative isomer composition	Relative carbon-number distribution, moles
C_2	1	1
C_3	1	$2a$
C_4 { n - C_4	1	$2a^2(1+f)$
2-methyl- C_4	f	
C_5 { n - C_5	1	$2a^3(1+2f)$
2-methyl- C_5	$2f$	
C_6 { n - C_6	1	$2a^4(1+3f+f^2)$
2-methyl- C_6	$2f$	
3-methyl- C_6	f^2	
2,3-dimethyl- C_6	f^2	

The best values of computed isomer distributions, obtained by assigning values to a and f by a trial-and-error method, are compared with observed values from iron and cobalt catalysts in table 7. Figures 10 and 11 show plots of equation (7) for data from iron catalysts in fluid-bed⁶⁰ and fixed-bed operation.⁶¹

⁵⁴ Storch, H. H., Columbic, N., and Anderson, R. B., Fischer-Tropsch and Related Syntheses: John Wiley & Sons, Inc., New York, N.Y., 1951, 610 pp.

⁵⁵ Anderson, R. B., Friedel, R. A., and Storch, H. H., Fischer-Tropsch Reaction Mechanism Involving Stepwise Growth of Carbon Chain: Jour. Chem. Phys., vol. 19, 1951, pp. 313-319.

⁵⁶ Herington, E. P. G., The Fischer-Tropsch Synthesis Considered as a Polymerization Reaction: Chem. and Ind., vol. 65, 1946, pp. 345-347.

⁵⁷ Friedel, R. A., and Anderson, R. B., Composition of Synthetic Fuels. I. Product Distribution and Analysis of C_2 - C_6 Paraffin Isomers From Cobalt Catalysts: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 1212-1215, 2307.

⁵⁸ Weller, S., and Friedel, R. A., Isomer Distribution in Hydrocarbons from the Fischer-Tropsch Process: Jour. Chem. Phys., vol. 17, 1949, pp. 801-803.

⁵⁹ See footnote 55, p. 19.

⁶⁰ Weitkamp, A. W., Seelig, H. S., Bowman, N. J., and Cady, W. E., Products of the Hydrogenation of Carbon Monoxide Over an Iron Catalyst: Ind. Eng. Chem., vol. 45, 1953, pp. 343-349.

⁶¹ Anderson, R. B., Catalysts for the Fischer-Tropsch Synthesis: Chap. 2 in Catalysis, vol. IV (P. H. Emmett, ed.), Reinhold Publishing Corp., New York, N.Y., 1956, pp. 29-255.

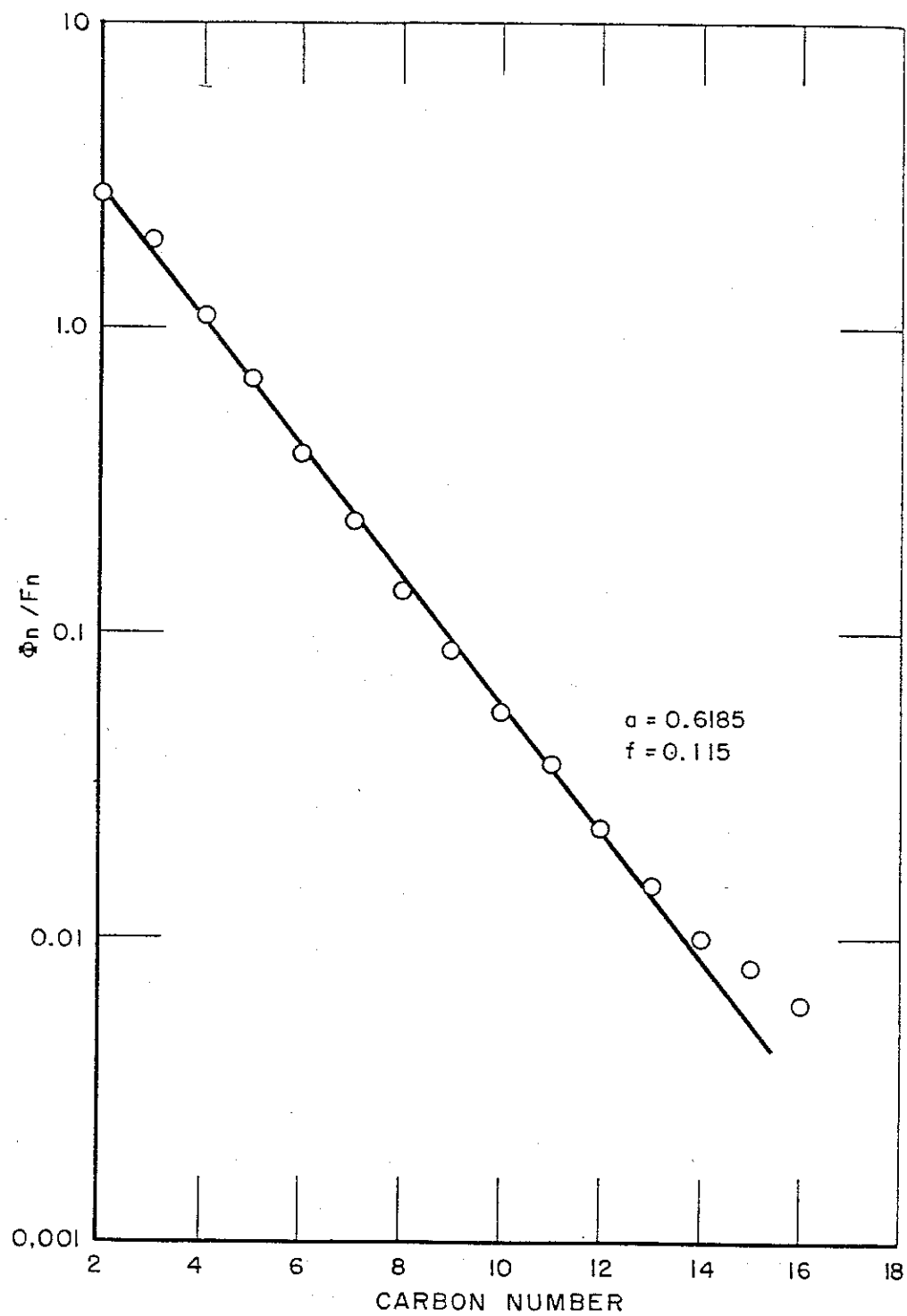


FIGURE 10.—Plot of Equation [7] for Data From Synthesis With Fluidized Iron Catalyst (Standard Oil).

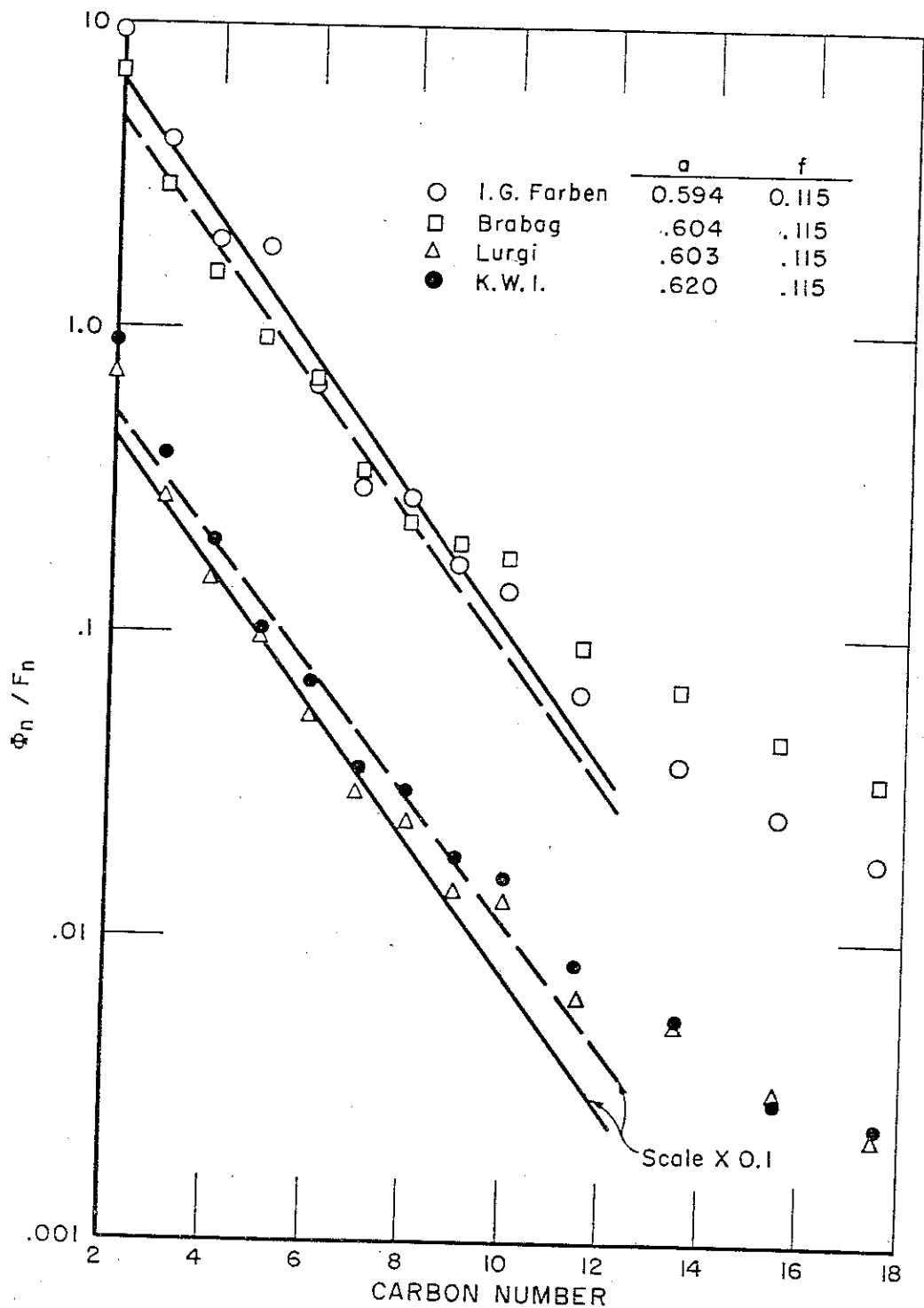


FIGURE 11.—Plots of Equation 7 for Data From Schwarzheide Tests of Iron Catalysts.

TABLE 7.—Chain structures of hydrocarbons from cobalt and iron catalysts

Carbon chain	Mole percent in fraction			
	Cobalt catalyst		Iron catalyst	
	Observed	Com-puted	Observed ¹	Com-puted
		$f=0.035$		$f=0.115$
C ₄ n-C ₄	97.0	96.6	89.4	89.7
2-methyl-C ₃	3.0	3.4	10.6	10.3
C ₅ n-C ₅	95.0	93.4	81.2	81.3
2-methyl-C ₄	5.0	6.6	18.8	18.7
n-C ₆	89.6	90.2	78.8	73.5
2-methyl-C ₅	5.7	6.4	11.2	16.9
C ₆ 3-methyl-C ₅	4.7	3.2	9.5	8.5
2,3-dimethyl-C ₄	0	2	4	9
n-C ₇	87.7	87.3	66.0	66.0
2-methyl-C ₆	4.6	6.2	13.1	15.4
C ₇ 3-methyl-C ₆	7.7	6.2	19.1	15.4
2,3-dimethyl-C ₅	0	2	1.6	1.7
2,4-dimethyl-C ₅	0	1	3	8
n-C ₈	84.5	84.4	61.0	60.5
C ₈ 2-methyl-C ₇	3.9	6.0	36.4	34.7
3-methyl-C ₇	7.2	6.0		
4-methyl-C ₇	4.4	3.0	2.6	4.8
dimethyl-C ₆ 's.....	0	6		

¹ Bruner, F. H., Quality of Synthetic Gasoline From Natural Gas: Ind. Eng. Chem., vol. 41, 1949, pp. 2511-2515.

² Data available for only these chain structure types.

Deviations of the linear plots at high carbon numbers are large for products from fixed-bed tests.

Storch, Golumbic, and Anderson⁶² proposed

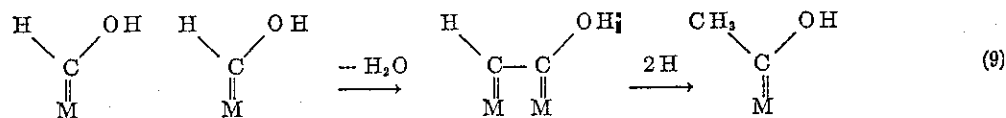
⁶² See footnote 54, p. 19.

Initiation of chains:

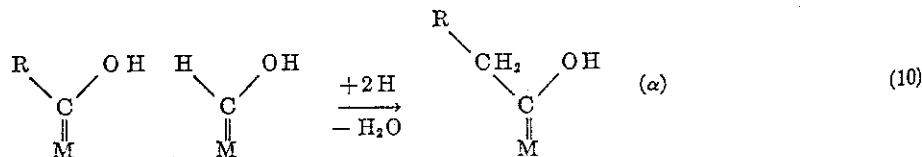


Growth of chains:

(a) At end carbon—



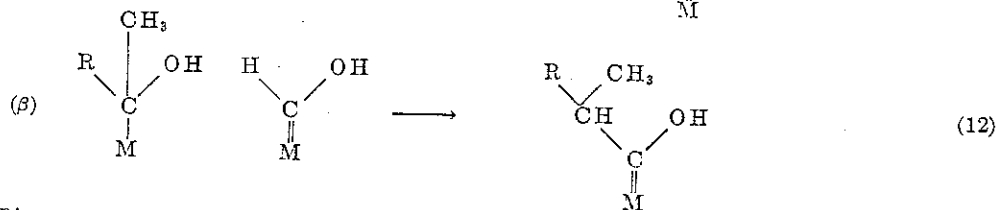
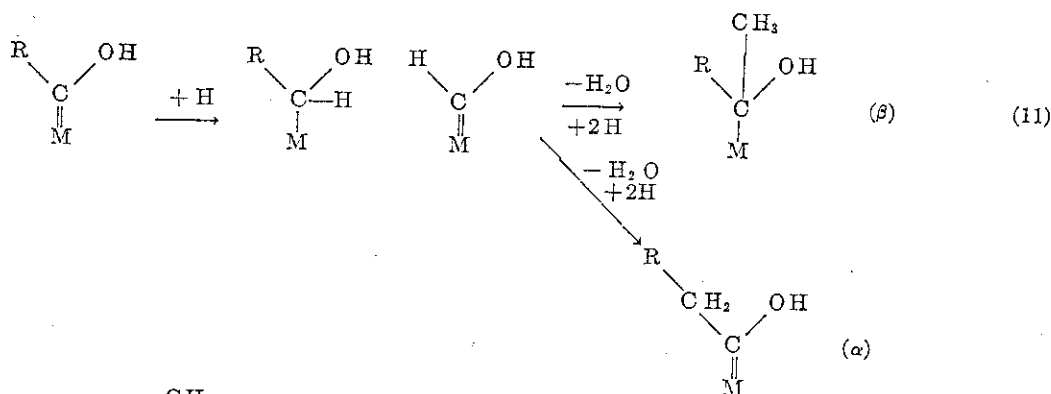
and



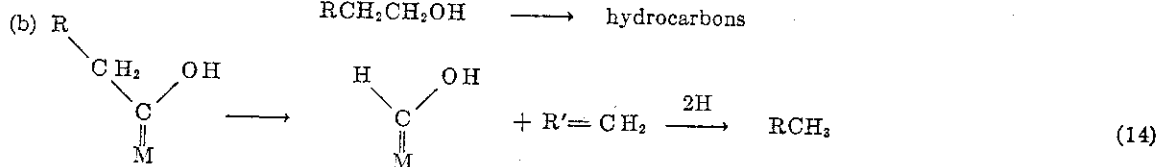
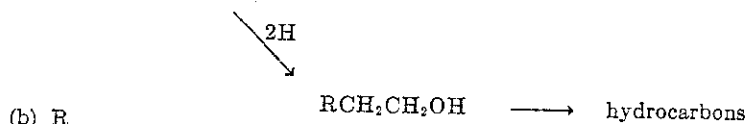
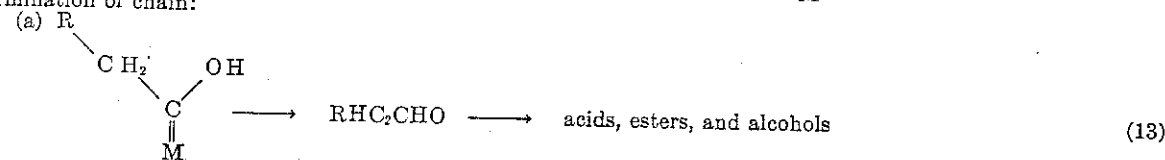
an oxygenated intermediate mechanism that was consistent with the chain-growth mechanism described above. The following assumptions were made: (a) Hydrogen is adsorbed as atoms on surface metal atoms; (b) chemisorption of carbon monoxide occurs on metal atoms with bonding similar to that in metal carbonyls; and (c) adsorbed carbon monoxide is partly hydrogenated according to equation (8).

Chain building may occur in two ways, at the end carbon (equations 9 and 10) and at the adjacent-to-end carbon (equations 11 and 12). In these steps the double bonds between carbon and metal atoms are assumed to be more resistant to hydrogenation if the carbon atom is also attached to a hydroxyl group. Growth processes leading eventually to chain branching involve partial hydrogenation of the carbon-metal bond, according to equations (11) and (12). Intermediate α is the same as in equation (10), but intermediate β may produce a chain with a methyl branch according to equation (12). Various equations, such as (13) and (14), can be proposed for terminating the growing chain to give aldehydes, alcohols, olefins, and paraffins. Acids and esters may result from Cannizzaro reactions of aldehyde-like intermediates or from other side reactions.

(b) At penultimate carbon—



Termination of chain:



Emmett and coworkers⁶³⁻⁶⁶ studied the incorporation of alcohols and other oxygenated molecules in the synthesis with iron catalysts at atmospheric pressure using alcohols tagged with C¹⁴. When primary alcohols are introduced at low concentration (1.5 percent by volume), they are largely incorporated into synthesis products, presumably by having become intermediates in the synthesis. The important result is that the radioactivity of the hydrocarbon product per mole (for carbon numbers greater than that of the alcohols) is essentially constant, as figure 12 shows.

[†] Kummer, J. T., Podgurski, H. H., Spencer, W. B., and Emmett, P. H., Mechanism Studies of the Fischer-Tropsch Synthesis. Addition of Radioactive Alcohol: Jour. Am. Chem. Soc., vol. 73, 1951, pp. 564-569.

[‡] Kummer, J. T., and Emmett, P. H., Fischer-Tropsch Synthesis Mechanism Studies. The Addition of Radioactive Alcohols to the Synthesis Gas: Jour. Am. Chem. Soc., vol. 75, 1953, pp. 5177-5182.

[§] Hall, W. K., Kokes, R. J., and Emmett, P. H., Mechanism Studies of the Fischer-Tropsch Synthesis. The Addition of Radioactive Methanol, Carbon Dioxide, and Gaseous Formaldehyde: Jour. Am. Chem. Soc., vol. 79, 1957, pp. 2985-2989.

[¶] Kokes, R. J., Hall, W. K., and Emmett, P. H., Fischer-Tropsch Synthesis Mechanism Studies. The Addition of Radioactive Ethanol to the Synthesis Gas: Jour. Am. Chem. Soc., vol. 79, 1957, pp. 2989-2996.

These data suggest that primary alcohols initiate chains that grow by a stepwise mechanism. For isopropanol the radioactivity per mole of hydrocarbon decreased with increasing carbon number. Analyses of the C₄ products from the incorporation of normal and isopropanol indicated that straight-chain butane and butenes were predominantly formed from propanol-1 and isobutane and isobutylene from propanol-2. Incorporation of radioactive methanol was smaller, and the radioactivity of hydrocarbon products per mole increased with increasing carbon number, suggesting that methanol acts as both a chain initiator and a chain-building unit. With ethanol and higher alcohols 40 to 60 percent of the hydrocarbon chains were initiated by the alcohol.

On cobalt catalysts with 2H₂+1CO plus 1.5 percent radioactive ethanol, the radioactivity of C₃⁺ hydrocarbons per mole was relatively constant; however, the alcohol initiated only