

A Comprehensive Mechanism for the Fischer-Tropsch Synthesis

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I. Introduction

Hydrocarbons and oxygenated compounds can be produced catalytically from synthesis gas ($\text{CO} + \text{H}_2$) at atmospheric pressure or above and at a few hundred degrees Celsius. The production of chemical feedstocks or motor fuels from any combustible carbon-containing source, including coal, biomass, or garbage, would be an attractive alternative to politically unstable petroleum supplies. In addition, the Fischer-Tropsch synthesis has the potential for producing chemical feedstocks or motor fuels without the production of the environmentally harmful compounds encountered in direct hydrogenation. However, the Fischer-Tropsch



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synthesis is now utilized on a large scale only in the South African Sasol plants.

The process could be improved in several areas. The production of a range of compounds indicates that the synthesis might be used to supply several chemical feedstocks, but it also requires extensive refining of the product stream. Catalyst deterioration is another significant difficulty. A more detailed understanding of the process should lead to greater flexibility of application.

A more theoretical approach may be of use in further improving the Fischer-Tropsch synthesis. Although the synthesis has been studied for more than 50 years,¹⁻¹⁷ no understanding of its mechanism exists that is sufficient to predict products under various conditions or to unify the observations in a detailed way.

Many of the features of the synthesis indicate that the mechanism is not simple. Extensive reaction, including dissociation to adsorbed atoms, must take place to transform the reactants, CO and H_2 , to compounds containing several C-C and C-H bonds. Numerous products are obtained that vary in both carbon chain length and type of functional groups;^{1,2,7,9,11,12} the different functional groups imply different paths and different intermediates. Relative amounts of the products vary with the catalyst, temperature, and pressure;^{1,2,5,7,11} different paths must be favored by different sets of conditions.

Large amounts of data have been generated on product distribution for different operating conditions and on experiments intended to elucidate the mecha-

nism. The sheer volume of data makes correlations difficult, with an enormous number of possible combinations of catalyst, temperature, and pressure. Several reaction mechanisms have been proposed.^{3,7,8,10,12,14-16,18-24} Most are constructed around a single critical intermediate or reaction,^{3,8,12,18-20,23,24} although multiple paths have also been considered.^{7,10,14-16,21,22} All of the intermediates proposed have evidence to support them, but contradictory data also exist for all of them.

The question in formulating a mechanism for the Fischer-Tropsch synthesis appears to be less which intermediate is the critical intermediate than to what degree each type of intermediate contributes. The difference between these two questions is the difference between two approaches to chemical mechanisms. The first approach has been predominant in previous studies. The second will be pursued in this review.

The second approach leads to a set of elementary reactions that describe a network of paths, whereas the first approach leads to a more linear system. Most of the steps and intermediates that have been proposed by other workers are included, some new steps have been added, and several steps have been proposed as possibilities for future inclusion.

The mechanism proposed here provides a preliminary basis for unifying the many observations relating to the Fischer-Tropsch synthesis; a definitive statement of all elementary reactions is not possible at this time. Steps can be added or subtracted as new information becomes available. This mechanism provides a structure by which studies of various sorts of model systems (metal complexes, surfaces) can be related to each other and by which relationships among several synthesis-gas processes may be explored. It is also a starting point for calculational analysis of the mechanism. Many of the elementary reactions are of such a form that rate constants can be calculated or estimated; the mechanism as a whole is treatable by kinetics codes and sensitivity analysis codes. The calculation of relative stabilities of intermediates can also contribute to and benefit from this type of mechanistic treatment.

The elementary reactions that make up this mechanism are those that have some support in experiment. The types of evidence that will be considered are, in decreasing order of relevance to the mechanism: direct observation of reactions or intermediates on surfaces, kinetic evidence for elementary reactions on surfaces, kinetic evidence and product distributions for combinations of elementary reactions on surfaces, direct observation of reactions or intermediates in complexes, kinetic evidence from complexes, and analogy to organic reactions.

The metals that will be considered as substrates, again in order of decreasing relevance, are iron, cobalt, nickel, ruthenium (the metals commonly used as Fischer-Tropsch catalysts); other group 8 metals; group 7 and 6 metals; and other transition metals, lanthanides, and actinides. If sufficient evidence is available from the more relevant categories to support an elementary reaction, evidence from the less relevant categories will not be included.

The relevance of complex chemistry to heterogeneous catalysis has been discussed in some detail,²⁵⁻³⁰ and opinion as to its usefulness as a model system differs.

I will assume that the observation of a reaction or an intermediate in a metal complex implies that the reaction or intermediate can occur on a surface, although rates may differ.

Evidence for the reactions will be reviewed with emphasis on that published from 1975 through 1980. Many of the subtopics touched on here have themselves been the subject of reviews, which will be referenced to the greatest extent possible. Primary references will also be used extensively. The capabilities and limitations of the experimental techniques cannot be discussed here; specialized reviews will be referenced as appropriate.

The Fischer-Tropsch synthesis will be defined here as the catalytic polymerization and hydrogenation of CO to give hydrocarbons and oxygenated products having various chain lengths; CO₂ and H₂O are the side products. This definition agrees with some that have appeared recently^{15,16} and differs slightly from others.^{5,10,12}

This discussion will be focused on the mechanism of the heterogeneous Fischer-Tropsch synthesis, because homogeneous reactions giving Fischer-Tropsch products may be mechanistically distinct; this point is not now clear.^{17,24} Similarly, mechanisms for zeolite catalysts will not be discussed, although it seems likely that the mechanism for them is similar to that for the normal heterogeneous synthesis, with spatial limitations imposed on the products by the zeolite.³¹

The approach to chemical reaction mechanisms used here will first be discussed in some detail. Next, the mechanism and supporting evidence for the elementary reactions will be presented. The reactions of the mechanism are grouped by a "time sequence" in the synthesis, in the sense of following a single CO molecule through its possible reactions from absorption on the surface to the formation of stable product molecules. Under steady-state conditions, however, all elementary reactions proceed simultaneously. The relation of this mechanism to other proposed mechanisms will be discussed, and its relation to other synthesis-gas reactions will be explored.

II. Viewpoints on Chemical Mechanisms

The mechanism of a chemical reaction can be understood in a number of ways, all of them reducing to the same elements. The extremes of viewpoint can be illustrated by two definitions:

The mechanism of a reaction is simply the path the molecules follow in going from reactant to product.³²

The "mechanism" of a complex reaction is the list of elementary chemical reactions postulated to explain the observed rates and products.^{33a}

Obviously, the path the molecules follow can be represented by appropriate elementary chemical reactions, while the list of elementary chemical reactions is arrived at by examining paths that the molecules might follow in going from reactant to product. Although the two viewpoints may refer to the same set of facts, each gives a different kind of insight. The first has been emphasized in previous discussions of Fischer-Tropsch mechanisms, usually with identification of a probable intermediate or reaction and its implications for a possible path. In this paper, a set of elementary

chemical reactions will be proposed. This approach has been used for other catalytic systems.^{34,35} However, it has not been applied in detail to the Fischer-Tropsch synthesis. The set of elementary reactions presented here can explain the products; further development should allow an analysis of observed rates.

In this mechanism, some intermediates are produced by more than one path, and an intermediate may yield more than one product. Thus, the appropriate spatial image for the mechanism is a network of paths. Previously, when multiple paths have been considered for Fischer-Tropsch mechanisms, the image has been of parallel paths or of forking late in the mechanism to produce multiple products from a few intermediates.^{7,14,15,16,21,23} Unfortunately, it is much more difficult to gain an intuitive feeling for the outcome of a network of reactions than for parallel paths or forks. A thorough analysis of such a system can only be done by computing the solutions of the appropriate set of differential equations. This complexity is the reason that few systematics have emerged from the study of the Fischer-Tropsch synthesis.

For example, the determination of Arrhenius parameters for the overall synthesis has shed little light on the mechanism.¹⁰ There are two possible reasons for this. First, the heterogeneous reactions of adsorption and desorption may be slow enough relative to chemical reactions on the surface that they dominate the overall kinetics, although this can usually be recognized from the form of the Arrhenius parameters and appears not to be the case here. Second, and more likely in this case, the concept of a rate-determining step may not be as useful in such a complex mechanism.^{33b} The inability to reduce the kinetics to a single rate-determining step can lead to the fractional concentration dependences observed in the Arrhenius analyses of Fischer-Tropsch syntheses,¹⁰ or to misinterpretations of seemingly interpretable data.^{33b} The complexity of the isotope effect when D_2 is substituted for H_2 in methanation³⁶ and in the Fischer-Tropsch synthesis³⁷ may also derive from this type of nonsimplifiability.^{37,38}

The concept of a zero effective relative rate may be more useful in understanding the Fischer-Tropsch mechanism. For a set of elementary reactions, it is possible that under particular conditions the rates of some reactions will effectively become zero relative to the rates of others. Concentrations of intermediates may change, or the rates themselves may change, to give effective relative rates of zero. Then the products from that part of the network will disappear or decrease, depending on the number and efficiency of other paths to them. It is important to recognize that the disappearance of a product indicates an effective relative rate of zero, but does not require the removal of that step or path from the mechanism. The rates for the elementary reactions of that path may remain what they were for conditions leading to those products, but the rates of elementary reactions in other paths may have increased, or the rate of a single reaction leading to a crucial intermediate may have decreased. Conceptually, however, the elementary reactions must remain in the mechanism, although their contributions to the differential equations may become negligible. Only by their retention can further changes in conditions be understood.

The complexity of the mechanism and the possibility of zero effective relative rates lead to difficulties in disproving a particular reaction path. Under a given set of conditions, a given reaction path may have an overall effective rate of nearly zero, and therefore the experiment will appear to disprove the participation of a particular intermediate. However, that result may apply only to that set of conditions and is not a disproof of that intermediate for all conditions. Many investigators have recognized this limitation, but it is often lost in later discussion of mechanisms. For example, ^{14}C tracer experiments³⁹ have often been cited as proving that methylene intermediates do not participate in carbon-carbon bond formation. The conclusion drawn by the authors of that study, however, is that "the mechanism of hydrocarbon production proposed by Fischer and his co-workers plays only a minor role in the synthesis of hydrocarbons under the conditions and over the catalyst studied in the present work, provided one assumes that the surface is uniformly active in the synthesis".³⁹ The qualifications are at least as important as the conclusion in this case.

Relative rates of the elementary reactions have been manipulated reasonably successfully in the empirical development of the industrial Fischer-Tropsch syntheses producing motor fuels. The rates for the paths in the reaction network leading to oxygenated products and extremely long carbon chains have been reduced relative to the rates of the paths leading to hydrocarbons. In most applications it would be desirable to reduce rates for paths leading to methane and to carbon deposition on the catalyst to a greater degree than has been achieved empirically. If the Fischer-Tropsch synthesis is to be modified to produce industrial feedstocks from coal, then relative rates of the elementary reactions leading to oxygenated products or alkenes will need to be enhanced; the relative rates of paths to other products will need to be reduced.

Cases in which a particular relative rate is effectively zero can be used to extract information on the mechanism from otherwise hard to handle data. For example, the existing data on hydrocarbon production represent a network in which the relative rates for the paths leading to oxygenated products are zero. Comparisons of these systems with those producing oxygenates in various quantities may lead to an understanding of the types of intermediates and changes in rates that are leading to the different product distributions. This type of analysis has been done in an empirical way in the industrial development of the synthesis. It should also be useful in reconsidering some of the subsidiary experiments that have been done to elucidate the mechanism. A computer code incorporating this mechanism would be the most helpful development in this type of data analysis.

If the multitudinous phenomena gathered under the Fischer-Tropsch umbrella are to be represented by a single mechanism, it will have to be a set of elementary reactions, some of which will have effective relative rates of zero under some conditions. Subsets of these reactions may be written for particular conditions, but this approach will lead to a different mechanism (set of elementary reactions) for every pressure, temperature, or catalyst condition that gives different products. This more limited approach cannot give a unified under-

standing of the Fischer-Tropsch synthesis and related synthesis-gas reactions. Subsets of the elementary reactions presented here can also represent other synthesis-gas reactions, such as carbon monoxide disproportionation, the water-gas shift reaction, methanation, and other syntheses closely related to Fischer-Tropsch.

III. The Mechanism

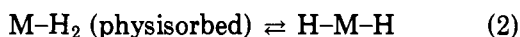
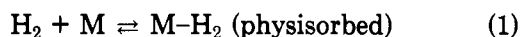
In order to write elementary reactions involving a surface, certain conventions beyond ordinary chemical notation are necessary. For this discussion, it will be desirable to indicate which atom of an adsorbed intermediate is bound to the surface, but not the details of its bonding, such as the type of active site to which it is bound. Most recent experimental findings show only small energy differences for chemisorption on different planes of the same metal (see, for example, ref 40-42). Under the high coverage conditions typical of the Fischer-Tropsch synthesis, these differences are likely to be even smaller. Other aspects of the bonding of the intermediate to the surface will be ignored or emphasized as appropriate; these will be noted as they occur. It is also desirable to have a compact notation that lends itself to the writing of elementary reactions in a linear form. Metal surface atoms will be indicated by M; the chemisorptive bond will be represented by a hyphen, which may represent any bond order. In most cases, no attempt will be made to represent multiple bonding to the surface, which may be to one or more surface atoms. Proximity of chemisorbed species is indicated by bonding to a single metal atom or is understood as being necessary for two intermediates to react; thus, H-M-CO is equivalent to M-H + M-CO; no necessary relation to metal complexes is intended by this notation.

All reactions will be assumed to proceed in both directions, by the principle of microscopic reversibility, and therefore the reverse reactions will not be written explicitly, although rates for the forward and reverse reactions can be expected to differ.

A. Adsorption Steps

1. Hydrogen Adsorption

Dihydrogen is first physisorbed and then dissociated on most transition metals:⁴⁰⁻⁵³



No distinction will be made between hydrogen adsorbed in a bridged mode (between two metal atoms) and hydrogen adsorbed atop a single metal atom.

Bonding of hydrogen atoms to a transition-metal surface appears to involve charge transfer from the metal to hydrogen;⁴¹ the hydrogen atoms are hydridic. The degree of participation of metal electrons in the bond differs from one metal to another. Ultraviolet photoelectron spectra show that bonding of H to nickel and iron involves the d bands of the metals less than does the bonding of H to palladium and platinum.^{52,54}

Most investigations of hydrogen adsorption have been carried out for pure metals. However, Fischer-Tropsch catalysts are generally supported or promoted metals, that is, systems of more than one metal. The catalytic properties of promoted and unpromoted metals differ

sufficiently that studies of adsorption on promoted metals and of the difference between supported and unsupported metals are important for understanding the synthesis.

Potassium carbonate on iron was one of the earliest catalysts studied by Fischer and Tropsch,² and the potassium-iron system is the only one in which the effect of a promoter on hydrogen adsorption has been studied. A potassium adlayer on a Fe(100) surface displayed greater binding energy for chemisorbed hydrogen than a clean Fe(100) surface.⁴⁷ An earlier study of K₂O adsorbed on iron gave the opposite result: hydrogen was more weakly adsorbed.⁵⁵ It has been suggested⁴⁷ that the difference was due to a layer of oxide on the iron surface in the earlier study. This difference illustrates both the difficulty of characterizing metal-promoter systems and the sensitivity of their catalytic properties.

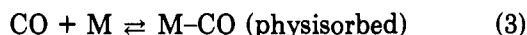
The effect of the support on hydrogen adsorption has been more studied, although in most cases not in direct relation to the Fischer-Tropsch synthesis.⁵⁶ Under some conditions, hydrogen atoms chemisorbed on a supported metal can migrate to the support, which then acts as a hydrogen atom reservoir even though it is itself incapable of dissociating H₂. The possibility of this sort of interaction was recognized by Sinfelt, Lucchesi, and Carter^{57,58} and was named "spillover" by Boudart, Vannice, and Benson.⁵⁹ Experimental evidence relating to hydrogen spillover has been extremely difficult to interpret.⁵⁶ An apparently unambiguous proof of such hydrogen was given by the comparison of temperature-programmed desorption curves for hydrogen from alumina-supported metals (platinum and nickel) with curves for hydrogen atoms deposited on alumina by a high-frequency discharge.⁶⁰

The mechanism of spillover is unclear. Water or another hydroxylic solvent appears to be necessary for it to occur.⁶¹ This finding suggests that hydrogen is transferred to the support as a proton, which is consistent with the form of hydrogen adsorption most likely on metal oxides. Infrared evidence⁶² indicates the presence of additional hydroxyl groups on alumina resulting from hydrogen spillover. However, since hydrogen chemisorbed on metals is hydridic, it should be repelled by the electron density around the oxygens of the support. An oxidation-reduction couple between hydrogen chemisorbed to the metal and oxidized metal at the interface between the metal and the support⁶³ or a cell-like situation involving the metal, the hydrogen, the water, and the support⁶⁴ may account for the conversion of hydridic hydrogen to a proton. In a related experiment, support and promoter effects were combined. Mössbauer effect studies showed that an equilibrium among H₂, Fe²⁺, H⁺, and Fe⁰ can exist on iron catalysts supported on alumina, but this equilibrium is suppressed by a potassium promoter.⁶⁵ Migration of hydrogen atoms from metal to support also has some experimental support.^{66,67} In any case, the presence of mobile protons on the support and mobile hydridic hydrogens on the metal might be expected to lead to a rapid recombination to H₂ at the interface (reverse of reaction 2), although this is not observed.

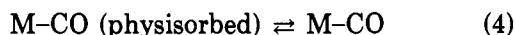
For later steps in the mechanism, both hydridic and protonic hydrogen atoms will be assumed to be available.

2. Carbon Monoxide Adsorption

In contrast to the relatively simple situation of dissociative chemisorption for hydrogen, CO may be adsorbed both molecularly and dissociatively, and there is reason to believe that more than one molecularly adsorbed species is important in the Fischer-Tropsch synthesis. A physisorption step is first:

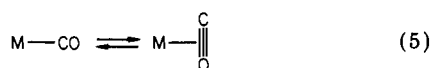


This species is rapidly converted to the chemisorbed species:



Carbon monoxide is predominantly adsorbed on the metal in a carbonyl-like mode, bonded to one or more metal atoms through the carbon by donation of CO 5σ electrons to the metal and backbonding by the donation of metal d electrons into the CO 2π antibonding orbital.⁶⁸⁻⁷² As more metal atoms participate in the bonding, the metal-carbon bond will strengthen and the C-O bond will weaken, making the CO more susceptible to hydrogenation and other reactions, although this species appears to be difficult to hydrogenate from the evidence of cluster compounds.⁷³

A more strongly adsorbed form of CO has been suggested to be bonded side-on to the metal by Muetterties^{15,73} and Masters.¹⁶ This species should be more activated toward hydrogenation and carbon-carbon bond formation.^{15,73} A side-on species seems likely to be an intermediate in CO dissociation:



The more strongly chemisorbed CO can interact with two or more metal atoms, which may belong to the catalyst metal. An infrared band at 1620 cm^{-1} has been assigned to CO coordinated to at least three nickel atoms, one of which is coordinated to the oxygen.⁷⁴ A CO stretch of 1520 cm^{-1} has been observed for CO adsorbed at steps on a nickel surface,⁷⁵ which would be suitable sites for side-on adsorption, perhaps combined with end-on interactions. Ultraviolet photoelectron spectroscopy of CO adsorbed on a carbonized osmium surface is consistent with side-on bonding.⁷⁶ Cluster compounds of iron⁷⁷ and manganese⁷⁸ have been prepared in which CO is coordinated end-on to one metal atom and side-on to another.

Carbon monoxide may also be complexed between two dissimilar metal atoms, which, in a synthesis catalyst, might be in the catalyst and the promoter or in the catalyst and the support. Bimetallic complexes have been prepared in which the carbon of the CO is complexed to a metal capable of donating electrons and the oxygen complexed to a metal capable of accepting electrons.⁷⁹⁻⁸¹ The CO stretching frequency in these compounds is lowered relative to its value in the carbonyl complexes. Complexes with CO coordinated through both carbon and oxygen are summarized in Table I. Carbocations can also react with the oxygen of carbonyl CO in a Lewis acid-base fashion. Both iron⁸² and cobalt⁸³ carbonyls have been reacted with carbocations to produce new complexes.

For a metal on an oxide support, the carbon of the CO could be coordinated to one or more of the metal

atoms, and the oxygen to a metal or metalloid atom in the oxide support. This type of CO adsorption may be related to the strong metal-support interactions observed in catalyst systems⁸⁴⁻⁸⁶ and to differences in Fischer-Tropsch activity observed in systems that might be capable of these interactions.⁸⁷⁻⁹¹ If the side-on CO complexed between two dissimilar metals is particularly active in carbon-carbon bond formation, then the catalytic activity of a metal that, unsupported, is a methanation catalyst should be shifted toward Fischer-Tropsch activity (more two-carbon and heavier hydrocarbons) by support on the oxide of an early transition metal, with empty d orbitals to complex the carbonyl oxygen. This shift has been observed for nickel on a TiO_2 support,^{87,88} and other combinations of this type have shown enhanced carbon-carbon bond formation.^{89,90} When a compound is formed between the metal and support,^{86,92} CO adsorption would be expected to be suppressed because the metals are sharing electrons directly rather than through a complexed CO.

A few studies have been performed on CO adsorption on potassium-promoted iron.^{47,55,93} A higher binding energy is observed than for iron alone, and the saturation coverage of CO increases. The CO appears to be adsorbed end-on to the iron through the carbon, although no conclusions were drawn about the participation of the potassium in the active site.⁹³

A study of CO interaction with potassium-promoted alumina⁹⁴ showed that, although CO is poorly adsorbed, it can exchange oxygen with the alumina, probably through the formation of a CO_2^- intermediate.

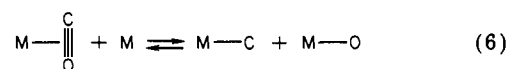
Carbonization of the metal surface, which may occur during the synthesis, weakens the bonding of CO to the surface in the case of nickel⁹⁵ but causes a side-on bonding with interactions of the metal with both C and O in the case of osmium.⁷⁶ This contradictory behavior in two group 8 metals may be significant in their differing activity for the synthesis.

A species of CO molecularly adsorbed end-on through the oxygen has been postulated⁹⁶ to explain some of the observations relating to the Fischer-Tropsch synthesis, but there appears to be no experimental or theoretical evidence for the existence of this species.

The two types of molecularly adsorbed CO will be distinguished only where there appears to be good reason to write separate reactions for the two types.

3. Carbon Monoxide Dissociation

Dissociation of CO on the metal surface is possible for the common Fischer-Tropsch catalyst metals at the temperatures of the synthesis.^{69,97-110}



The side-on CO must be the precursor to dissociation, because breaking of the C-O bond in end-on CO should lead to loss of the oxygen to the gas phase, which does not seem to occur.

The metals used as Fischer-Tropsch catalysts occupy a border area in the transition series;⁹⁷ for these metals, both dissociative and molecular CO chemisorption occur at temperatures near room temperature. For metals to the left in the periodic chart, CO chemisorption is dissociative at room temperature, and for metals to the

TABLE I. C- and O-Coordinated Carbon Monoxide

parent metal complex	bonding to C	Lewis acid	stoichiometry (acid/complex)	CO stretch for -CO-	ref
Fe compounds					
HFe(CO) ₁₁ ⁻	Fe ₂	H ⁺	1		a
[(η ⁵ -C ₅ H ₅)Fe(CO)] ₄	Fe ₃	BF ₃	1	1365	b
			2	{1405}	b
				{1435}	
[(η ⁵ -C ₅ H ₅)Fe(CO) ₂] ₂	Fe ₂	BCl ₃	1	1463	b
	Fe ₃	BCL ₃	1	1292	b
[(η ⁵ -C ₅ H ₅)Fe(CO)] ₄			2	{1327}	b
				{1360}	
[(η ⁵ -C ₅ H ₅)Fe(CO) ₂] ₂	Fe ₂	BBr ₃	1	1438	b
[(η ⁵ -C ₅ H ₅)Fe(CO)] ₄	Fe ₃	BBr ₃	1	{1301}	b
				{1312}	
			2	1320	b
				1365	
(η ⁵ -C ₅ H ₅)Fe(CO) ₂	Fe	Mg(C ₅ H ₅ N) ₄	0.5	1711	c
[(η ⁵ -C ₅ H ₅)Fe(CO)] ₂	Fe ₂	Al(C ₂ H ₅) ₃	2	1682	b, d-f
		Al(<i>i</i> -C ₄ H ₉) ₃	1	1680	f
[(η ⁵ -C ₅ H ₅)Fe(CO)] ₄	Fe ₃	Al(C ₂ H ₅) ₃	4	1527	e
		AlBr ₃	1	1392	b
			2	{1368}	
				{1395}	b
				{1415}	
			3	{1439}	b
				{1470}	
			4	1473	b
Fe ₂ (CO) ₉	Fe ₂	AlBr ₃	1	{1523}	b
				{1557}	
Fe ₃ (CO) ₁₂	Fe ₂	AlBr ₃	1	1548	b
[(η ⁵ -C ₅ H ₅)Fe(CO) ₂] ₂	Fe ₂	Sm(η ⁵ -C ₅ H ₄ Me) ₃	2	1700	g
		Sm(η ⁵ -C ₅ H ₅) ₃	2	1700	g
Fe-Ni compounds					
(η ⁵ -C ₅ H ₅)Ni(CO) ₂ ⁻	FeNi	Ho(η ⁵ -C ₅ H ₄ Me) ₃	2	1738	g
		Gd(η ⁵ -C ₅ H ₄ Me) ₃	2	1738	g
Fe(η ⁵ -C ₅ H ₅)(CO)					
Co compounds					
Co ₃ (CO) ₁₀	Co ₃	BF ₂ N(C ₂ H ₅) ₃	1		h
		BCl ₂ N(C ₂ H ₅) ₃	1		i-k
		BBr ₂ N(C ₂ H ₅) ₃	1		i
		BI ₂ N(C ₂ H ₅) ₃	1		h
		Mg(C ₅ H ₅ N) ₄	0.5	1751	c
Co(CO) ₄	Co	AlCl ₂ N(C ₂ H ₅) ₃	1		h
Co ₃ (CO) ₁₀	Co ₃	AlBr ₂ N(C ₂ H ₅) ₃	1		i
		AlBr ₃	1	1600	b
Co ₂ (CO) ₈	Co ₂	SiR ₃ , R = Me, Ph	1		l-n
Co ₃ (CO) ₁₀	Co ₃	SiR ₃ , R = Cl; R ₃ = MeCl ₂	1		m
		SiR ₂ [Co(CO) ₄], R = Me, Ph	1		o
		Ti(Cl)(η ⁵ -C ₅ H ₅) ₂	1		p, q
		Ti(η ⁵ -C ₅ H ₅) ₂	0.5		p
		Ti(η ⁵ -C ₅ H ₅)[Co(CO) ₄]	1		r
		Zr(Cl)(η ⁵ -C ₅ H ₅) ₂	1		p
		Zr(η ⁵ -C ₅ H ₅) ₂	0.5		p
		Hf(Cl)(η ⁵ -C ₅ H ₅) ₂	1		p
		Hf(η ⁵ -C ₅ H ₅) ₂	0.5		p
Co ₂ (CO) ₈	Co ₂	Sm(η ⁵ -C ₅ H ₄ Me) ₃	2	1781	g
Co ₃ (CO) ₁₀	Co ₃	U(η ⁵ -C ₅ H ₅) ₃	1		s
Ni compounds					
(η ⁵ -C ₅ H ₅)Ni ₃ (CO) ₂	Ni ₃	Al(C ₂ H ₅) ₃	1	1637	f
[(η ⁵ -C ₅ H ₅)Ni(CO)] ₂	Ni ₂	Al(C ₂ H ₅) ₃	1	1761	f
		Al(<i>i</i> -C ₄ H ₉) ₃	1	1761	f
		Er(η ⁵ -C ₅ H ₄ Me) ₃	1	1780	g
		Sm(η ⁵ -C ₅ H ₄ Me) ₃	2	1780	g
Ru compounds					
Ru ₃ (CO) ₁₂	Ru ₂	AlBr ₃	1	1535	b
[(η ⁵ -C ₅ H ₅)Ru(CO) ₂] ₂	Ru ₂	Al(<i>i</i> -C ₄ H ₉) ₃	2	1679	f, t
Mn compounds					
Mn(CO) ₅	Mn	Mg(C ₅ H ₅ N) ₄	0.5	1721	c
(η ⁵ -C ₅ H ₄ Me)Mn(CO) ₃	Mn	Sm(η ⁵ -C ₅ H ₄ Me) ₃	1	1868	g
		Er(η ⁵ -C ₅ H ₅) ₃	1	1868	g
		Yb(η ⁵ -C ₅ H ₅) ₃	1	1868	g
		Nd(η ⁵ -C ₅ H ₄ Me) ₃	2	1865	g

TABLE I (Continued)

parent metal complex	bonding to C	Lewis acid	stoichiometry (acid/complex)	CO stretch for -CO-	ref
Mo compounds					
(η^5 -C ₅ H ₅)Mo(CO) ₃	Mo	Mg(C ₅ H ₅ N) ₄	0.5	1664	<i>c</i>
(η^5 -Ph ₃ PC ₂ H ₄)Mo(CO) ₃	Mo	Al(CH ₃) ₃	1	1665	<i>u</i>
Mo(phen)(PPh ₃) ₂ (CO) ₂	Mo	Al(C ₂ H ₅) ₃	2	1633	<i>v</i>
		Al(<i>i</i> -C ₄ H ₉) ₃	2	1633	<i>v</i>
Mo(5,6-dmphen)-(PPh ₃) ₂ (CO) ₂	Mo	Al(C ₂ H ₅) ₃	2	1627	<i>v</i>
Mo(phen) ₂ (CO) ₂	Mo	Al(C ₂ H ₅) ₃	2	1565	<i>v</i>
W compound					
(η^5 -C ₅ H ₅)W(CO) ₃	W	Al(C ₄ H ₉ O) ₃	1/3	1670	
				1605	<i>w</i>
				1570	

^a Hodali, H. A.; Shriver, D. F.; Ammlung, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 5239. ^b Kristoff, J. S.; Shriver, D. F. *Inorg. Chem.* **1974**, *13*, 499. ^c Ulmer, S. W.; Skarstad, P. M.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 4469. ^d Kim, N. E.; Nelson, N. J.; Shriver, D. F. *Inorg. Chim. Acta* **1973**, *7*, 393. ^e Nelson, N. J.; Kim, N. E.; Shriver, D. F. *J. Am. Chem. Soc.* **1969**, *91*, 5173. ^f Alich, A.; Nelson, N. H.; Strope, D.; Shriver, D. F. *Inorg. Chem.* **1972**, *11*, 2976. ^g Crease, A. E.; Legzdins, P. *J. Chem. Soc., Chem. Commun.* **1972**, 268; *J. Chem. Soc., Dalton Trans.* **1973**, 1501. ^h Schmid, G.; Bätzel, V.; Etzrodt, G.; Pfeil, R. *J. Organomet. Chem.* **1975**, *86*, 257. ⁱ Schmid, G.; Bätzel, V. *Ibid.* **1972**, *46*, 149. ^j Bätzel, V.; Müller, U.; Allman, R. *Ibid.* **1975**, *102*, 109. ^k Schmid, G.; Stutte, B. *Ibid.* **1972**, *37*, 375. ^l Mann, C. D. M.; Cleland, A. J.; Fieldhouse, S. A.; Freeland, B. H.; O'Brien, R. J. *Ibid.* **1970**, *24*, C61. ^m Nicholson, B. K.; Simpson, J. *Ibid.* **1978**, *155*, 237. ⁿ Ingle, W. M.; Preti, G.; MacDiarmid, A. G. *J. Chem. Soc., Chem. Commun.* **1973**, 497. ^o Fieldhouse, S. A.; Cleland, A. J.; Freeland, B. H.; Mann, C. D. M.; O'Brien, R. J. *J. Chem. Soc. A* **1971**, 2536. ^p Stutte, B.; Bätzel, V.; Boese, R.; Schmid, G. *Chem. Ber.* **1978**, *111*, 1603. ^q Schmid, G.; Bätzel, V.; Stutte, B. *J. Organomet. Chem.* **1976**, *113*, 67. ^r Schmid, G.; Stutte, B.; Boese, R. *Chem. Ber.* **1978**, *1239*. ^s Stutte, B.; Schmid, G. *J. Organomet. Chem.* **1978**, *155*, 203. ^t Alich, A.; Nelson, N. J.; Shriver, D. F. *J. Chem. Soc., Chem. Commun.* **1971**, 254. ^u Kutz, J. C.; Turnipseed, C. D. *Ibid.* **1970**, 41. ^v Shriver, D. F.; Alich, A. *Inorg. Chem.* **1972**, *11*, 2984. ^w Petersen, R. B.; Stezowski, J. J.; Wan, C.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1971**, *93*, 3532.

right, it is molecular. Related to this observation is the fact that dissociation becomes more likely as the heat of adsorption for molecular CO increases.^{89,98} These relationships have been explained in terms of the heats of formation of the transition-metal carbides and oxides.^{111,112}

In this borderline group of metals, a small change in energy can change the mode of adsorption from molecular to dissociative; adsorption may be molecular on one crystal plane of a metal and dissociative on another. Increasing temperature also promotes CO dissociation. However, although adsorption may be predominantly molecular or dissociative at different temperatures, a temperature range will exist over which both molecular and dissociated CO will be present on the metal surface. For example, in the case of iron, CO adsorbs molecularly at 100 to 300 K and slowly dissociates; at 350 K and above, it is predominantly dissociated both on the metal¹⁰¹⁻¹⁰⁴ and on iron supported on alumina.¹⁰⁵ Even in the case of predominantly dissociative adsorption, however, molecularly adsorbed CO will be present as an intermediate between gaseous CO and surface carbon and oxygen atoms. Further, the side-on CO will be present as an intermediate which can be intercepted between adsorption and dissociation if the rates of its reactions with hydrogen and other intermediates allow. The kinetics of interconversion of the various types of adsorbed CO will determine the paths leading to the products of the overall synthesis, and different balances of intermediates will be favored by different conditions. For example, higher surface coverage (higher gas pressure) increases the amount of molecularly adsorbed CO relative to dissociated CO.^{113,114}

Carbon monoxide adsorption on ruthenium may be an exception to the generalization of dissociation at synthesis temperatures. Some question exists as to whether CO is dissociated¹⁰⁰ or molecularly adsorbed.¹¹⁵ Although this question is not now resolved, two types

of adsorbed CO are known to exist on ruthenium, and they may correspond to the two types of molecularly adsorbed CO discussed in section II.A.2.

Other factors affect the dissociation of CO on metal surfaces. Irregularities in the surface promote dissociation; steps and kinks on a platinum surface promote dissociation of adsorbed CO, even though platinum surfaces with low Miller indices exhibit molecular adsorption exclusively.^{113,116,117} Similarly, CO adsorbed at steps and kinks on a nickel surface has a lowered C-O stretching frequency⁷⁵ and dissociates more readily than CO adsorbed on low-index planes.¹¹⁸ Silica-supported ruthenium-platinum bimetallic clusters with a cluster composition of 10 atom % ruthenium dissociate CO.¹¹⁹

The effect of supports and promoters on CO dissociation has been little studied. The probability of CO dissociation is greater on potassium-promoted iron than on clean iron, but the temperature of dissociation is unchanged.⁹⁸ Supports are sometimes used in investigations of CO dissociation, but their effect (or lack of effect) has not been studied systematically. Investigations of support effects on CO dissociation would be useful, particularly in view of recent observations of metal-support interactions affecting CO adsorption⁸⁴⁻⁸⁶ and catalysis^{87,88,91,120-125} and earlier work indicating changes in the stretching frequencies of adsorbed CO with changes in support.¹²⁶

Coadsorption of hydrocarbons, which are produced by the synthesis and can be expected to be present on the catalyst, with CO on nickel and platinum shifts the CO vibration to lower frequencies, indicating a weakening of the C-O bond.¹²⁷ A carbon layer on rhodium¹²⁸ or osmium⁷⁶ surfaces also appears to promote dissociation of CO, although the formation of a carbide layer on cobalt^{109,110} or nickel⁹⁴ inhibits the dissociation of CO.

The disproportionation of CO to CO₂ and surface carbon is sometimes suggested as an alternative or additional source of surface carbon. However, because the

TABLE II. Adsorption Reactions and Intermediates Produced

reaction	eq no.
$H_2 + M \rightleftharpoons M-H_2$ (physisorbed)	1
$M-H_2$ (physisorbed) \rightleftharpoons H-M-H	2
$CO + M \rightleftharpoons M-CO$ (physisorbed)	3
$M-CO$ (physisorbed) \rightleftharpoons M-CO	4
$M-CO \rightleftharpoons M-\overset{C}{\parallel}$	5
$M-\overset{C}{\parallel} + M \rightleftharpoons M-C + M-O$	6
Intermediates	
M-H ₂ (physisorbed)	M-CO M-H
M-CO (physisorbed)	M- $\overset{C}{\parallel}$ M-C M-O

disproportionation is heterogeneous and takes place under conditions similar to those for the Fischer-Tropsch synthesis, the chemisorption and dissociation of CO are probably a part of its mechanism.¹²⁹⁻¹³⁵ In other words, disproportionation of CO is a single possible path in the overall mechanism of the Fischer-Tropsch synthesis. This path will be discussed in section V.A.

For later steps in the mechanism, both M-C and M-O will be assumed to be available for reaction. Table II summarizes the physisorption and chemisorption reactions and the intermediates produced.

B. Initial Reactions among Chemisorbed Species

The division between this section and the next is somewhat arbitrary; the word "initial" refers only to the fact that the reactants for the elementary reactions discussed in this section are the intermediates generated in the adsorption steps of section III.A. and result in intermediates rather than stable products. These "initial" reactions will, in fact, be taking place throughout a Fischer-Tropsch synthesis. Similar re-

actions have been proposed previously; these reactions and the type of evidence on which they have been based are given in Table III. In some cases in Table III, individual elementary reactions have been combined; all reactions have been translated into the notation used here to facilitate comparisons. Not all of the previously proposed reactions will be discussed individually. The discussion in the rest of section III will be directed toward establishing those reactions that are best supported by the currently available experimental evidence.

In order for reactions to take place among adsorbed species, those species must be mobile on the surface. Little direct evidence is available for or against the mobility of adsorbed species of the type of interest here.¹³⁶ CO and H ligands are extremely mobile on metal cluster compounds,^{25,137} and evidence is available for the mobility of a combination of CO, H, and hydrocarbon ligands in a ruthenium complex.¹³⁸ It is not clear, however, whether these observations are transferable to surfaces.^{15,73} A recent study indicates little mobility for CO on tungsten.¹³⁹ However, the presence of attractive potentials among adsorbed species or for particular sites on the surface may change the situation. Carbon monoxide appears to diffuse toward coordinatively unsaturated sites (kinks and steps) on a platinum surface.¹¹³ For CO or H adsorbed alone on a metal surface, the interactions among the adsorbates appear to be repulsive, as indicated by the common observation of decreasing adsorption energy with increasing coverage. The interaction between adsorbed CO and H appears to be slightly attractive on the Fischer-Tropsch catalyst metals¹⁴⁰⁻¹⁴⁹ and different from their interactions on other transition metals.^{141,150,151} For example, the interaction on rhodium appears to be repulsive enough that the CO and H form separate "islands" at low pressures.¹⁵¹ The extent and significance of these differences among the metals are not yet clear.

Most adsorption studies are necessarily done at pressures of adsorbing gases well below 1 atm, while the operating conditions of the Fischer-Tropsch synthesis

TABLE III. Previously Proposed Reactions Corresponding to Initial Reactions of Chemisorbed Species

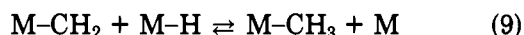
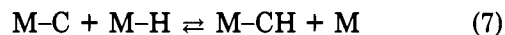
reaction	type of evidence	ref
$M-C + H_2 \rightleftharpoons M-CH_2$	product distribution	19
	product distributions, kinetics	20
$M-C + 2H_2 \rightleftharpoons M + CH_4$	CO adsorption experiments	131
$M-C + M-H \rightleftharpoons M-CH + M$	CO, H ₂ adsorption properties	133, 353
	transient experiments	22, 135, 167, 170
	isotope tracer experiments	172
	kinetics	165, 176
$M-C + H_2O \rightleftharpoons M-CHOH$	combination	7, 14, 37
$M-O + H_2 \rightleftharpoons M + H_2O$	combination	23
	CO adsorption experiments	131
$M-O + M-H \rightleftharpoons M-OH + M$	combination	37
	CO adsorption experiments	353
	CO, H ₂ adsorption experiments	133
	kinetics	165
	transient experiments	170
$M-CO^+ + M-H_2^- \rightleftharpoons M-HCOH^+ + M + e^-$	combination	299
$M-CO + M-H_2 \rightleftharpoons M-CH_2O$ (surface complex with undefined structure)	combination	6
	kinetics	121
$M-CO + M-H \rightleftharpoons M-CHO + M$	complex chemistry	12, 16, 21
	combination	7
$M-CO + M-H \rightleftharpoons M-COH + M$	kinetics	135
$M-CO + 2M-H \rightleftharpoons M-CHOH + M$	complex chemistry	3
$M-CHO + M-H \rightleftharpoons M-CH_2=O + M$	complex chemistry	12
$M-CHO + H_2 \rightleftharpoons M-CH_2OH$	complex chemistry	18
$M-CH_2=O + M-H \rightleftharpoons M-CH_2OH + M$	complex chemistry	12
$M-CHO + M-H \rightleftharpoons M-CH_2O-M$	combination	7

are 1 atm or above. Differences exist between the two regimes, the most important of which is that thermodynamics favor the formation of hydrocarbons from synthesis gas at the higher pressures, but not at the lower pressures.¹²⁸ The formation of some of the intermediates may also be thermodynamically unfavorable at low pressures. Kinetic studies of dynamic catalytic systems at atmospheric pressure and above are being done,^{151a,152} but detailed monitoring of surface species under reaction conditions is still not possible. Combinations of these techniques with some of the new laser light-scattering techniques, perhaps with Fourier transform analysis,¹⁵³ may eventually prove helpful in elucidating the nature of surface species under synthesis conditions. Several techniques are available for examining surface species (for example, see ref 154-160); intermediates in slow reactions have been observed.^{161,162} However, not all of the observed phenomena in systems of this type are well understood.^{163,164}

It may be helpful at this point to visualize the catalyst surface under the conditions of the synthesis. Immediately next to (and bonded to) the metal surface is the most active layer, containing C, O, and H atoms and at least two types of adsorbed CO; next to these is a layer of physisorbed CO, H₂, and desorbing products. The intermediates to be discussed in this section and the next are also present in the surface layer, as are some physisorbed CO, H₂, and product molecules. The physisorbed layers will be several molecules deep, requiring diffusion through them for transfer between the gas phase and the catalyst surface. The molecules in the physisorbed layers, in electronic structure and therefore in chemical reactivity, resemble molecules in the gas phase, although they will be perturbed by van der Waals interactions and other liquid-like forces. No distinction will be made here between physisorbed and gas-phase molecules, since energy differences are likely to be small.

1. Reactions of C and O with H

Carbon atoms from the dissociation of CO can react with adsorbed hydrogen:



In this case, and in some of the others following, an adsorbed reactive species could also react with dihydrogen:



The hydrogen atom liberated in this reaction could then react with other molecules in the physisorbed layer in a chain fashion; the chain would be terminated by reaction of a radical with the surface to give one of the adsorbed species or by recombination of the radical with another radical or a surface species to give a product molecule. This type of reaction would give unpredictable products, depending largely on the proximity of various molecules in the physisorbed layers. However, it may well play a minor or insignificant part, since in the reactions that have been researched in detail, reaction between adsorbed species is found to predomi-

nate over reaction with an unadsorbed molecule.

Adsorbed carbon atoms are known to exist on catalyst surfaces and to react readily with hydrogen. In addition, other types of surface carbon may contribute to this reaction. Four types of surface carbon have been shown to exist on nickel supported on alumina.¹⁶⁵ In decreasing order of reactivity toward hydrogen, they are identified as: chemisorbed carbon atoms, bulk nickel carbide, amorphous carbon, and crystalline (graphitic) elemental carbon. The more reactive carbons are converted to the less reactive carbons by heating.

Other studies have identified a reactive carbon that may be adsorbed carbon atoms. Auger electron spectroscopy indicates that a readily hydrogenated form of carbon remains on the surface of iron foils¹⁶⁶ and of polycrystalline rhodium¹²⁸ during the synthesis of hydrocarbons. Infrared studies of silica-supported ruthenium led to similar conclusions.¹⁶⁷ An active carbon layer was also identified on ruthenium and nickel by Auger electron spectroscopy.^{168,169} Kinetic evidence from transient-method studies also implicates a reactive carbon intermediate for fused iron¹⁷⁰ and supported iron¹⁷¹ catalysts. Other kinetic evidence^{131,133,135,172,173} and isotopic distributions^{133,172} imply that adsorbed carbon atoms can be readily hydrogenated. Isotopic studies indicate that carbon deposited by disproportionation of CO on ruthenium and cobalt hydrogenates to methane, but another intermediate is implicated in addition for the reaction on ruthenium.¹⁷⁴

A carbon species identified as a surface carbide may also contribute to the hydrogenation reactions. Bulk carbides of iron and nickel form under synthesis conditions^{165,170,175,176} and can be hydrogenated to methane.^{165,172,177} However, it is not clear that the carbon sometimes referred to as carbidic is different from what has been discussed here as adsorbed atomic carbon, following the classification of McCarty and Wise.¹⁶⁵ Auger studies of carbon deposits on iron^{178,179} show a carbidic phase that behaves similarly to what has been discussed here as adsorbed atomic carbon, and a readily hydrogenated superficial carbide of nickel¹⁸⁰ is deposited by CO disproportionation, a method concluded by other workers to deposit adsorbed carbon atoms.¹³¹ This apparently semantic difficulty arises from a difficult chemical distinction. Is there a difference between an adsorbed carbon atom and a surface carbide?

There are no simple answers to this question, and it is possible that no distinction can be made.³⁹ However, both terms carry implicit assumptions about the nature of the bond between the carbon and the metal. A classification of surface species that might help to clarify this question has been suggested by Madix,¹⁸¹ but more information is necessary on the chemical states of the various types of surface carbon before this classification can be applied.

The amorphous and crystalline carbon species appear to act mainly as poisons to hydrogenation,^{166,178,179} that is, their effective rates of hydrogenation will be zero relative to hydrogenation of the other forms of carbon. If the elemental carbon is in intimate contact with metal particles, its rate of hydrogenation is increased,¹⁸² perhaps due to surface interactions forming the more active types of carbon.

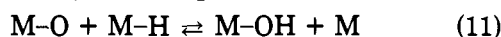
Another form of carbon that has been observed in deposits on catalysts includes hydrogen.^{167,179} This

deposit also hydrogenates rapidly, although it is fairly stable to the hydrogen isotopic substitution that might be expected of $M-CH_n$ species. It is not clear whether the hydrogen in these deposits is chemically bonded to the carbon or physically included in the deposit.

Several types of evidence point to the existence of hydrocarbon-like intermediates, although some of this evidence may result from carbonaceous deposits containing hydrogen or from adsorbed products rather than from true intermediates. Infrared spectroscopy showed C-H stretches for coadsorbed CO and H_2 heated on silica-supported nickel,¹⁸³ iron,^{184,185} and ruthenium¹⁶⁷ and for alumina-supported ruthenium.¹⁸⁵ However, inertness to isotopic substitution^{167,186} and the band growth structure¹⁸⁵ imply that these bands arise from adsorbed products as well as intermediates. The reaction of alkenes with surface intermediates on ruthenium gives evidence for the presence of alkyl and alkylidene groups as intermediates.¹⁸⁷

Few metal complexes that give reactions similar to reactions 7-10 have been prepared,¹⁵ although numerous complexes containing hydrocarbon ligands are known. Alkylmetal complexes are well-known.¹⁸⁸⁻¹⁹¹ Alkylidene^{192,193} and alkylidyne¹⁹⁴ complexes have been studied mainly for the earlier transition metals, but cobalt alkylidynes are well-known,¹⁹⁵ iron alkylidene complexes have been observed spectroscopically¹⁹⁶ and isolated,¹⁹⁷⁻¹⁹⁹ cobalt iron alkylidynes have been isolated,²⁰⁰ and an osmium alkylidyne has been isolated.²⁰¹ Several cluster complexes whose chemistry may prove to be more analogous to reactions 7-10 than that of the complexes previously known have recently been synthesized.^{138,202-209}

Adsorbed oxygen atoms should react with adsorbed hydrogen atoms (or with H_2):



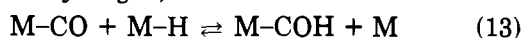
The formation of hydroxyl is known to proceed rapidly on nickel from atomic oxygen,²¹⁰ although it is not clear whether H_2 or the adsorbed atom is the reactive species. The reaction of oxygen and hydrogen on rhenium,²¹¹ iridium,²¹² platinum,²¹³⁻²¹⁵ and palladium²¹⁶ and of oxygen and deuterium on platinum²¹⁷ appears to proceed as in reaction 11. There is some indication that other mechanisms may contribute at temperatures below that of the synthesis.^{218,220} Hydroxyl groups have been observed by infrared spectroscopy on platinum, iridium, rhenium, nickel, cobalt, and iron as a result of the reaction of oxygen and hydrogen.²²¹ Under synthesis conditions, this reaction appears to be very rapid, since oxygen is observed to be removed rapidly from iron¹⁷⁸ and rhodium,¹⁶⁷ giving water as a product.

2. Reactions of Undissociated CO

Chemisorbed molecular CO^{167} and CO in metal carbonyls^{15,73,222} appear not to react directly with dihydrogen. Therefore, only reactions with adsorbed hydrogen atoms will be considered here. Molecularly adsorbed CO should yield two intermediates upon addition of a hydrogen atom. For hydridic hydrogen,



For protonic hydrogen,



The $M-CHO$ intermediate would have the formyl

structure I, and the $M-COH$ intermediate, an alcoholic structure (II). The triple bond may in fact represent



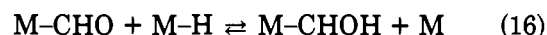
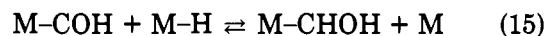
bonds to three metal atoms. Analogy to the aldol equilibrium in organic compounds suggests that the two intermediates should be able to interconvert tautomericly, although no metal complex analogue or surface reaction has been observed:



The evidence for the addition of hydridic and protonic hydrogen to CO in metal complexes has been reviewed recently.²²² The reverse of reaction 12 has been observed in metal complexes, but the equilibrium favors the left-hand side of that reaction.^{12,223} Complexing of the carbonyl oxygen to a Lewis acid (discussed in section III.A.2; see also ref 224) activates the carbonyl carbon to nucleophilic attack, for example, by hydride, to give the $M-CHO$ intermediate. For this reason, a second reaction, or rate constant for reaction 12, may be necessary to represent the reaction of the more strongly adsorbed CO. Because the carbonyl oxygen can act as a Lewis base, attack by a proton is possible at that point to give an $M-COH$ intermediate.^{82,225,226} A study of methanation over alumina-supported metal carbonyls also suggests that protonic hydrogen may be active in hydrogenation of undissociated CO.²²⁷

Similar reactions have been observed for CO complexed to more electron-deficient metals, such as zirconium²²⁸ and the actinides,²²⁹ and have been postulated for titanium.²³⁰ The relatively empty d orbitals of these metals allow the formation of π bonds between the metal and the product formyl ligand. However, these metals are sufficiently different from the Fischer-Tropsch catalyst metals to raise a question of the relation of these reactions to the Fischer-Tropsch synthesis.

Further hydrogenation of I and II, which will be assumed to be by adsorbed atomic hydrogen rather than by H_2 , yields alcoholic intermediates:



Both hydridic^{138,231-236} and protonic²³⁷ hydrogen can participate in reactions of this type in metal complexes.¹⁵ Carbon monoxide in rhenium complexes has been reduced to $M-CHO$, $M-CHOH$, and $M-CH_2OH$ ligands.²²³ Reduction of a formyl ligand to methyl has been reported.^{231,235} A formyl ligand has been identified spectroscopically in the reduction of an osmium carbonyl complex to a carbene, and a reaction sequence analogous to reactions 16 and 17 was postulated.²³⁶ Reduction to hydroxymethyl has also been reported by two methods, a disproportionation and one involving hydride.^{231,233,234} A strongly acidic solution of an iron cluster compound known to protonate at a carbonyl oxygen gave methane as a product,²³⁷ this may include steps 15 and 17.

Adsorbed intermediates containing C, H, and O have been produced by the interaction of CO and H_2 on ruthenium¹⁴⁵ and nickel,¹⁴⁶ although their structures are

not known. Auger spectroscopy gives evidence for small amounts of oxygen in the surface reactive layers on Fe(110) during CO hydrogenation.¹⁷⁹ Its chemical state is not unambiguous, but at least some of it appears to be bonded to carbon. Dipole moments corresponding to two different C-H-O complexes produced by the interaction of CO and H₂ on ruthenium have been observed; they appear to correspond to an aldehydic (I) or alcoholic (II) intermediate and a surface complex between chemisorbed CO and protonic hydrogen atoms;¹⁸¹ similar results have been obtained for nickel.²³⁸ An O-H band (3500 cm⁻¹) was observed as a result of heating coadsorbed CO and H₂ on silica-supported nickel¹⁸³ and on silica-supported iron;¹⁸⁴ this could represent the OH of an alcoholic intermediate or a hydroxyl intermediate formed by reaction 11; no C-O vibrations were observed, however, tending to support the interpretation of a hydroxyl intermediate or adsorbed water. Vibrational frequencies (2920, 1440, and 1360 cm⁻¹) for species resulting from coadsorption of CO and H₂ on Ni(111) suggest that the species may be M-CHO or formate.²³⁹ Interaction of reactive species with a nickel catalyst pretreated with CO and H₂ gave products indicating a formyl intermediate.^{240,241}

A formate intermediate could be formed by reaction of molecularly adsorbed CO with hydroxyl. Adsorbed formate species have been observed in the adsorption of CO on silica-supported nickel¹⁰⁸ and in the coadsorption of H₂ and CO.^{108,184,239,242} An analogous reaction, although with hydroxide ion, has been observed for carbonyl complexes of group 6 and 7²⁴³⁻²⁴⁶ and group 8²⁴⁵⁻²⁵² metals. However, the reaction is observed only at high pH with an iron carbonyl; when olefins are present, hydroformylation occurs preferentially at a pH of 10.7 or less.²⁵³ The difference in nucleophilicity between hydroxide and a surface hydroxyl may be compensated for by the activation of the carbonyl carbon to nucleophilic attack by a stronger form of adsorption, such as complexing of the carbonyl oxygen. Water appears to be the nucleophile in acid solution.²⁴³ Another possible path to formate is hydrogenation of adsorbed CO₂.²⁵⁴ Formate and carbonate formation is suppressed by the presence of H₂.¹⁰⁸

An infrared ellipsometric study of CO methanation on Ni(110) shows that CO does not dissociate during the reaction at low temperatures.²⁵⁵ Similarly, carbonyls of transition metals supported on alumina yielded methane in flowing H₂ under conditions in which dissociation of the CO was unlikely.²⁵⁶ These studies suggest that paths represented by reactions 12-17 must be relevant to the Fischer-Tropsch synthesis at least at lower temperatures.

The reactions proposed in this section and the intermediates produced are summarized in Table IV. These reactions are all hydrogenations; undissociated CO can add a hydrogen atom at either the carbon or the oxygen.

C. Reactions of Hydrocarbon and H-C-O Intermediates

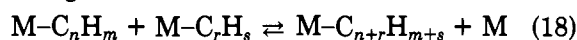
As in section III.B, only reactions giving intermediates will be discussed in this section. Reactions previously proposed by other investigators are given in Table V. Generalized reactions can be written for many of the reactions presented here; they can be

TABLE IV. Initial Reactions and Intermediates Produced

reaction	eq no.
M-C + M-H ⇌ M-CH + M	7
M-CH + M-H ⇌ M-CH ₂ + M	8
M-CH ₂ + M-H ⇌ M-CH ₃ + M	9
M-O + M-H ⇌ M-OH + M	11
M-CO + M-H ⇌ M-CHO + M	12
M-CO + M-H ⇌ M-COH + M	13
M-COH + M-H ⇌ M-CHOH + M	15
M-CHO + M-H ⇌ M-CHOH + M	16
M-CHOH + M-H ⇌ M-CH ₂ OH + M	17
Intermediates	
M-CH, M-OH, M-CHO, M-CHOH	
M-CH ₂ , M-COH, M-CH ₂ OH	
M-CH ₃	

written in several ways, depending on their intended use. R will be used to represent a hydrocarbon residue or hydrogen.

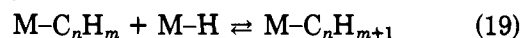
Carbon-carbon bond formation should be possible between hydrocarbon intermediates hydrogenated to various degrees:



where $n, r \geq 1$ and $0 \leq m, s \leq [2(n, r) + 1]$. As written, reaction 18 is extremely general and is intended to be indicative of a set of reactions. For $n = r = 1$, ten reactions can be written with $0 \leq m, s \leq 3$; these can easily be permuted and need not be included here. The forms of the reactions represented by reaction 18 for larger n and r will vary with the intended application. If both hydrocarbon intermediates are saturated, with methyl groups at the ends, the reaction will form a stable hydrocarbon molecule that can desorb from the surface. This reaction will be discussed further in section III.D. If one intermediate has a methyl group at the end, one of the metal sites will be freed, but if both are unsaturated at the ends, both metal sites may remain occupied.

A closely related reaction is the insertion of an alkene into a metal-carbene bond to give a metallocyclobutane intermediate. This reaction apparently occurs on the surfaces of several transition metals²⁵⁷ and has been invoked to explain product distributions from a Fischer-Tropsch synthesis over a supported iron carbonyl catalyst.²⁵⁸

Hydrogenation of these intermediates can then occur analogously to reactions 7-9:



where $n \geq 1$ and $0 \leq m \leq 2n$. Rearrangement of hydrogen in an unsaturated chain and hydrogen abstraction from other intermediates may also be possible. However, if these processes were significant, they would lead to branching of the hydrocarbon chains. They cannot be altogether eliminated from consideration, but will be ignored for the rest of this discussion. The relative lack of chain branching also puts further limits on the values of n, m, r , and s in reaction 18. Unsaturated chains have the potential for branching at the point of unsaturation; therefore, it may be justified to restrict reaction 18 to intermediates of the type M-(CH₂)_n and M-(CH₂)_nCH₃, with the possible inclusion of M-CH(CH₂)_n and M-CH(CH₂)_nCH₃.

The evidence for hydrocarbon intermediates was discussed in section II.B.1 and may include intermediates containing more than one carbon atom. The

TABLE V. Previously Proposed Reactions Corresponding to Reactions of Hydrocarbon and H-C-O Intermediates

reaction	type of evidence	ref
M-CH + M-CH \rightleftharpoons M-CHCH + M	surface studies	353
M-CH ₂ + M-CH ₂ \rightleftharpoons M-CH ₂ CH ₂ -M	kinetics, product distribution	19, 20
M-CH ₂ + M-CH ₃ \rightleftharpoons M-CH ₂ CH ₃ + M	kinetics, product distribution	19, 20
	diazomethane reaction	260
	combination	172
M-R + M-CH _n \rightleftharpoons M-CH _n R + M	isotopic studies	37, 172
M-CH ₂ + M-CH ₂ \rightleftharpoons M-CHCH ₃ + M	surface chemistry	167
M-CHR + M-CH ₂ \rightleftharpoons M-CHCH ₂ R + M	surface chemistry	167
M-CHR + M-H \rightleftharpoons M-CH ₂ R + M	combination	18, 21
M-CH ₂ + RCH=CH ₂ \rightleftharpoons M-CH ₂ CH ₂ CHR	complex chemistry	257, 258
M-CH ₃ + M-CO \rightleftharpoons M-C(O)CH ₃	complex chemistry	16
	transient experiments	170
	combination	7, 12
M-R + M-CO \rightleftharpoons M-C(O)R	complex chemistry	21
	ir spectroscopy of surfaces	283
	combination	7, 14
M-C(O)CH _n + mM-H \rightleftharpoons H ₂ O + M-CH _{m-2} CH _n + mM	combination	14, 22
M-C(O)CH ₃ + H ₂ \rightleftharpoons M-CH(OH)CH ₃	complex chemistry	12, 18
M-C(O)CH ₃ + 2M-H \rightleftharpoons M-CH(OH)CH ₃ + 2M	transient experiments	170
M-C(O)R + M-H \rightleftharpoons M-CH(OH)CH ₃	combination	21
M-C(O)R + 2M-H \rightleftharpoons M-OCH ₂ R	combination	281
M-C(O)R + M-H + H ₂ O \rightleftharpoons M-C(R)(OH)O-M	combination	7
M-C(O)R + M-H \rightleftharpoons M-CH(R)O-M	combination	7
M-CH(OH)CH ₃ + H ₂ \rightleftharpoons M-CH ₂ CH ₃ + H ₂ O	combination	12
M-CH(OH)CH ₃ + 2M-H \rightleftharpoons M-CH ₂ CH ₃ + H ₂ O	transient experiments	170
M-CHOH + H ₂ \rightleftharpoons M-CH ₂ + H ₂ O	combination	299
M-C(OH) ₂ + H ₂ \rightleftharpoons M-CHOH + H ₂ O	combination	299
M-CHOH + nM-H \rightleftharpoons M-CH _n + H ₂ O	kinetics	121
M-COH + M-H \rightleftharpoons M-C + M + H ₂ O	kinetics	135
M-CH(OH)CH ₃ \rightleftharpoons M-CH=CH ₂ + H ₂ O	organic dehydration reaction	18
M-OR + M-CO \rightleftharpoons M-O ₂ CR	combination	283, 297
2M-CHOH \rightleftharpoons M-CHC(OH)-M + H ₂ O	combination	3, 23
M-CHC(OH)-M + 2M-H \rightleftharpoons M-C(OH)CH ₃ + 3M	combination	3
M-C(OH)R + M-CHOH \rightleftharpoons M-C(R)C(OH)-M	combination	3

structure of most of these intermediates has not been determined beyond evidence of C-H and sometimes C-C bonds; however, an ethylidene intermediate has been identified on an alumina-supported rhodium catalyst by tunneling spectroscopy²⁴² as a result of the adsorption of CO, although the source of hydrogen was not evident.

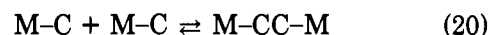
It is clear, however, that carbon-carbon bond formation can occur without the participation of an oxygenated intermediate. Carbon deposited on Fischer-Tropsch catalyst metals has been hydrogenated to ethane, propane, and butane in the absence of CO.^{131,134,167,172} Carbon-carbon bond formation has also been observed between surface intermediates on a ruthenium catalyst and added olefins,¹⁸⁷ a process that may take place similarly to reaction 18, with the olefin adsorbed on the surface as an alkylidene; olefins also add to an iron methylene complex.¹⁹⁹ The fact that relatively short-chain products are observed in these experiments raises the question of whether *n* and *r* in reaction 18 are limited in some way or whether the reaction is a hydrogenation of a short-chain carbon fragment.

An ethynyliron complex has been reduced to a neopentylidene complex by addition of methyl from methyl fluorosulfonate; intermediates have been isolated.²⁵⁹

The reaction of diazomethane and hydrogen on transition-metal surfaces to produce hydrocarbons²⁶⁰ has been interpreted as evidence in favor of this type of carbon-carbon bond formation. However, the surface intermediates have not been experimentally identified, and this approach is subject to the uncertainties inherent in the study of back reactions of stable product

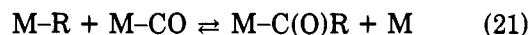
molecules (see discussion of reaction 31) plus the further difficulty that diazomethane is not a Fischer-Tropsch product. This evidence, therefore, falls short of the criteria listed in the Introduction, although it appears to support reactions of the class represented by reaction 18.

A special case of reaction 18 is for *m* and *s* both equal to 0:

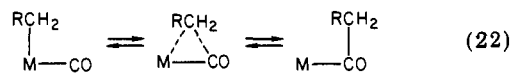


This is probably a step in the formation of carbon deposits, which will be discussed in section III.D.4.

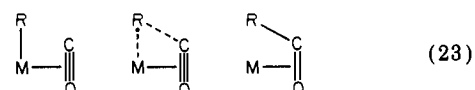
Complex chemistry offers evidence for the insertion of CO into an alkyl-metal bond (or migration of the alkyl to CO) as a way of forming carbon-carbon bonds:^{7,12,14-16}



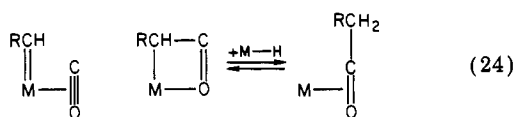
When the mechanism of alkyl migration is considered in detail, it has been treated as bond-breaking between the alkyl carbon and the metal accompanied by bond-making between the alkyl and carbonyl carbons:²⁶¹



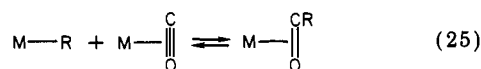
If CO is complexed side-on, the mechanism can be written in analogy to the mechanisms proposed for Ziegler-Natta polymerization. Analogy to Cossee's mechanism²⁶² gives



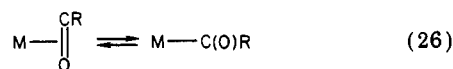
Analogy to the mechanism of Ivin et al.²⁶³ gives a different type of carbonyl insertion:



The product acyl in this case would be expected to be π bonded to the metal through the acyl double bond:



The η^2 -acyl complex will then be able to convert to the σ -bonded form:²⁶⁴



Carbon monoxide insertion is a well-known reaction in complex chemistry^{189,191,265,266} and has been studied theoretically in some detail.²⁶¹ However, it has not been observed unambiguously on surfaces. The reaction of the more strongly adsorbed form of CO (reaction 25) would be expected to be more rapid than that of the end-on CO (reaction 21), from several types of evidence. Alkyl migration in an iron complex has been found to be catalyzed by Lewis acids such as alkali metal cations²⁶⁷ and protons²⁶⁸ which complex the oxygen of the carbonyl ligand. For manganese complexes, AlBr₃ has been shown to play the same role as the alkali metal cations; an intermediate has been isolated that contains a Mn-CO-Al-Br ring.^{269,270} Further, the same sort of interaction appears to take place between the manganese complexes and an alumina surface, with oxygen from the alumina taking the place of bromine in the ring.²⁷¹

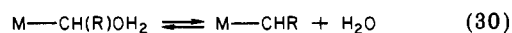
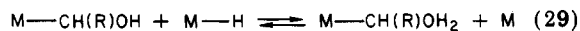
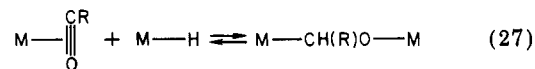
As was the case for hydrogenation of CO, the earlier transition metals also facilitate alkyl migration to CO complexed to them. Zirconium complexes have been the most studied,²²⁸ but facile alkyl migration has been observed for complexes of uranium and thorium,^{272,273} titanium,^{274,275} hafnium,²⁷⁶ and tantalum.²⁷⁷ Most of these reactions result in η^2 -acyl products, as might be expected from reaction 25.

An η^2 -acyl derivative of ruthenium is also known,²⁷⁸ and acyls with oxygen and carbon coordinated to two different metals have also been characterized,²⁷⁹ in one case having been prepared by CO insertion into an alkyl-metal bond.²⁸⁰

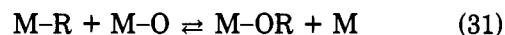
Acyl intermediates have been formed by the interaction of CO and alkenes adsorbed on metal surfaces.²⁸¹⁻²⁸⁴ However, isotopic evidence suggests that the formation of the oxygenated species is by oxygen transfer rather than alkyl migration.²⁸⁴

The acyl intermediate must be hydrogenated to an alkyl to continue chain growth. The probable mechanism is through an alcoholic intermediate with loss of water. Several sequences of hydrogen addition can be written for this reaction; the overall reaction from acyl to alkyl has been observed in a complex,^{16,285} but the detailed mechanism has not been elucidated. Some analogous intermediates have been isolated in the case of reduction of formyl ligands (section III.B.2). The reduction appears to require coordination of the acyl

oxygen,^{16,286} so that reaction probably takes place from the η^2 -acyl. A possible sequence is⁷

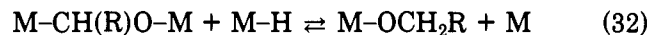


Rhenium acyls have been protonated to give hydroxycarbene ligands,²⁸⁷ an alternative to reaction 27, yielding M-C(R)OH. Alkoxy intermediates may also be formed under the conditions of the synthesis, but the evidence for their formation is of a different type than given earlier. The formation of alkoxy intermediates might be expected to occur by the reaction of an alkyl intermediate with an adsorbed oxygen atom:



However, this reaction has not been directly observed in either the forward or reverse direction. Most of the evidence comes indirectly from studies of alcohol adsorption on surfaces. Stable metal alkoxide complexes are well-known,²⁸⁶ but they are not formed by reactions analogous to reaction 31. Although alcohols adsorbed on iron,²⁸⁸ nickel,^{290,291} and silica-supported iron, cobalt, and nickel²⁹² can give alkoxy intermediates, these observations support reaction 31 only in an indirect way. Somewhat less indirect is the observation that alcohols adsorbed on Fe(100) gave CO, H₂, aldehydes, and hydrocarbons.²⁹³ The formation of the reactants of the Fischer-Tropsch synthesis and hydrocarbon products suggests that alkoxy intermediates can be considered to play a part in the Fischer-Tropsch synthesis and constitutes evidence for reaction 31 by an argument based on the principle of microscopic reversibility.

The adsorption reaction can be considered to be the reverse of the reaction forming alcohols as products (section III.D.1). If hydrocarbons are formed through the alkoxy intermediates, the oxygen must be lost at some point. One path to oxygen loss that would lead to alkanes would be formation of alkyl intermediates through the reverse of reaction 31, followed by product formation. However, ethane may be a product of the adsorption of ethanol on iron, but its presence could not be confirmed.²⁹³ Ethylene was confirmed as a product. Elimination of OH from alkoxy intermediates would yield alkenes, but this reaction has no other support. Another route to alkoxy intermediates would be hydrogenation of the product of reaction 27 with hydridic hydrogen:



Again, the evidence is not inconsistent with the reverse of this reaction. A difficulty in interpreting reactions in which products of the synthesis are inserted into synthesis conditions is in the network of paths open to them and the intermediates formed from them and in the current uncertainty of the nature of the intermediates corresponding to a late stage of reaction. Although alcohols added to the feed stream have been shown to participate in chain growth to a greater extent than do added alkenes,^{294,295} these results cannot simply be interpreted in terms of a single intermediate or path. The relative participations of the two added products

may rather be related to the rates of the reactions that give the chain-forming intermediates from the added products.

Evidence for the participation of carboxyl intermediates suffers from the same difficulties. Adsorbed carboxyl species have been observed in the coadsorption of alkenes and CO₂²⁸³ and in the adsorption of acetaldehyde.²⁴¹ Carboxylic acids adsorb on Fe(100) to give carboxylate intermediates which decompose to CO, H₂, and CO₂,²⁹⁶ but the same difficulty arises here in interpreting these experiments as in the alcohol adsorption experiments. Another possible path to carboxylate intermediates may be alkyl migration to chemisorbed CO₂.²⁵⁴

The roles of alkoxy and carboxyl intermediates in the synthesis need to be clarified with more direct evidence with respect to the mechanism of their formation and their further reactions. They have been suggested to be the predominant intermediates in the Fischer-Tropsch synthesis,^{283,297,298} but the present evidence is too slender to include their reactions in this mechanism.

Numerous other reactions can be written, particularly for elimination of water from oxygenated intermediates. Some reactions can be removed from consideration by the assumption that chains grow only at one end, and that end is the precursor of the functional groups in the products; the end not bonded to the metal is an alkyl. This assumption is commonly made in discussions of the Fischer-Tropsch mechanism, but it is not the only one possible. The predominance of unbranched hydrocarbon chains with functional groups most often in the 1-position is consistent with chain growth at one end only. However, there appears to be no a priori reason why reactions of the type



could not take place. Then further reaction, such as elimination of water or readsorption of the functional group on the surface, could take place at the free end as well. However, the formation of reactive loci in the chain would produce more branched products and products with functional groups in positions other than the 1-position. Since some of these products are seen, these types of reactions cannot be completely ruled out, although the fact that these are minor products argues that these paths are minor. At present, there is no direct evidence for or against double-ended chain growth.

The last several reactions in Table V also have no direct evidence and relatively little indirect evidence that can be interpreted in their favor. Most of them are based on analogies to well-known organic reactions; thus, they remain possibilities. The hydroxycarbene polymerization mechanism proposed by Storch, Golumbic, and Anderson³ is not supported by observed surface species; few metal hydroxycarbene complexes have been identified.^{223,287} Some authors have postulated intermediates of this type to explain kinetics of methanation,^{121,299-301} but the evidence as a whole appears not to support these reactions sufficiently to include them in this mechanism.

The reactions proposed in this section and the resulting intermediates are summarized in Table VI. These reactions include two types of carbon-carbon bond-forming steps; the hydrogenation steps are analogous to the reactions of Table IV.

TABLE VI. Reactions of Hydrocarbon and H-C-O Intermediates

reaction	eq no.
$M-C_nH_m + M-C_rH_s \rightleftharpoons M-C_{n+r}H_{m+s} + M$	18
$M-C_nH_m + M-H \rightleftharpoons M-C_nH_{m+1}$	19
$M-R + M-CO \rightleftharpoons M-C(O)R + M$	21
$M-R + M-\begin{array}{c} C \\ \\ O \end{array} \rightleftharpoons M-\begin{array}{c} CR \\ \\ O \end{array}$	25
$M-\begin{array}{c} CR \\ \\ O \end{array} \rightleftharpoons M-C(O)R$	26
$M-\begin{array}{c} CR \\ \\ O \end{array} + M-H \rightleftharpoons M-CH(R)O-M$	27
$M-CH(R)O-M + M-H \rightleftharpoons M-CH(R)OH + M$	28
$M-CH(R)OH + M-H \rightleftharpoons M-CH(R)OH_2 + M$	29
$M-CH(R)OH_2 \rightleftharpoons M-CHR + H_2O$	30
Intermediates	
$M-CH(CH_2)_nCH_3$	$M-CH(R)O-M$
$M-CH_2(CH_2)_nCH_3$	$M-CH(R)OH$
$M-C(O)R$	$M-CH(R)OH_2$
$M-\begin{array}{c} CR \\ \\ O \end{array}$	

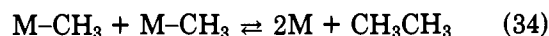
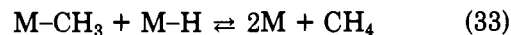
D. Product Formation

Although some of the previously proposed mechanisms have been discussed in terms of primary and secondary products, this distinction becomes somewhat arbitrary in a mechanism of the type proposed here. The customary distinction is that primary products are those produced directly by the reactions of the mechanism, and the secondary products are those produced by readsorption and further reaction of the primary products. However, if all the reactions, including the product desorption reactions, are reversible, as they must be by the principle of microscopic reversibility, then the readsorption of stable product molecules will give intermediates that are indistinguishable from intermediates that have not undergone desorption and readsorption and therefore will lead to the same kinds of products. A distinction can be made on the basis of relative amounts of different products with different conversions, but this distinction seems not to be useful in this discussion. Although some products may be observed to form earlier than others in the synthesis, this may simply result from the kinetics of the formation of the various products.

In addition to the reactions giving the organic products, the generation of the side products H₂O, CO₂, graphite, and metal carbides and oxides will also be discussed in this section. In every case where a product is formed, a desorption reaction can also be written, but the desorption reactions will be omitted here. Previously proposed product-forming reactions are given in Table VII.

1. Organic Products

Two reactions are possible for the formation of methane and other alkanes:



or, more generally,

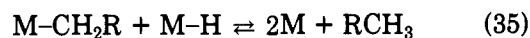
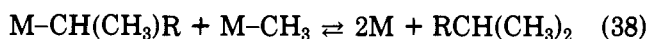
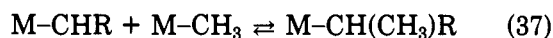


TABLE VII. Previously Proposed Product-Forming Reactions

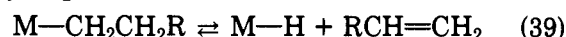
reaction	type of evidence	ref
$M-C + 2H_2 \rightleftharpoons M + CH_4$	transient experiments	131
	surface species	165
$Ni_3C_{surf} + 2H_2 \rightleftharpoons 3Ni + CH_4$	combination	180
$M-CH_n + H_2 \rightleftharpoons M + CH_4$	kinetics	121
$M-CH_2 + H_2 \rightleftharpoons M + CH_4$	combination	167
$M-CH_3 + M-H \rightleftharpoons 2M + CH_4$	surface species	178
	kinetics	135
	transient experiments	170
	combination	133
$M-CHR + 2M-H \rightleftharpoons 3M + RCH_3$	combination	167
$M-CH_2R + H_2 \rightleftharpoons M + RCH_3$	complex chemistry	18
$M-CH_2R + H_2 \rightleftharpoons M-H + RCH_3$	kinetics, product distribution	20
$M-CH_2R + M-H \rightleftharpoons 2M + RCH_3$	combination	7, 16, 22, 37
	transient experiments	170
$M-(CH_2)_n-M \rightleftharpoons 2M + RCH=CH_2$	kinetics, product distribution	20
$M-CH=CHR + H_2 \rightleftharpoons M + RCH=CH_2$	complex chemistry	18
$M-CH_2CH_2R \rightleftharpoons M-H + \pi-M-CH_2=CHR$	combination	7, 21
$\pi-M-CH_2=CHR \rightleftharpoons M + RCH=CH_2$	combination	7, 21
$M-CH_2\dot{C}H_2R \rightleftharpoons M-H + RCH=CH_2$	complex chemistry	12
$M-OR + M-H \rightleftharpoons 2M + ROH$	combination	7, 21
$M-CH(OH)R + H_2 \rightleftharpoons M + RCH_2OH$	complex chemistry	18
$M-CH(OH)R + M-H \rightleftharpoons 2M + RCH_2OH$	transient experiments	170
	complex chemistry	12
$M-C(O)R + M-H \rightleftharpoons 2M + RC(O)H$	combination	21
$M-O + H_2 \rightleftharpoons M + H_2O$	combination	166, 167
	transient experiments	131
	H_2 , CO absorption properties	134
$M-OH + M-H \rightleftharpoons 2M + H_2O$	combination	133
$M-O + CO \rightleftharpoons M + CO_2$	combination	135, 166, 167
	transient experiments	131
	CO absorption properties	134
$M-O + M-CO \rightleftharpoons 2M + CO_2$	transient experiments	170
	combination	135
$nM-C \rightleftharpoons nM + C_n(\text{graphite})$	surface species	178
$nM-C \rightleftharpoons nM + C_n(\text{amorphous})$	surface species	165
$C_n(\text{amorphous}) \rightleftharpoons C_n(\text{graphite})$	surface species	165
$M-C + CO + H_2 \rightleftharpoons M-CC + H_2O$	combination	166
$M-C + 2CO \rightleftharpoons M-CC + CO_2$	combination	166
$M-C + 2Fe \rightleftharpoons Fe_3C$	transient experiments	170
$M-C + 3Ni \rightleftharpoons Ni_3C_{bulk}$	surface species	165
$C_{interstitial} + 3Ni \rightleftharpoons Ni_3C_{surface}$	hydrogenation of carbides	180

The formation of 2-methyl-substituted alkanes probably takes place through a succession of two reactions of the form of reaction 36, where R' is methyl:

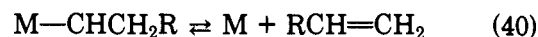


The evidence for hydrogenation (reaction 33) has been discussed in section III.B.1. In metal alkyl complexes, reactions 35 and 36 are called reductive eliminations and have been observed for numerous metals.^{189,190,302-304} Dihydrogen has also been observed to react with metal carbene complexes to cleave the $M=C$ bond and give hydrocarbons.^{199,236,305,306} Reactions between iron dimers and methane,³⁰⁷ nickel clusters and pentane,³⁰⁸ and copper atoms and methane³⁰⁹ in low-temperature matrices to give the metal alkyls may be the reverse of reaction 33. The apparent reverse of the hydrogenation of carbon atoms to methane (reactions 7-9, 33) has been observed in the adsorption of methane on nickel single-crystal surfaces.³¹⁰ The lack of significant branching in the carbon chains beyond 2-methyl must be explained in this mechanism by competing rates of hydrogenation and carbon-carbon bond formation and will be discussed in detail in section IV.B.

Alkene formation can occur from alkyl intermediates by β -hydrogen elimination:^{189,190}

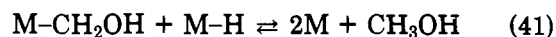


or from less saturated intermediates by rearrangement:

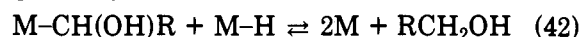


Ethylene has been shown by electron energy loss spectroscopy, interpreted in terms of adsorbate vibrational spectra, to adsorb on platinum as a $-CHCH_3$ species,^{311,312} the reverse of reaction 40. Results from the adsorption of ethylene on Fe(100) are consistent with the platinum results, but the structure of the intermediate was not identified conclusively.²⁹⁶ The product from reaction 40 may be formed as a π complex.^{7,21}

Alcohols, like alkanes, can be formed by hydrogenation of the appropriate intermediates:



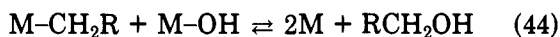
More generally,



Reactions of this type have been observed for chromium complexes in acidic aqueous solution, protons being the source of hydrogen.³¹³ If alkoxy intermediates are present, they may be hydrogenated to alcohols:

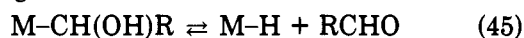


The reverse of this reaction has been observed on iron, nickel, and cobalt surfaces.^{289,293} However, the formation of alkoxy intermediates has not been well supported (section III.C), and their role in the synthesis is not clear. Reaction of alkyl intermediates with surface hydroxyls may also occur:

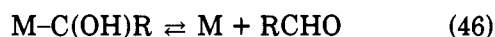


Certain similarities and differences among reactions 42, 43, and 44 remain to be understood. Reaction 44 is a nucleophilic attack of hydroxyl at the alkyl carbon bonded to the surface; reaction 42 might be expected to occur through nucleophilic attack by hydride, but the single experimental observation is of electrophilic attack by a proton. Hydrogenation of alkoxy intermediates (reaction 43) should also require protonic hydrogen.

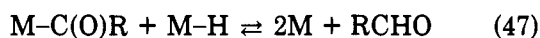
For the formation of aldehydes, kinetic evidence for an α -hydroxymethyl intermediate in a reaction of manganese complexes to give benzaldehyde³¹⁴ and the thermal decomposition of a hydroxymethylene rhenium complex to give acetaldehyde²⁸⁷ suggest that a product-forming reaction is



or

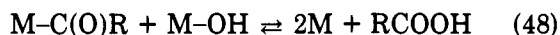


Aldehydes may also be formed by hydrogenation of acyl intermediates:



However, no direct evidence is available for this reaction.

The formation of acids can also be accounted for by reaction of the available intermediates:



Esters could be formed through an analogous reaction, with alkoxy intermediates replacing hydroxyl.

2. Water

The evidence for the formation of surface hydroxyl (section III.B.1) also supports the reaction of chemisorbed intermediates to form water



rather than the reaction of H_2 with adsorbed oxygen atoms. Water may also be formed in the hydrogenation of acyls to alkyls (reaction 30).

3. Carbon Dioxide

The reaction between CO and O to produce CO_2 probably takes place through the adsorbed species on metal surfaces:³¹⁵⁻³¹⁷



rather than through a collision of an unadsorbed CO molecule with an adsorbed oxygen atom. The kinetics of the reaction have been studied mainly on rhodium, palladium, iridium, and platinum. Of the Fischer-Tropsch metals, only ruthenium and cobalt have been studied. The results for ruthenium did not eliminate either mechanism from consideration,³¹⁸ and the reaction appears to have some different characteristics from that on the other metals studied.^{315,319,320} The results

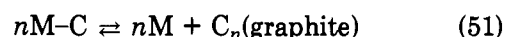
for cobalt³²¹ were consistent with reaction 50.

Metal oxides can also serve as substrates for CO oxidation. On iron,³²² mixed cobalt magnesium,^{323,324} and mixed nickel magnesium³²⁵ oxides, the oxidation takes place at the metal ions, through ionic intermediates. This path is also a possibility in supported catalyst systems in which the metal at the interface between metal and support is oxidized and for systems in which metal oxides are formed during the synthesis.

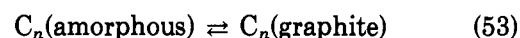
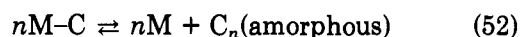
4. Unreactive Carbon

Carbon deposition is one of the major routes of deactivation of the Fischer-Tropsch catalysts.^{166,178,326-329} Carbon blocks adsorption of H_2 and CO ^{330,331} and some forms are difficult to hydrogenate (section III.B.1). In addition, carbon deposited on the catalyst is removed from paths to desired products.

Carbon atoms are produced by dissociation of CO (reaction 6). At least four types of carbon have been identified on the surface of catalysts, some of them reactive enough to be considered intermediates (section III.B.1). The carbon to be discussed here is the inert carbon that is effectively an end product of the synthesis. The formation of this carbon may be directly from adsorbed atoms:^{178,332}



The transformation of surface carbon atoms to graphite has also been observed to proceed through amorphous carbon:¹⁶⁵



The amorphous carbon may also be a poison, because it hydrogenates slowly, although not as slowly as the graphitic carbon.¹⁶⁵ On the other hand, it appears to oxidize more rapidly than carbidic carbon.³³³

Studies of the disproportionation of CO over iron,³³⁴ nickel,³³⁵ and cobalt³³⁵ catalysts and studies of coke formation on dehydrogenation (iron-chromium) catalysts³³⁶ indicate that graphite deposits can also be formed by the breakdown of an intermediate metal carbide. Although these studies were carried out at higher temperatures than typical synthesis conditions, this path should also be considered as a possibility for formation of unreactive carbon.

Because the strengths of the metal-carbon bonds for the various metals should influence the rates of reactions 51 and 52, it has been speculated that one of the functions of promoters is to decrease the formation of graphite deposits. However, promoters have been shown to have little or no effect on the specific activity of iron catalysts for carbon deposition.³²⁶

Carbon deposition has also been studied by pyrolysis of hydrocarbons over catalysts.³¹⁰ Although these studies are typically carried out at higher temperatures than those of the Fischer-Tropsch synthesis, this path should also be considered for carbon deposition. It would be represented by the reverse of the hydrocarbon formation reactions and hydrogenation reactions and by the reactions for the formation of unreactive carbon discussed in this section; thus, these studies can also contribute to the understanding of carbon deposition in the Fischer-Tropsch synthesis, but will be subject to some of the same types of difficulties in interpreta-

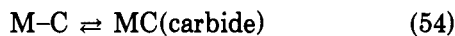
tion discussed in section III.C with respect to alkoxy intermediates.

5. Metal Carbides and Oxides

Although the definition of a catalyst requires that it be unchanged at the end of a reaction, the Fischer-Tropsch catalysts have been found to have been converted from the metal to the carbide or the oxide at the end of a synthesis. In addition, the metal oxides and carbides themselves possess catalytic activity for various parts of the synthesis and can participate in product-forming reactions. Therefore, their formation during a synthesis may change rate constants for elementary reactions.

The formation of metal oxides may be slightly beneficial in removing oxygen by another path than reaction with H_2 or CO , although this cannot be a large contribution, in view of the relative amounts of catalyst and reactants. The formation of metal carbides, unless it provides new catalytic paths or improved rate constants, will be detrimental in removing carbon from the product-forming paths, although, again, only to a small degree.

The formation of carbides and oxides of iron and nickel is thermodynamically favorable under the conditions of the Fischer-Tropsch synthesis.³³⁷⁻³³⁹ However, the kinetics of the processes involved may be slow enough relative to other reactions in the mechanism³²⁹ that the reactions



may be sufficient to indicate the removal of carbon and oxygen from other paths.

The behavior of the particular metal in the catalyst will need to be taken into consideration to represent the mechanism over a particular catalyst. Whereas the metal may change the rates of earlier reactions by the metal-intermediate bond strengths, the formation of oxides and carbides proceeds through different compounds with different stoichiometries and phases, and therefore must be represented by different sets of elementary reactions. Reactions 54 and 55 will be regarded as sufficient here. However, the available literature relevant to the kinetics of carbide and oxide formation under Fischer-Tropsch conditions will be reviewed here to give a starting point for further studies to show the amount of detail needed for including these reactions in the mechanism.

A complete set of elementary reactions describing the transformation of oxygen or carbon into a metal oxide or carbide, from surface atom to bulk compound, is not available for any system. Nickel has been the most studied.^{333,340,341} The sequence appears to be surface atom, dissolved atoms that diffuse into the bulk, and formation of compound. This sequence has been postulated for nickel carbide formation,^{132,180,310} and it has some support in kinetics.^{342,343}

Metallic iron,^{327,328,344} ruthenium,³²⁸ and iron-ruthenium³²⁸ catalysts, silica-supported iron,^{175,345-347} nickel,^{346,347} and iron-nickel^{175,346,347} catalysts, and iron intercalated in graphite³⁴⁸ have been studied by several methods to determine the phases of oxides and carbides formed under synthesis conditions. Several phases are observed, some of them at different times in the syn-

TABLE VIII. Product-Forming Reactions

reaction	eq no.
$M-CH_2R + M-H \rightleftharpoons 2M + RCH_3$	35
$M-R + M-R' \rightleftharpoons 2M + RR'$	36
$M-CH_2CH_2R \rightleftharpoons M-H + RCH=CH_2$	39
$M-CHCH_2R \rightleftharpoons M + RCH=CH_2$	40
$M-CH(OH)R + M-H \rightleftharpoons 2M + RCH_2OH$	42
$M-CH(OH)R \rightleftharpoons M-H + RCHO$	45
$M-C(OH)R \rightleftharpoons M + RCHO$	46
$M-OH + M-H \rightleftharpoons 2M + H_2O$	49
$M-CO + M-O \rightleftharpoons 2M + CO_2$	50
$nM-C \rightleftharpoons nM + C_n(\text{amorphous})$	52
$C_n(\text{amorphous}) \rightleftharpoons C_n(\text{graphite})$	53
$M-C \rightleftharpoons MC(\text{carbide})$	54
$M-O \rightleftharpoons MO(\text{oxide})$	55

thesis, indicating that the kinetics of the transformations from one phase to another may be significant in understanding the synthesis. Carbide formation appears to increase overall synthesis rates and to shift the activity toward formation of higher hydrocarbons;^{171,327,328,345} χ -iron carbide is the most active catalytic species at low temperatures.³⁴³

The cobalt (10 $\bar{1}2$) face has been found to allow oxygen from dissociation of CO to diffuse into it rapidly, while forming a surface carbide phase that may be Co_3C .^{109,110} This surface layer is capable of adsorbing CO , but not of dissociating it,^{109,110} and may therefore change the balance of reactions occurring.

Ruthenium does not form carbides and dissolves carbon over a limited range of composition.³⁴⁹ Adsorbed oxygen atoms have been found to diffuse into the Ru(001) plane in an early step in the formation of oxides.³¹³

The carbides and oxides themselves can participate in further reactions, mainly to produce CH_4 , H_2O , CO , CO_2 , and unreactive carbon.^{333,341} These reactions can be represented by elementary reactions already included in this mechanism, starting with the reverse of reactions 54 and 55 to form the reactive adsorbed carbon and oxygen atoms from the bulk carbides and oxides. Then the earlier hydrogenation and oxygenation reactions can take place.

The reactions proposed in this section are summarized in Table VIII. The hydrogenation and recombination reactions are analogous to the reactions of Tables IV and VI. In addition, the formation of alkenes and aldehydes may proceed through elimination reactions.

IV. Comparison with Previously Proposed Mechanisms

Parts of the mechanism for the Fischer-Tropsch synthesis have been discussed widely, but only five complete mechanisms have been proposed: the carbide mechanism,^{19,20} the Bureau of Mines mechanism,^{3,23} the Pichler-Schulz mechanism,^{7,21} mechanisms based on steps observed in complex chemistry,^{12,18} and a combined mechanism recently advanced by Ponac.^{14,22} Only the complete mechanisms will be discussed here. All of the mechanisms overlap to some degree. The object of this section is to provide an overview of the relationship among the mechanisms.

In general, the mechanism proposed here differs from previous mechanisms in that it includes more possible steps; in particular, two types of carbon-carbon bond formation (reactions 18, 21, and 25) are included here, whereas the others include either a hydrocarbon in-

intermediate recombination reaction or an alkyl migration to carbonyl, but not both. In addition, most of the other mechanisms do not include paths for the production of H_2O , CO_2 , unreactive carbon, and the metal carbides and oxides. The mechanism proposed here resembles the Pichler-Schulz and Ponc mechanism most closely of those previously proposed and differs most from the Bureau of Mines mechanism. The mechanisms will be discussed in the order of their historical development.

A. Carbide Mechanism

Fischer and Tropsch suggested that the mechanism of the synthesis involved the formation and hydrogenation of metal carbides to give methylene groups on the surface of the metal, which then polymerized and reacted further to give the observed products.¹⁹ Craxford and Rideal supported this idea through kinetic investigations.²⁰ This original formulation of the carbide hypothesis was so named because metal carbides were thought to be the major intermediates in the formation of hydrocarbons; parts of this mechanism, particularly the reaction of hydrocarbon intermediates to form carbon-carbon bonds, are included in the mechanism proposed here.

Part of the justification for carbides as intermediates was the observation that metal carbides react with acidic aqueous solutions to give higher hydrocarbons and methane. More recently, Fischer-Tropsch catalysts have been hydrolyzed with aqueous acid, and the gaseous products have been compared with the products of the synthesis.³⁵⁰ Although similarities are observed, they are not sufficient to support the carbide mechanism in its entirety. Water may well be dissociated on the surface of the carbides, or protons may participate in surface reactions of the type listed here. In that sense, the breakdown of carbides in aqueous acids may proceed by the same mechanism as the Fischer-Tropsch synthesis; however, this is not the same as saying that the metal carbides are essential intermediates in the synthesis. In addition, recent findings show that hydrogenation of metal carbides gives methane only.^{171,177}

The finding that hydrogenation of the bulk metal carbides produces only methane casts doubts on the overall carbide mechanism. In addition, ruthenium does not form stable carbides, but it is particularly efficient at forming carbon-carbon bonds in the synthesis. Further evidence felt to discredit the carbide mechanism included tracer experiments in which a metal carbide layer containing ^{14}C was formed on the catalyst and then reacted with synthesis gas.^{3,39} An analysis of ^{14}C in the products led to the conclusion that the carbide mechanism could account only for a minor part of the products. Part of the difficulty in interpreting these experiments is that the nature of the carbon involved was not well understood. Although a "surface carbide" was later postulated to be more reactive in the formation of hydrocarbons than bulk carbides, only the more recently developed surface techniques have allowed a more detailed understanding of the types of carbon that can exist on catalyst surfaces (section III.B.1).

Another shortcoming of the carbide mechanism is that it does not explain the formation of oxygenated products,³⁵¹ although it should be noted that Craxford

and Rideal explicitly intended only to explain the formation of hydrocarbons.²⁰ However, since methylene groups were to be formed by hydrogenation of CO with water removal, it could be argued that partial hydrogenation of CO combined with the condensation of methylene groups would give the oxygenated products.

Carbon atoms deposited on the catalyst could react to form metal carbides, which would then decompose back to carbon atoms or another form of reactive carbon (section III.D.5). However, this is unlikely to be a kinetically favorable path, although it would be a form of the original carbide mechanism.

An analysis of the similarities of the Fischer-Tropsch synthesis to the Haber ammonia synthesis³⁵² also postulated hydrocarbon intermediates that can react in ways suggested in section III.C.

A variant of the carbide mechanism has been proposed to take into account some of the recent findings of surface science.³⁵³ In this mechanism, methyldiyne groups, rather than methylene groups, are seen to be the primary carbon-carbon bond formers. This is consistent with the reactions proposed here, except that both types of hydrocarbon intermediates are allowed to be intermediates in carbon chain formation (section III.C).

A study of ^{13}C distribution in Fischer-Tropsch products appears to support a carbide-type mechanism rather than a hydroxycarbene or a carbonyl insertion mechanism.³⁵⁴ However, it would be difficult to exclude the mixed mechanism proposed here on this basis.

In summary, recent evidence on surface intermediates gives new likelihood to some of the reactions proposed in the carbide mechanism, particularly the recombination of hydrocarbon intermediates to form carbon-carbon bonds. However, bulk metal carbides are unlikely to provide a major path to the products of the synthesis, and the reactive carbon and hydrocarbon intermediates can be called carbides only at the potential risk of chemical and semantic confusion (section III.B.1).

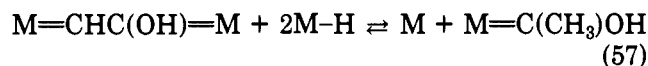
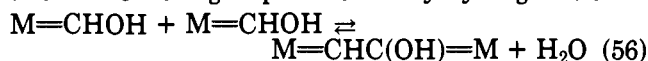
B. Bureau of Mines Mechanism

In response to the tracer experiments³⁹ and other factors that tended to discredit the carbide mechanism, workers at the U.S. Bureau of Mines developed a mechanism that explained the synthesis in more detail than the carbide mechanism.³ Eidus proposed a similar mechanism for similar reasons.⁶ This mechanism accounted for the formation of oxygenated products by making a hydroxycarbene intermediate, $\text{M}=\text{CHOH}$, responsible for carbon-carbon bond formation. However, this mechanism is difficult to justify under the conditions set forth in the Introduction to this review. Only two reactions proposed here, reactions 15 and 16, produce an intermediate of the $\text{M}-\text{CHOH}$ type, and little experimental justification is available for the existence of these intermediates. However, some of the hydrogenation and product-forming reactions are similar in the two mechanisms.

The observation that the carbon chains formed in the Fischer-Tropsch synthesis were primarily unbranched or 2-methyl branched was an impetus to the development of the Bureau of Mines mechanism. The challenge was to find a carbon-carbon bond-forming reaction that would allow only these two kinds of carbon-

carbon bond formation and prevent the formation of quaternary carbon atoms, which were not observed in the products. This observation was felt not to be explained satisfactorily by the carbide mechanism.

The Bureau of Mines mechanism postulated as the carbon-carbon bond-forming step the condensation of two M=CHOH groups followed by hydrogenation:



Condensation of a more hydrogenated species, M-CH(R)OH, with M=CHOH gave methyl branching.

A similar mechanism has again been proposed on the basis of several observations, including transient response of a reacting system, incorporation of olefins into products, and product distributions,²³ although with the hydroxycarbene species arising from the reaction of adsorbed carbon with water instead of from the reaction of dihydrogen with adsorbed CO.

The difficulty with this mechanism, in the terms of this review, is that the hydroxycarbene species M=C(R)OH has seldom been observed (sections III.B.2 and III.C). In addition, condensation reactions resembling reaction 56 have not been observed in organometallic compounds, although they have an analogy in organic condensation reactions.

However, it is necessary for any mechanism to account for the predominance of unbranched and 2-methyl-branched hydrocarbon chains in the Fischer-Tropsch synthesis. The carbide mechanism postulated methylene groups as the primary carbon-chain formers, leading to straight chains, with occasional reaction of an unhydrogenated carbon to give branching. The mechanism proposed here most resembles the carbide mechanism in its explanation of branching; it depends on relative rates to produce branched and unbranched products.

If carbon chains can be formed by the reaction of surface hydrocarbon intermediates or by alkyl migration to CO followed by hydrogenation, then all types of branching might be expected. However, although a more detailed explanation must await the availability of rate constants for the elementary reactions and computer analyses of various possible combinations, a qualitative explanation can be given here. If hydrogenation is rapid relative to carbon-carbon bond formation, then most intermediates will be relatively highly hydrogenated: methyl and methylene groups will predominate over methylenidene groups or unhydrogenated carbon; further, methyl and methylene groups will predominate over the longer carbon chains; and most groups will be attached to the metal at a single point, as was assumed in section III.C. Rapid hydrogenation relative to carbon-carbon bond formation is supported by the formation of large amounts of methane in the synthesis, although this could also result from more numerous paths to methane than to the higher hydrocarbons. A transient study found a relatively slow rate of chain growth,³⁵⁵ consistent with rapid hydrogenation relative to carbon-carbon bond formation.

A further constraint on the formation of tertiary and quaternary carbons lies in the (almost) two-dimensional nature of the catalyst surface and the tetrahedral geometry of sp³ carbon bonds. Steric hindrance to the

surface and to attacking groups will increase through the series M-CH₃, M-CH₂CH₃, M-CH(CH₃)₂, M-C(CH₃)₃, and reaction rate constants will accordingly decrease. In addition, increasing steric hindrance should lead to more rapid desorption of branched products before further branching can occur. An argument of this type has been put forward to explain the much greater stability of surface methoxide and ethoxide relative to isopropoxide on Fe(100).²⁸⁹ The competition among hydrogenation, carbon-carbon bond formation, and desorption should be able to account for the lack of branching in Fischer-Tropsch products.

Although it is desirable to be inclusive in a mechanism of this type, there seems to be no justification for including the Bureau of Mines condensation reaction in the mechanism at this time. However, a hydroxycarbene may be an intermediate in the reduction of CO to methane and in the reduction of acyls to alkyls.

C. Pichler-Schulz Mechanism

The Pichler-Schulz mechanism has been developed over a period of years and takes into account numerous types of experimental data, including product distributions from the synthesis and reactions of metal complexes.^{7,21} It accounts in more detail for the products of the synthesis than do the other mechanisms. The major difference between the Pichler-Schulz mechanism and the mechanism proposed here is that the mechanism proposed here includes both alkyl migration to carbonyl and recombination of hydrocarbon intermediates as routes to carbon chain formation whereas the Pichler-Schulz mechanism includes only alkyl migration. In other respects, the two mechanisms are very similar.

The formation of 2-methyl-branched compounds is somewhat difficult to explain in a mechanism that includes only alkyl migration as the carbon-carbon bond-forming reaction. In the Pichler-Schulz mechanism, 2-methyl branching is accounted for by partial hydrogenation of the acyl intermediate, with early loss of water to give an incompletely hydrogenated intermediate, which then can add two methyl groups. This sequence requires a more detailed understanding of the mechanism of the reduction of acyl ligands (section III.C) before it can be regarded as well-supported. As in the mechanism presented here, it relies on a combination of several rates; in fact, the reactions leading directly to branching (reactions 37 and 38) are nearly identical in both mechanisms.

D. Mechanisms Based on Complex Chemistry

Two similar mechanisms have been proposed on the basis of reactions observed in metal complexes.^{12,18} These mechanisms resemble the Pichler-Schulz mechanism, with some exceptions in the product-forming reactions. Again, the major difference between the mechanism proposed here and the complex chemistry mechanisms is that the mechanism proposed here includes the condensation of hydrocarbon intermediates as a carbon-carbon bond-forming step, and the complex chemistry mechanisms do not.

The greatest difference between the complex chemistry approach and the approach used in this paper is in the collection of supporting evidence for the elementary reactions. Although the reactions of metal

complexes may be indicative of processes on surfaces, significant differences do exist.²⁵⁻³⁰ The approach here has been to use information from complex chemistry as one type of supporting evidence, and not the most important. Complex chemistry may prove to be a more reliable analogue to the chemistry of the oxygenated intermediates, whereas surface chemistry may be more useful in elucidating the reactions of the simpler intermediates like adsorbed carbon atoms. The evidence for the reactions of the oxygenated intermediates (other than CO) given here rests mainly on complex chemistry; the evidence for reactions of the simpler intermediates rests more firmly on surface chemistry. New developments, however, may erase this distinction; the synthesis and study of cluster compounds containing carbon atoms (section III.B.1) are in an early stage and may provide more insight into the reactions of adsorbed carbon atoms than has so far been evident; new optical techniques may make it possible to investigate the more complex intermediates on surfaces.

Although parallels between surface chemistry and metal complex reactions can provide some information about possible paths, at this point of understanding the relation between metal complexes and surfaces, it seems safer to make use of as much information from surface chemistry as possible when trying to elucidate a surface mechanism.

E. Ponec Mechanism

Ponec and his co-workers have proposed a hybrid mechanism in which CO is dissociated on the surface to give carbon atoms, which are hydrogenated to methyl intermediates that can react with adsorbed undissociated CO by alkyl migration to form carbon-carbon bonds, with hydrogenation of the resulting acyl intermediates to alkyls.^{14,22} This sequence was proposed to take into account recent findings that CO dissociates readily on the Fischer-Tropsch catalyst metals (section III.A.3). Matsumoto and Bennett¹⁷⁰ proposed a similar mechanism on the basis of transient experiments. This mechanism is very close to the mechanism presented here, but, as in the case of the preceding two mechanisms, represents one of the many possible paths in the mechanism presented here. In addition, Ponec has presented less detail, particularly for the product-forming reactions, but puts more emphasis on the nature of the adsorption sites than has been done here. This is a complementary emphasis; the adsorption sites play some part in the detailed mechanism, but it is not clear that they need to be taken into account at this stage of understanding (section III.A).

F. The Fischer-Tropsch Synthesis as a Polymerization Reaction

The Fischer-Tropsch synthesis was defined here as a polymerization reaction, and it has been treated as such by several authors.^{12,279,356-362} However, it differs from most other polymerization reactions in that the adding group may be a fragment, rather than a complete molecule, or the growing chain must undergo other reactions after an addition of one unit has occurred and before the addition of the next is possible.

Although the Schulz-Flory distribution often applies reasonably well to the products of the synthesis,¹² the exceptions must be accounted for as well. Even if the

assumption is made that unbranched 1-alkenes are the primary product of the synthesis, higher production of CH₄ and lower production of C₂ and C₁₂ and higher hydrocarbons are observed than are predicted.¹² In addition, distributions completely different from the Schulz-Flory have been observed.³⁵⁷

Further, it may not be possible to delineate primary products of the synthesis in a way that is useful to understanding the mechanism (section III.D.). In this case, branched hydrocarbon chains must also be taken into account.^{356,361} Although it is commonly assumed (and has been for most of this discussion, although it is not necessary here) that 2-methyl branching is the only branching that occurs, other methyl-, dimethyl-, and ethyl-branched isomers are observed.^{7,21,356,363-367}

The differences between the Fischer-Tropsch synthesis and simple monomer addition make the application of the chain polymerization categories initiation, propagation, and termination somewhat arbitrary. For example, although alkyl migration to carbonyl to form an acyl intermediate (reactions 21 and 25) is a propagation reaction, the hydrogenation of the acyl (reactions 27-30) can lead to several product-forming reactions or to further growth of the chain. Whether they should be included as propagation or termination reactions is therefore not clear. Likewise, step polymerization is represented by a single type of reaction, for example esterification, rather than several reactions required to add a methylene unit to the carbon chain in the Fischer-Tropsch synthesis. This conditional nature of many of the reactions may require a more complex derivation of a distribution equation than the Schulz-Flory approach. Particle size effects may also require modifications to the Schulz-Flory treatment.^{368,369}

Qualitatively, several observations on the distribution of molecular weights can be made. The fact that Schulz-Flory (or nearly Schulz-Flory) distributions are observed in the Fischer-Tropsch synthesis can be accounted for in several ways: (1) there is a single carbon-carbon bond-forming step that, along with its associated steps, is kinetically well-behaved; (2) there are two or more carbon-carbon bond-forming steps that give well-behaved overall kinetics in combination with their associated steps; (3) one of two or more carbon-carbon bond-forming steps may predominate. The reasons for non-Schulz-Flory distributions would be, in effect, the inverse of reasons 1 through 3: (4) two or more carbon-carbon bond-forming steps whose kinetics combine in an unfavorable way; (5) the associated reactions have rate constants that combine in an unfavorable way; (6) a system with ill-defined initiation, propagation, and termination steps, which may not meet all the specifications for application of the Schulz-Flory equation,³⁵⁸ cannot be expected to give Schulz-Flory distributions.

At the present state of understanding, none of these possibilities can be ruled out. In particular, it is not possible to rule any out on the basis of a mechanism, since no mechanism is thoroughly enough proved to be used in this way. All of these reasons, except reason 1, are compatible with the mechanism presented here, and different reasons may be operative under different conditions. A Schulz-Flory distribution may indicate that several paths are reduced to zero effective relative rates under a particular set of conditions, as a conse-

quence of reason 3; however, reason 2 could give the same results. The Schulz-Flory distribution could be applied to the existing literature or to new experimental evidence as a scanning device to isolate conditions of interest for further study. Systems showing non-Schulz-Flory distributions may represent more complicated kinetic situations.

A further interpretation of the results obtained for carbon-chain distributions is possible. For a combined mechanism, such as that proposed here, it would be necessary to include the carbon-chain lengths of all products in testing the Schulz-Flory distribution. It is common in discussions of carbon-chain distributions to select alkanes or alkenes only; in particular, the oxygenates are often ignored. However, preliminary results appear to show that when the carbon chain lengths of all products, including oxygenates, are taken into account, a Schulz-Flory distribution that includes methane can result.³⁷⁰

V. Extension to Other Systems

Part of the utility of the type of mechanism presented here lies in its ability to unify information on closely related reactions. All of the following reactions have similarities to the Fischer-Tropsch synthesis in reaction conditions or catalysts. However, the conditions under which each reaction predominates are different. Carbon monoxide disproportionation, the water-gas shift reaction, and methanation have long been known to take place simultaneously with the synthesis of higher hydrocarbons from synthesis gas. Isosynthesis gives branched, short-chain hydrocarbons suitable for gasoline; the Kölbel-Engelhardt synthesis utilizes water in place of hydrogen, a desirable substitution from a cost viewpoint; both have been recognized as being closely related to the Fischer-Tropsch synthesis. The last section deals with a more controversial relationship, that of the heterogeneous Fischer-Tropsch synthesis to homogeneously catalyzed liquid-phase reactions; here the relationship is much less clear, although some parallels can be drawn between some features of the processes.

For delineation of the relationships among the processes, subsets of the elementary reactions given in section III have been assembled to represent the processes. Thus, there is an interplay between understanding these processes and understanding the Fischer-Tropsch synthesis: more information about the synthesis mechanism contributes to an understanding of the other processes in which those elementary reactions play a part, and more information about the elementary reactions of the other processes contributes to the understanding of the Fischer-Tropsch mechanism. This transfer of information could be particularly important from the simpler and more easily studied reactions, CO disproportionation, water-gas shift, and methanation, to the Fischer-Tropsch synthesis. For this reason, information on methanation, in particular, has been incorporated into the earlier discussion.

A. Carbon Monoxide Disproportionation

The disproportionation of CO, known as the Boudouard or Bell reaction, goes according to the overall stoichiometry:

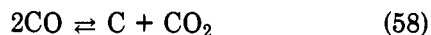


TABLE IX. Mechanism of CO Disproportionation

reaction	eq no.
$\text{CO} + \text{M} \rightleftharpoons \text{M-CO}$ (physisorbed)	3
M-CO (physisorbed) \rightleftharpoons M-CO	4
$\text{M-CO} \rightleftharpoons \text{M}-\overset{\text{C}}{\parallel}\text{O}$	5
$\text{M}-\overset{\text{C}}{\parallel}\text{O} + \text{M} \rightleftharpoons \text{M-C} + \text{M-O}$	6
$\text{M-CO} + \text{M-O} \rightleftharpoons 2\text{M} + \text{CO}_2$	50
$n\text{M-C} \rightleftharpoons n\text{M} + \text{C}_n$ (amorphous)	52
C_n (amorphous) \rightleftharpoons C_n (graphite)	53

Table IX gives the elementary reactions proposed here that could represent the mechanism of this reaction.

It might appear initially that CO disproportionation is a reaction that needs to be minimized, since it can lead to carbon deposition on the catalyst (reactions 52 and 53). However, the carbon resulting from the dissociation of CO (reactions 5 and 6) may also be hydrogenated to organic products (Tables IV and VI). Thus, CO disproportionation is not simply a beneficial or detrimental part of the Fischer-Tropsch synthesis.

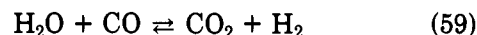
All of the Fischer-Tropsch catalyst metals catalyze CO disproportionation.^{334,335,371,372} Temperatures favoring CO disproportionation are somewhat higher than those for the synthesis. Disproportionation takes place over a large pressure range.

The thermodynamics of the reaction have been studied for nickel,^{373,374} cobalt,³⁷⁴ and iron.³⁷⁵ Fewer kinetic studies are available. The main question in the mechanism proposed here is the nature of the step in which CO reacts with oxygen: is the CO molecule adsorbed on the catalyst or does it come from the gas phase? Other investigations agree on the steps of chemisorption and dissociation of CO,¹²⁹⁻¹³⁵ but some favor a reaction with gas-phase CO¹²⁹ and some, adsorbed CO.¹³⁰ The evidence discussed in section III.D.3 for the reaction between CO and oxygen is predominantly for a reaction between two adsorbed species, as in reaction 50. However, this evidence was primarily for the other metals of group 8, so this conclusion cannot be considered to be firm for the Fischer-Tropsch catalyst metals.

The formation of carbides and oxides of the metal catalyst may also play a part in the disproportionation of CO, as was discussed in section III.D.5. Their exact role is not clear and may vary with the conditions and from metal to metal. Carburization retarded CO disproportionation for an iron catalyst from 240 to 370 °C but increased it for the same catalyst at higher temperatures.³⁷⁶ Oxides and carbides have been found not to catalyze the reaction, and in some cases to retard it,^{374,375} but, on the other hand, $\gamma\text{-Fe}_2\text{O}_3$ has been identified as a catalyst.³³⁴

B. Water-Gas Shift Reaction

The water-gas shift reaction is the equilibrium among H₂O, CO, CO₂, and H₂, all in the gas phase:



It is believed to shift the production of H₂O or CO₂ as the side product of the Fischer-Tropsch synthesis, and it is used to adjust the concentrations of CO and H₂ in the feed gas. To the extent that it takes place concurrently with the production of organic products, it can change the concentrations of the reactants. As in the

TABLE X. Mechanism of the Water-Gas Shift Reaction

reaction	eq no.
$H_2 + M \rightleftharpoons M-H_2$ (physisorbed)	1
$M-H_2$ (physisorbed) \rightleftharpoons H-M-H	2
$CO + M \rightleftharpoons M-CO$ (physisorbed)	3
$M-CO$ (physisorbed) \rightleftharpoons M-CO	4
$M-CO \rightleftharpoons M-\overset{C}{\parallel}\overset{O}{\parallel}$	5
$M-\overset{C}{\parallel}\overset{O}{\parallel} + M \rightleftharpoons M-C + M-O$	6
$M-O + M-H \rightleftharpoons M-OH + M$	11
$M-OH + M-H \rightleftharpoons 2M + H_2O$	49
$M-CO + M-O \rightleftharpoons 2M + CO_2$	50

case of the disproportionation of CO, its effect on the overall synthesis is neither favorable nor unfavorable. Table X gives the elementary reactions proposed here that could represent the mechanism of this reaction.

The water-gas shift reaction is catalyzed by a number of metals and their oxides.^{377,378} Oxide catalysts are used industrially. Of the Fischer-Tropsch catalyst metals, iron and cobalt are used for the water-gas shift reaction. The preferred temperature range is somewhat lower than typical Fischer-Tropsch temperatures, because the water-gas shift reaction is an equilibrium reaction, and the production of H_2 is favored at lower temperatures. The reaction can be carried out over a large pressure range.

Numerous empirical expressions have been derived for the kinetics of the overall reaction on iron chromium oxide catalysts,³⁷⁷ but these are not useful for an understanding of the elementary reactions. Further, the reaction mechanism over an iron chromium oxide may well be different from the mechanism over a Fischer-Tropsch metal catalyst.

Mechanisms have been proposed for several catalysts.³⁷⁸⁻³⁸⁷ All are similar to Table X; most of the reaction is believed to take place through adsorbed species. However, formate intermediates appear to be

a part of the shift reaction,^{378,381-383,385-387} whereas they are questionable intermediates in the Fischer-Tropsch synthesis (section III.C). This could be regarded as evidence for formate intermediates (and, by extension, carboxylate intermediates) in the synthesis. The single study³⁷⁸ of the water-gas shift over supported metals suggests the participation of formate intermediates, although the evidence is not unambiguous.

C. Methanation

Methanation has long been recognized as a part of the Fischer-Tropsch synthesis.^{299,388} Indeed, methane is usually a significant product in the synthesis. For this reason, evidence from methanation and reactions proposed for its mechanism have been included in the earlier sections of this paper. Methanation mechanisms can be divided into dissociative and associative mechanisms. Reactions for both are included in the mechanism presented here. Table XI gives the elementary reactions that can be included in a methanation mechanism. An "x" in the column for associative or dissociative mechanism indicates that the reaction should be included in that mechanism. It appears likely that all the reactions of Table XI contribute to methane formation in the Fischer-Tropsch synthesis and probably in methanation as well, although an associative or dissociative mechanism may predominate in a given situation.

The reactions given in Table XI are, on the whole, more thoroughly supported than the Fischer-Tropsch mechanism as a whole. The reason for this is their simplicity: the reactions of the more complex intermediates are more difficult to support. In the methanation mechanism, the reactions of the oxygenated intermediates are not as well supported as those of carbon from CO dissociation. Other published mechanisms have favored hydrogenation of carbon from CO dissociation,^{133,135,389,390} or an oxygenated intermedi-

TABLE XI. Mechanism of Methanation

reaction	no.	dissociative mechanism	associative mechanism
$H_2 + M \rightleftharpoons M-H_2$ (physisorbed)	1	x	x
$M-H_2$ (physisorbed) \rightleftharpoons H-M-H	2	x	x
$CO + M \rightleftharpoons M-CO$ (physisorbed)	3	x	x
$M-CO$ (physisorbed) \rightleftharpoons M-CO	4	x	x
$M-CO \rightleftharpoons M-\overset{C}{\parallel}\overset{O}{\parallel}$	5	x	
$M-\overset{C}{\parallel}\overset{O}{\parallel} + M \rightleftharpoons M-C + M-O$	6	x	
$M-C + M-H \rightleftharpoons M-CH + M$	7	x	
$M-CH + M-H \rightleftharpoons M-CH_2 + M$	8	x	
$M-CH_2 + M-H \rightleftharpoons M-CH_3 + M$	9	x	x
$M-O + M-H \rightleftharpoons M-OH + M$	11	x	
$M-CO + M-H \rightleftharpoons M-CHO + M$	12		x
$M-CO + M-H \rightleftharpoons M-COH + M$	13		x
$M-COH + M-H \rightleftharpoons M-CHOH + M$	15		x
$M-CHO + M-H \rightleftharpoons M-CHOH + M$	16		x
$M-CHOH + M-H \rightleftharpoons M-CH_2OH + M$	17		x
$M-CH_2OH + M-H \rightleftharpoons M-CH_2OH_2 + M$	29		x
$M-CH_2OH_2 \rightleftharpoons M-CH_2 + H_2O$	30		x
$M-CH_3 + M-H \rightleftharpoons 2M + CH_4$	33	x	x
$M-OH + M-H \rightleftharpoons 2M + H_2O$	49	x	
$M-CO + M-O \rightleftharpoons 2M + CO_2$	50	x	
$nM-C \rightleftharpoons nM + C_n$ (amorphous)	52	x	
C_n (amorphous) \rightleftharpoons C_n (graphite)	53	x	
$M-C \rightleftharpoons MC$ (carbide)	54	x	
$M-O \rightleftharpoons MO$ (oxide)	55	x	

ate.^{121,128,299,391,392} A comparison of cobalt and ruthenium showed that the dissociative mechanism predominated on cobalt, and an oxygenated intermediate was implicated in the reaction on ruthenium.¹⁷⁴

Carbon dioxide can also be hydrogenated to methane, with a lower overall activation energy than for CO.^{299,388,392-394} Carbon dioxide is adsorbed on nickel dissociatively, to give CO and oxygen atoms,^{392,393} the reverse of reaction 50. If the CO is formed in the more strongly adsorbed state, it could be more easily hydrogenated and would eliminate reactions 3-5 from the mechanism. This change could give the difference in overall activation energy. Another possibility for the methanation of CO₂ is through a formate intermediate.^{254,395} Small amounts of higher hydrocarbons have been observed in CO₂ methanation.^{394,396} This finding points to similarities to the mechanism of the Fischer-Tropsch synthesis.

The mechanism for methanation presented in Table XI differs from previously proposed mechanisms in including both associative and dissociative paths. The difference may be simply that of purpose: the earlier studies were primarily intended to account for observations in particular systems, whereas this mechanism is intended to relate methanation to the Fischer-Tropsch synthesis and to serve as a generalized mechanism that, with appropriate rate constants, can represent methanation under many conditions.

D. Isosynthesis and Kölbel-Engelhardt Synthesis

Isosynthesis uses oxide catalysts to give short-chain, highly branched alkanes suitable for gasoline.^{3,11} Much less work has been devoted to understanding the mechanism of this synthesis than to the Fischer-Tropsch synthesis, on the assumption that the processes are similar. As in the case of the water-gas shift reaction, however, it may not be possible to transpose the discussion of metal catalysts and their elementary reactions to oxide catalysts in the present state of understanding. In a general overview, however, following the argument of section IV.B for the formation of unbranched chains, if the mechanism is substantially similar to that presented here, in isosynthesis the rate of carbon-carbon bond formation must be increased relative to the rate of hydrogenation.

The Kölbel-Engelhardt synthesis uses catalysts, temperatures, and pressures similar to those for the Fischer-Tropsch synthesis, but water is substituted for hydrogen in the feed gas.⁵ Water dissociates on iron,³⁹⁷ cobalt,³⁹⁸ and nickel^{399,400} at temperatures below those of the synthesis to give hydroxyl intermediates and hydrogen atoms, the reverse of reaction 49. Therefore, the mechanism proposed here also describes the Kölbel-Engelhardt synthesis. Differences between the products of the two syntheses most likely result from differences in the concentrations of intermediates due to the greater abundance of water under Kölbel-Engelhardt conditions.

E. Homogeneously Catalyzed Reactions

Although the major focus of this paper is on the heterogeneous Fischer-Tropsch synthesis, some relation to homogeneous systems has been assumed in the use of evidence from metal complexes. The only related

homogeneously catalyzed reaction that is understood in any detail is the hydroformylation reaction;⁴⁰¹ homogeneous catalysis of the water-gas shift reaction is being investigated,²⁴³⁻²⁵³ a number of homogeneous systems producing hydrocarbons and oxygenated products from synthesis gas have been reported, with little detail on mechanisms; and a mechanism has been proposed for homogeneous hydrogenation of CO to alcohols and esters.²⁴ Several points of similarity and difference between the homogeneous and heterogeneous systems will be discussed here; the state of understanding of the mechanisms of both does not yet allow detailed comparisons to be made.

Hydroformylation is the addition of one molecule each of CO and H₂ to an alkene to give an aldehyde. It is one of the few commercial processes in which homogeneous catalysis is used. The catalysts are typically rhodium and cobalt carbonyl complexes. The mechanism most generally accepted⁴⁰¹ involves complexing of the alkene to the metal with partial hydrogenation to give a metal alkyl, which then can participate in a migration to carbonyl to give an acyl complex (reaction 21 or 25), which is then hydrogenated to the aldehyde. Addition of CO to the metal complex after the alkyl migration and addition of hydrogen during the acyl hydrogenation regenerate the catalyst. The details of hydrogenation to aldehyde have not been elucidated.

The similarity to the mechanism proposed here is in the alkyl migration reaction, and perhaps in the following hydrogenation reactions, although the question that must arise is why hydroformylation conditions do not allow the hydrogenation to proceed to the alkyl, which can then participate in further chain-lengthening. An answer that has been suggested is that reactive hydride is more available in the homogeneous systems, and dimerization of the cobalt complexes provides a driving force for early product formation.⁴⁰² Another possibility is that hydridic hydrogen is required for reducing the acyl to the aldehyde, and protonic hydrogen is necessary for further reduction to alkyl. Both types of hydrogen should be available in the heterogeneous system, but only hydride is available in the homogeneous system. If the hydride is the only species responsible for the reduction to alkyl, a higher concentration should promote this reduction. Reactions 28 and 29, however, require protonic hydrogen, whereas attack at carbon to give an aldehyde requires hydride.

Homogeneous catalysis of the water-gas shift reaction can take place in acidic or basic solution, with carbonyl complexes of the group 6-8 metals.²⁴³⁻²⁵³ The mechanism in basic solution involves nucleophilic attack of hydroxyl on the carbonyl carbon to form a carboxyl group, which then decomposes to CO₂ and a metal hydride. Although carboxyl groups can be formed on the heterogeneous synthesis catalysts, their role in the synthesis is not clear. Thus, although this reaction is partial supporting evidence for the participation of carboxyl intermediates in the heterogeneous synthesis (section III.B.2), parallels between these two processes cannot be drawn at this time.

Homogeneous rhodium catalysts produce ethylene glycol and other alcohols from synthesis gas under high pressures.^{17,403} This mechanism appears to involve migration of an hydroxyalkyl ligand to a carbonyl carbon followed by hydrogenation.^{17,24,403-405} Again, the

TABLE XII. State of Experimental Support for Elementary Reactions in Mechanism

excellent	good	fair	poor
1, 2, 3, 4, 11, 49, 50	5, 6, 7, 8, 9, 12, 13, 18, 19, 21, 25, 35, 36, 39, 40	15, 16, 17, 26, 27, 42, 45, 46, 52, 53	28, 29, 30, 54, 55

major difference between this reaction and the heterogeneous Fischer-Tropsch synthesis is in the degree to which hydrogenation of the ligands proceeds.

Although CO can be reduced to methanol⁴⁰⁶ and methane^{230,407} by homogeneous catalysts, the distinctive feature of the Fischer-Tropsch synthesis is carbon-carbon bond formation. Higher hydrocarbons and alcohols have been formed in a few homogeneous systems. Ethane has been formed by reaction of $\text{Cr}(\text{CO})_6$ with $(\eta^5\text{-C}_5\text{H}_5)\text{NbH}_3$,⁴⁰⁸ unbranched alcohols have been formed by reduction of CO complexed to zirconium by aluminum hydrides,⁴⁰⁹ aliphatic hydrocarbons have been formed from synthesis gas with an $\text{Ir}_4(\text{CO})_{12}$ catalyst,⁴¹⁰ and primary alcohols have been formed from synthesis gas with a cobalt carbonyl catalyst.⁴¹¹ Of these four reactions, the last two have the greatest resemblance to the heterogeneous synthesis in the metals used and in being truly catalytic. Few mechanistic details are available for these reactions. The solvent for the $\text{Ir}_4(\text{CO})_{12}$ system was molten $\text{NaCl}\cdot 2\text{AlCl}_3$, which may have provided complexing of the carbonyl oxygens⁴¹⁰ as discussed in sections III.B.2 and III.C. The cobalt reaction appears to be related to hydroformylation and the rhodium-catalyzed ethylene glycol formation.⁴¹¹ These reactions provide mixed evidence for the thesis that metal cluster complexes are better analogues of surfaces than mononuclear complexes,^{15,29} because the cobalt complexes all appear to be mononuclear.⁴¹¹

VI. Summary and Prospects for Future Research

The mechanism presented here summarizes current knowledge about the elementary reactions of the Fischer-Tropsch synthesis and illuminates a number of areas in which more information would be desirable. Experimental support for the elementary reactions proposed ranges from excellent to poor. Although a few reactions have been proposed in the text with no experimental evidence, they have not been included in the summary tables. Table XII summarizes the state of experimental support for the various reactions. This evaluation refers to quantity and type of support according to the hierarchy given in the Introduction, and is not intended to be an evaluation of individual studies.

The mechanism proposed here differs both in approach and in detail from those proposed earlier, although there are many points of similarity. This set of elementary reactions takes into account many different kinds of experimental evidence, with emphasis on evidence from surface chemistry. Writing the mechanism in this way leads to several general observations. One path does not necessarily preclude another; in fact, the network character of this mechanism makes it difficult to separate one path from another, because many paths have common intermediates. Evidence obtained under the simplified conditions of low

pressures and single-crystal metal surfaces may be incorporated into the mechanism insofar as it represents elementary reactions. This kind of evidence is most available for the adsorption of H_2 and CO (section III.A) and for the formation of CO_2 and H_2O (sections III.D.2,3).

In detail, writing the mechanism in this way shows where more information is needed. Many of these areas have been noted in earlier sections of this paper, and investigators in the various fields will recognize still more possibilities for future research. In general, the earlier reactions of adsorption and dissociation are supported by the most detailed evidence from surface science; for the intermediate reactions, less evidence is available from surface science, but additional evidence is available from complex chemistry. The product-forming reactions are the most poorly supported of the entire mechanism; what evidence is available for them is mostly from complex chemistry. The product-forming reactions are also the most difficult to study; both the forward and back reactions on surfaces are complicated by the presence of all the other intermediates of the synthesis. Much of the justification for them has been analogy to better understood reactions in complex and organic chemistry. However, more direct evidence would be highly desirable. The contribution (or lack of contribution) of alkoxy and carboxy intermediates to the synthesis needs to be understood.

In addition to these particular areas in which information is needed, some larger questions are posed by the mechanism and by some of the experimental findings on which it is based.

Throughout the reactions, it appears at times in hydrogen additions that attack by a proton is more favorable and at other times that attack by hydride is more favorable. Can polarization of the hydrogen-metal bond by through-metal interactions between the hydrogen and the intermediate with which it is reacting account for these differences, or is one type of hydrogen contributed by the metal and one by the support?

Some investigators have suggested that oxygen, carbon, and hydrogen may be "stored" by the catalyst, and hydrogen storage compounds have been found to act as methanation catalysts.⁴¹²⁻⁴¹⁶ Although it appears that the hydrogen storage compounds break down into a metal and an oxide during methanation, they show some initial catalytic activity. If the catalyst stores one component of the reaction, how does this affect the kinetics? Or is the apparent storage of a given intermediate a result of the kinetics of the later reactions?

The early transition metals and actinides simulate in solution some of the reactions that take place on the group 8 metals in heterogeneous systems. The reactions of the early transition metals and actinides, however, tend to be stoichiometric rather than catalytic. Given the large differences in electronic configuration and chemistry between the early transition metals and the group 8 metals, why are these reactions so analogous?

Much more information must be collected before a definitive mechanism for the Fischer-Tropsch synthesis can be put forth. However, the framework presented here allows for future changes in ways that previously proposed mechanisms do not. It is a starting place for future work as much as a summary of what has been done.

VII. Acknowledgments

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