sis of ammonia solutions of $NaGe(C_6H_5)_3$, it was found[22] that the amount of nitrogen liberated was almost equivalent to the amount of $(C_6H_5)_3GeH$ produced (the other anode product being $(C_6H_5)_3GeGe(C_6H_5)_3$) if a platinum anode was used, whereas on a mercury anode the amount of nitrogen produced was much less. Perhaps more significant are the experiments of Browne and Holmes[23] who found that upon electrolysis of an ammonia solution of ammonium azide, the ratio of hydrogen to nitrogen produced was high (as high as 1.8) when a platinum anode was used, indicating considerable oxidation of the solvent, whereas with a graphite anode the ratio was about 0.33, indicating virtually quantitative oxidation of the azide ion and no solvent discharge.

Summary.—It can now be seen that the expected analogy between the anodic discharge of oxy anions in water solution to give peroxy anions and the anodic discharge of amides in ammonia to give hydrazine derivatives is established. In the case of the hydrazo compounds, however, further oxidation takes place so readily as to preclude isolation of the hydrazine derivatives, the corresponding azo compounds being found instead.

With improvement of yields, this should be an attractive route to many azo compounds, both known and unknown.

LAFAYETTE, INDIANA

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[CONTRIBUTION FROM THE MELLON INSTITUTE]

Mechanism Studies of the Fischer–Tropsch Synthesis: The Incorporation of Radioactive Ethylene, Propionaldehyde and Propanol

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When a 1:1 = H_2:CO synthesis gas containing 1 to 1.25 mole % radioactive ethylene is passed over an iron catalyst at 224°, about 12% of the hydrocarbons formed at 1 atm. stem from the ethylene. At 100 p.s.i., about 6% of the hydrocarbons are formed from ethylene. When 1.5% radioactive propanol or propionaldehyde is added to the synthesis stream, at one atmosphere almost half of the hydrocarbons come from the additive. In the case of 1-propanol the butanes and butenes formed from the additive are predominantly straight chain. These results, taken as a whole, show that ethylene can act as a chain initiator although not to the same extent as primary alcohols. The available data for such tracer experiments are reexamined in view of this new result, and a mechanism is suggested for iron catalysts which is consistent with the tracer experiments and with the available kinetic data for the Fischer–Tropsch synthesis and for the carbiding of iron catalysts This mechanism successfully predicts the isomer and carbon number distributions found for Fischer–Tropsch products.

Introduction

In spite of the apparent complexity of the Fischer–Tropsch reaction, it is possible to explain many experimental facts on the basis of the relatively simple mechanism postulated by Storch, Golumbic and Anderson,[2a] as modified by Kummer and Emmett.[3] According to this picture, the carbon monoxide and hydrogen react on the surface to form a species similar to adsorbed methanol.[2a] These C_1 surface complexes then react by splitting out water to form a C_2 complex similar to adsorbed ethanol.[3] The production of higher molecular weight products is presumed to occur by the reaction of C_n with C_1 complexes to form water and C_{n+1} complexes. The synthesis products may be formed by direct desorption of these complexes or by dehydration, dehydrogenation, hydrogenation, etc., followed by desorption. It has been shown[4] that this mechanism leads to a two parameter equation which quite adequately describes the isomer and carbon number distributions of the hydrocarbon products obtained from synthesis over iron and cobalt catalysts.

Recent tracer experiments[3,5–7] have furnished support for this picture and, in addition, have made apparent several additional features of the mechanism. These experiments have definitely shown that primary alcohols tend to act as chain initiators for the synthesis of higher molecular weight hydrocarbons. With adsorbed methanol, the C_1 complex formed acts (more often) as a chain initiator, but also as a chain build-in unit; a similar result was obtained with gaseous formaldehyde, suggesting that the C_1 chain initiator may not be identical with the C_1 build-in unit and that several distinct C_1 complexes exist. Also in the case of the C_2 complex, some species (possibly ethylene) other than adsorbed ethanol acts as a chain initiator.[7]

In an effort to clarify further the reaction mechanism over iron catalysts, a series of tracer experiments has been carried out with radioactive ethylene to determine whether or not it can function as a C_2 chain initiator. In addition, an earlier tracer experiment was repeated to check a result of Kummer and Emmett,[3] that indicated (in conflict with the simple theory[2,3]) that when labeled 1-propanol was added to the synthesis stream, some

[1] John Hopkins University, Baltimore, Maryland.

[2] H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer–Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951; (a) p. 591 ff.; (b) p. 538 ff.

[3] J. T. Kummer and P. H. Emmett, THIS JOURNAL, **75**, 5177 (1953).

[4] R. B. Anderson, R. A. Friedel and H. H Storch, *J. Chem. Phys.*, **19**, 313 (1951).

[5] J. T. Kummer, H. H. Podgurski, W. B. Spencer and P. H. Emmett, THIS JOURNAL, **73**, 564 (1951).

[6] W. K. Hall, R. J. Kokes and P. H. Emmett, *ibid.*, **79**, 2983 (1957).

[7] R. J. Kokes, W. K. Hall and P. H. Emmett, *ibid.*, **79**, 2989 (1957).

TABLE I

SYNTHESIS VARIABLES FOR TRACER EXPERIMENTS

Catalyst No.	614	614	D3001	614	614
Pressure, atm.	1	1	7.5	1	1
SVH[a]	288	288	100	200	240
Temperature, °C.	224	236	249	241	239
Contraction, %	34	24	63	19	21
Duration, hr.	27	23	22	23	24
Vol. % additive	1.25	1.25[b]	1.0	1.5	1.5
Additive	C_2H_4	C_2H_4	C_2H_4	$CH_3CH_2\overset{*}{C}H_2OH$	$CH_3\overset{*}{C}H_2CH_2O$
Activity (c./min./cc.)[c]	5910	5910	9200	3780	3000
Total liq. products, g.	7.2	10.0	....	12.0	11.8
CO_2 produced, g.	34.3	26.1	....	16.8	13.3
Gaseous hydrocarbons produced, cc. S.T.P.	7370	6860	....	2900	2100

[a] SVH = volumes of gas/volume of catalyst per hr. The synthesis gas was 1:1 = H_2:CO. [b] In this run the synthesis gas contained 1.8% water. [c] Activity of the additive in counts per minute per cc.

radioactivity appeared in the iC$_4$ fraction. Also, a tracer experiment with labeled propionaldehyde was made to see whether aldehydes function differently from alcohols when added to the Fischer–Tropsch synthesis. Finally, a semi-quantitative theory of the reaction kinetics has been developed, which accounts for many of the known experimental facts concerning the synthesis over iron catalysts.

Experimental

Most of the techniques as well as the bench scale reactors used in these studies have been described in detail elsewhere.[3,5-7]

In the runs with radioactive propionaldehyde and propanol, the synthesis gas was passed through a saturator filled with the additive. The saturator was thermostated at appropriate temperatures to give concentrations of 1.5 volume % in the gas stream. The radioactive ethylene was first mixed with CO and introduced into a tank under pressure. This gas then was blended with H_2 to obtain a 1:1 = H_2:CO synthesis gas containing the indicated amount of ethylene.

The gaseous products were fractionated on a Podbielniak column. The various cuts then were analyzed for radioactivity before and after the absorption of the olefins in H_2SO_4–$HgSO_4$ solution. With the aid of mass spectrographic analyses of these cuts, it was possible to calculate the molar radioactivity (hereafter simply called activity) of the individual gaseous olefins and paraffins. A more detailed radioactive analysis of the C_4 cut was obtained using the chabazite procedure described by Kummer and Emmett.[3] The hydrocarbon liquid was cut into fractions, burned to CO_2 in an excess of O_2 and the CO_2 counted. In the process the carbon number was determined; hence, the activity in counts per minute per cc. (NTP) of hydrocarbons (c./min./cc.) could be computed.

Two catalysts were used in these studies. Catalyst No. 614 was a singly promoted iron catalyst containing 0.64% Al_2O_3 and 2.00% ZrO_2 in addition to iron oxide (Fe_3O_4). Catalyst D3001[8] was a doubly promoted iron catalyst containing 0.6% SiO_2, 0.6% Cr_2O_3, 4.6% MgO and 0.6% K_2O.

Results

(1) **Ethylene Experiments.**—The data listed in Tables I and II for the experiments where radioactive ethylene was added to the synthesis gas clearly show that ethylene incorporates in the Fischer–Tropsch synthesis to form higher hydrocarbons over iron catalysts and that the build-in takes place stepwise, *i.e.*, the ethylene is not merely polymerized to form products having an even number of carbon atoms but forms hydrocarbons by the addition of one carbon atom at a time. The average incorporation in these experiments (6 to 15%) was lower than that found with ethanol (~30%) but was by no means small. The activity of the methane (Table II) was low. This clearly shows that hydrocracking of hydrocarbon polymers on the surface, even when produced from ethylene, is not an important reaction in the Fischer–Tropsch synthesis. This is of particular interest in view of Gibson's finding[9] that most of the C_3 fraction formed, when ethylene and hydrogen reacted over a *cobalt* catalyst in the presence of 5% concentrations of radioactive CO, was formed from the ethylene alone and involved the breaking of the ethylene molecule into single carbon units. It is also of considerable interest to note that in the atmospheric experiment without water essentially all of the radioactive ethylene reacted as it passed through the catalyst bed. This indicates that over a singly promoted iron catalyst (which has a higher hydrogenating activity than a doubly promoted catalyst)[10] the ethylene either builds-in to form higher hydrocarbons, hydrates to oxygenated organic compounds or hydrogenates to ethane. The principal reaction judging from the product distribution was the hydrogenation to ethane. It was apparent, therefore, that in order to obtain a more realistic estimate of the intrinsic chain building potential of ethylene, tracer runs should be made under conditions such that less hydrogenation took place. To this end 1.8% water vapor was added in an experiment in which the conditions were otherwise kept as nearly identical as possible. Also, another experiment was carried out at 100 p.s.i. over a doubly promoted catalyst. In these experiments, the activity of the ethylene in the product was found to be of the same order as the ethane, rather than zero. At 100 p.s.i. the average incorporation was found to be about 6% or about half that obtained with the singly promoted catalyst at one atmosphere. For a similar change in pressure and catalyst, in ethanol tracer experiments[7] the incorporation decreased to about one quarter of its value at one atmosphere. Also, in contrast to the one atmosphere runs, the activity fell off strongly with increasing carbon number, reminiscent of the behavior observed earlier with labeled ethanol.[7]

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(8) W. K. Hall, W. H. Tarn and R. B. Anderson, THIS JOURNAL, **72**, 5436 (1950); **56**, 688 (1952).

(9) E. J. Gibson, *Chem. & Ind.* (*London*), **21**, 649 (1957).

(10) P. H. Emmett and J. Gray, THIS JOURNAL, **66**, 1338 (1944).

TABLE II

SUMMARY OF PRODUCT RADIOACTIVITY

Radioactive additive activity (c./min./cc.)[b]	$CH_2{=}CH_2$ 5910		$CH_2{=}CH_2$[a] 5910		$CH_2{=}CH_2$[c] 9200		$CH_3CH_2C^{14}H_2OH$ 3780		$CH_3C^{14}H_2CHO$ 3000	
Product	Av. C no.	C./min./cc.[b]	Av. C no.	C./min./cc.[b]	Av. C no.	C./min./cc.[b]	Av. C no.	C./min./cc.[b]	Av. C no.	C./min./cc.[b]
CO		5		5		..		..		0
CO_2		17		17		..		..		0
CH_4		43		54		15		35		0
C_1		43		54		15		35		0
C_2H_4		0		1985		4700		48		81
C_2H_6		4470		5180		5100		28		138
C_2		4120		4740		4960		41		100
C_3H_6		1024		1145		700		1563		862
C_3H_8		692		1035		838		1720		1530
C_3		875		1115		731		1598		987
n-C_4H_8		692		1040		635		1691		1287
i-C_4H_8								606		
n-C_4H_{10}		1045		1180		713		2120		1150
i-C_4H_{10}								745		
C_4		814		1083		664		1983		1260
C_5H_{10}		554		890		558		1890		1107
C_5H_{12}		1410		975		610		986		990
C_5		810		1105		569		1795		1025
Liquids	5.12	670	4.61	760	6.94	385	5.49	1710	5.53	1085
	5.98	792	5.05	765	..		5.44	1805	5.12	1050
	6.36	758	5.40	815[d]	..		5.95	1965	6.05	1165
	6.46	668			7.52	418	5.63	1845	5.23	950
	7.16	810			7.94	385	6.52	2070	5.65	1020
	7.63	668							6.95	1140
									7.02	1137
									7.99	1130

[a] In this run the synthesis gas contained 1.8% H_2O. [b] Counts per minute per cc. of gaseous hydrocarbon S.T.P. [c] Run made at 7.5 atm. The mass spectrographic analysis was unsatisfactory; the values for olefins and paraffins were computed on the basis of the amount of olefin adsorbed in an olefin scrubber. [d] This last sample exhausted the supply of liquid and indicated a lower average molecular weight for the product of this run than for the one without added H_2O.

(2) **1-Propanol Experiment.**—Kummer and Emmett[3] made two separate experiments in which the synthesis gas contained about 1.5% 1-propanol. They found that the radioactivity of the isobutylene was 20 and 32% of the activity of the 1-butene; they also found that in one of these runs, although the activity of the n-butane was comparable to that of the 1-butene, the activity of the isobutane was negligible. It was suggested[3] that skeletal isomerization of the butenes might have occurred during the separation and analysis of the C_4 hydrocarbons and that the added 1-propanol yielded only straight chain C_4 hydrocarbons in the actual hydrocarbon synthesis. In the course of the present work, a series of experiments was made which showed that no skeletal isomerization occurred in the separation procedure outlined by Kummer and Emmett[3] or in the hydrogenation of the C_4 olefins to their corresponding saturated hydrocarbons over iron catalysts at or below 100°. In view of these results the activities of the various components of the C_4 cut were redetermined.

The data for the propanol experiment given in Tables I and II are quite similar to those previously reported.[3] The incorporation in this run was about 50% compared to 40 and 60% in the earlier experiments. Cracking of the propanol also took place to about the same extent. Detailed analysis of the C_4 cut, however, showed that in contradistinction to the earlier work, the activities of *both* the isobutylene and isobutane were about 34% of the activities of the corresponding straight chain hydrocarbons.

(3) **Propionaldehyde Experiment.**—The results obtained with propionaldehyde show that its behavior in the synthesis is quite similar to that with propanol but that cracking occurs to a slightly higher extent. Since the middle carbon atom of the propionaldehyde was labeled, the formation of radioactive ethane rather than radioactive methane results. (The activities of the methane and ethane formed in the 1-propanol experiment were approximately equal since the carbinol carbon was labeled.) The incorporation in this run was about 37%. In all respects, therefore, the data obtained with propionaldehyde are explicable with the assumption that the propionaldehyde adsorbs and hydrogenates to form the same complex as 1-propanol. It is unfortunate that a detailed activity analysis of the C_4 cut is not available, as this would obviously yield added information on this point.

Discussion

The mechanisms proposed by Storch, Golumbic and Anderson[2a] and by Kummer and Emmett[3] involved a type of adsorbed alcoholic complex. Ethylene could form such a complex by known reactions if it (a) hydrated to form ethanol or (b) underwent hydroformylation to 1-propanol. There is evidence that neither of these reactions occurred. If reaction a occurred in the ethylene ex-

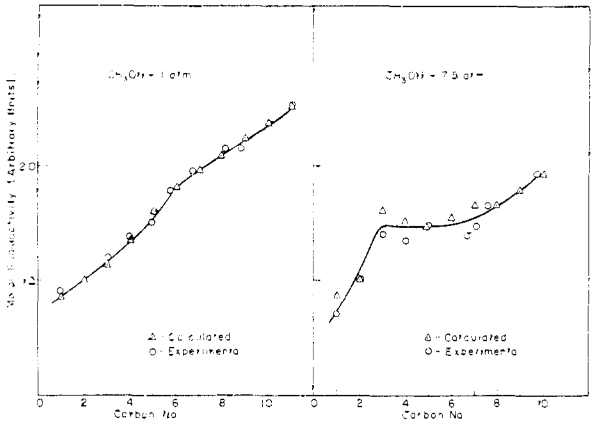


Fig. 1.—Comparison of calculated and experimental data for methanol tracer runs.

periments, it should also have occurred with the radioactive ethylene formed in the ethanol experiments.[5] Thus, with methylene labeled ethanol

$$CH_3C^{14}H_2OH \rightleftarrows CH_2{=}C^{14}H_2 + H_2O \rightleftarrows C^{14}H_3{-}CH_2OH \quad (1)$$

would be expected so that the position of the radioactive carbon relative to the hydroxyl group would have changed in a portion of the alcohol during synthesis. Examination of the unreacted radioactive ethanol, recovered from the products, showed that this had not occurred. If (b) occurred, the radioactivity distribution in the C_4 products should resemble that observed in 1-propanol tracer experiments, *i.e.*, the activity of the branched C_4 hydrocarbons should be about 33% the activity of the straight chained hydrocarbons. Actually, the activity of the branched C_4 hydrocarbons was found to be 72% of the activity of the straight chain C_4 hydrocarbons. It appears, therefore, that the complex formed from adsorbed ethylene need not resemble the alcohol-type complexes suggested previously.[2a,3]

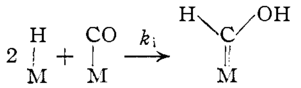
If ethylene does in fact form a different complex from that formed from ethanol, it becomes necessary to re-examine the alcohol experiments already reported.[3,5–7] Let it be assumed that chain building complexes can be formed from adsorbed alcohols and that a different type of complex can also be formed from ethylene, but, for the moment, that other olefins do not form such complexes. In this situation, whenever a radioactive C_1 or C_2 alcohol is added to the synthesis, the resulting distribution of radioactivity in the products should be a weighted summation of those stemming from the alcohol and those from ethylene. Thus, for ethanol, by taking the value of the activity observed for the C_2 fraction as the contribution per mole to all hydrocarbons of higher carbon number and adding on the experimentally observed contribution from the ethylene, by proper weighting the qualitative features of the experimentally determined curves[7] for both atmospheric and pressure runs can be reproduced. Similarly, methanol reacts to give radioactive C_2 complexes like those formed in ethanol tracer experiments. All C_{2+} hydrocarbons are formed *via* these C_2 complexes by addition of one or more radioactive chain building units. In this simple case the activity *vs.* carbon number curve should be calculable from the radioactivity of the chain-building complex and the actual data from an ethanol tracer experiment. Specifically, these activities should be those found in an ethanol tracer experiment plus $(n - 2)\Delta$ where n is the carbon number and Δ is the activity of the chain building complex. In Fig. 1, the calculated points are compared to the points for the experimental data obtained at atmospheric pressure and at 100 p.s.i. In each case, the "equivalent activity" of the ethanol was fixed by the activity of the C_2 hydrocarbons from the corresponding methanol tracer experiment. Likewise, the value of Δ was determined from the slope of the plot of the data at high carbon numbers. The agreement is quite good. It implies, of course, that the C_2 complexes formed from methanol are the same as those formed from ethanol but does nothing to define its nature.

If it is now supposed that propylene is also capable of build-in, similar to ethylene, when present in large concentrations, an explanation is available for the appearance of radioactivity in the iC_4 fraction when 1-propanol is added to the synthesis.

From the above it appears that the principal features of the Fischer–Tropsch experiments are explicable in terms of the mechanism suggested by Storch, Golumbic and Anderson[2a] as modified by Kummer and Emmett.[3] For a more detailed explanation of the results, however, it must be assumed that in addition to complexes formed on the surface by adsorption of alcohol, another formed from ethylene is also capable of "building-in," to form high molecular weight hydrocarbons.[11]

In spite of the shortcomings of the simple picture developed through earlier work,[2–7] the assumption that adsorbed alcohols are intermediates in the Fischer–Tropsch synthesis does explain many of the features of the tracer experiments with iron catalysts. It is therefore worthwhile to consider in some detail the consequences of the approach as applied to the experimental data available for the normal synthesis. For the sake of specificity, detailed equations for the formation of the complexes, for the chain build-in steps and for complex destruction will be written, but in many cases the same conclusions would follow even when reactions other than those described below take place.

The formation of the single carbon complex and the subsequent build-in steps can be represented by the equations



$$2\,\underset{M}{\overset{H}{|}} + \underset{M}{\overset{CO}{|}} \xrightarrow{k_1} \underset{M}{\overset{H\diagdown\ \diagup OH}{\underset{\|}{C}}} \qquad (2a)$$

For the sake of brevity, the adsorbed n carbon primary alcohol complex may be represented by X_n and the corresponding secondary alcohol complex by Z_n. Obviously X_n complexes can react to form either X_{n+1} or Z_{n+1} by (2b) or (2c), but Z_n can only yield an X_{n+1} complex by (2d). Furthermore, for $n \leqslant 3$ only X_n complexes exist whereas for $n \geqslant 3$

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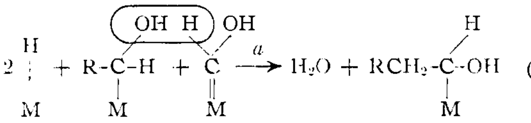
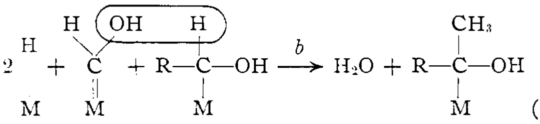
[11] See also the Discussion of ref. 7 concerning the way in which ethylene build-in can explain the propane pyrolysis experiments made in connection with ethylene tracer runs.



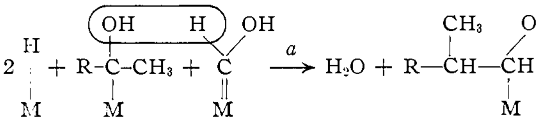
$$2\,\underset{M}{H} + \underset{M}{R\text{-}C\text{-}H} + \underset{M}{\overset{OH}{C}} \xrightarrow{a} H_2O + \underset{M}{RCH_2\text{-}\overset{H}{C}\text{-}OH}$$

(X$_n$) (2b)



$$2\,\underset{M}{H} + \underset{M}{\overset{H}{C}} + \underset{M}{R\text{—}\overset{H}{C}\text{—}OH} \xrightarrow{b} H_2O + \underset{M}{R\text{—}\overset{CH_3}{C}\text{—}OH}$$

(Z$_n$) (2c)



$$2\,\underset{M}{H} + \underset{M}{R\text{-}\overset{OH}{C}\text{-}CH_3} + \underset{M}{\overset{H}{C}} \xrightarrow{a} H_2O + R\text{—}\overset{CH_3}{CH}\text{—}\underset{M}{\overset{OH}{CH}}$$

(X$_n$) (2d)

both X_n and Z_n complexes exist. The scheme allows for methyl branching only.

Destruction of the complex may take place by a variety of reactions. Some of the more evident are

$$X_n \text{ or } Z_n + H_2 \xrightarrow{k_1} \text{alcohols} \quad (3a)$$

$$X_n \text{ or } Z_n + H_2 \xrightarrow{k_2} \text{paraffins} + H_2O \quad (3b)$$

$$X_n \text{ or } Z_n + CO \xrightarrow{k_3} CO_2 + \text{olefins} \quad (3c)$$

$$X_n \text{ or } Z_n + H_2 \xrightarrow{k_4} \text{olefins} + H_2O \quad (3d)$$

$$X_n \text{ or } Z_n \xrightarrow{B} \text{decomposition to other products} \quad (3e)$$

The amounts of H_2 required for (a), (b) and (d) will depend on the nature of the binding of the alcohol to the metal. It will be seen that it is not critical whether or not the bonding is actually dissociative as indicated in (2); therefore the equations for the destruction of the complex may be written as if the bonding were non-dissociative, *i.e.*

$$-\left[\frac{d(X_n \text{ or } Z_n)}{dt}\right] = [k_1(H_2) + k_2(H_2) + k_3(CO) + k_4(H_2) + B](X_n \text{ or } Z_n) \equiv S(X_n \text{ or } Z_n) \quad (4)$$

where S is a function of the synthesis variables. The X_n complex may be formed by (2b) and (2d); it may be removed by (2b) and (2c) as well as by (4). Hence, in the steady state

$$\frac{dX_n}{dt} = 0 = aX_1(X_{n-1} + Z_{n-1}) - (a + b)X_nX_1 - SX_n \quad (5)$$

The Z_n complex can only form by (2c) and on further condensation must form X_{n+1} by (2d); it may also be destroyed by (4). Hence

$$\frac{dZ_n}{dt} = 0 = bX_1(X_{n-1}) - aZ_nX_1 - SZ_n \quad (6)$$

This yields for the X_n complex

$$X_n = \frac{aX_1(X_{n-1} + Z_{n-1})}{(a + b)X_1 + S} = f(X_{n-1} + Z_{n-1}) \quad (7)$$

where f is a function of the synthesis variables. Similarly for the Z_n complex

$$Z_n = \frac{bX_1(X_{n-1})}{aX_1 + S} = gX_{n-1} \quad (8)$$

where g is a function of the synthesis variables. On this basis the rate of formation of products will be

$$\frac{d(C_n)}{dt} = k_s(X_n + Z_n) = k_sP_n \quad (9)$$

where C_n is the concentration of n carbon products. In the simplest approximation, $k_s \equiv S$. The two parameters are carried through separately, however, to allow for (a) the possibility that X_n or Z_n may decompose to other than C_n products, *i.e.*, by (3e) and (b) a change in units between (4) and (9). Since k_s is assumed to be the same for all complexes, the fractional yield of C_n products will be proportional to P_n. It follows from (7) and (8) that

$$P_n = fP_{n-1} + gfP_{n-2} \quad (10)$$

Thus, from (7), (8) and (10) it is possible to calculate the isomer and carbon number distributions in the products by assuming values for the parameters f and g; the distributions are derived following the method of Anderson, Friedel and Storch.[4] In column 4 of Table III, the isomer distribution calculated on the basis of the present scheme is compared with the experimental values for iron catalysts found by Bruner.[12] The agreement is quite good. For the sake of comparison, the values calculated using one of the schemes suggested by Anderson, *et al.*,[4] [*i.e.*, scheme a] are listed.

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED ISOMER DISTRIBUTION

Hydrocarbon	Exptl.[a]	Calcd.[b]	Calcd.[c]	Calcd.[d]
n-Butane	89.4	90.3	89.7	91.7
Isobutane	10.6	9.7	10.3	8.3
n-Pentane	81.2	81.6	81.3	83.2
Isopentane	18.8	18.5	18.7	16.8
n-Hexane	78.8	73.5	73.5	75.0
2-Methylpentane	11.2	16.7	16.9	15.5
3-Methylpentane	9.5	8.8	8.5	8.7
2,3-Dimethylbutane	0.4	0.9	0.9	0.8
n-Heptane	66.0	66.4	66.0	65.7
2-Methylhexane	13.1	15.1	15.4	13.8
3-Methylhexane	19.1	15.9	15.4	18.0
2,3-Dimethylpentane	1.6	1.8	1.7	1.8
2,4-Dimethylpentane	0.3	0.8	0.8	0.7
n-Octane	61.0	59.8	60.5	57.0
All methylheptanes	36.4	35.1	34.7	37.8
All other isomers	2.6	5.0	4.8	5.4

[a] Ref. 12. [b] Calculated using equations 7, 8 and 10, taking $g/f = 0.12$. [c] Scheme A of Anderson, *et al.*, ref. 4. [d] Multiple build-in scheme: $f/g = 7$, $h = 5$; see Appendix II.

As already indicated, both chain-building theories make quite similar predictions. This is to be expected as they both use the same steady-state treatment in their derivation. They differ in an important way only in the following respect. Anderson's scheme does not distinguish between X_n and Z_n type complexes; the present scheme has, therefore, nearly twice as many *distinguishable* complexes. The results of the calculations are not, however, identical; *e.g.*, whereas the present scheme predicts slightly different concentrations for 2- and 3-Me-hexane, Anderson's predicts the same.

The ability of the present scheme to predict the carbon number distribution has been tested graphically. As shown in Appendix I, (10) can be written in the form

$$\frac{P_n}{F_n(g/f)} = f^{n-1}X_1 \quad (11)$$

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[12] F. Bruner, *Ind. Eng. Chem.*, **41**, 2511 (1949).

where $F_n(g/f)$ is a polynomial in g/f which varies with carbon number. Using I-17 from Appendix I to evaluate $F_n(g/f)$, (11) was tested using Weitkamp's experimental values of P_n.[13] It was found that the fit of the data obtained was *at least* as good as the results of similar calculations based on the development of Anderson.[4]

It is convenient to restrict the discussion in the present paper to stepwise chain growth involving the addition of one carbon atom at a time to the growing chain, *viz.*, reaction of an n carbon complex, X_n or Z_n with an X_1 complex—as indicated by equations 2. If, however, it is assumed that a complex containing any number of carbon atoms, X_i, can react with any other, X_j, equations similar to (7), (8), (10) and (11) can be obtained (with certain simplifying assumptions) and, hence, carbon number and isomer distributions can be obtained. The results of such calculations are compared to those for the single carbon build-in schemes in Table III, the necessary equations being developed in Appendix II. There are two principal results from this work. These are: (a) "multiple build-in" can and possibly does occur in the Fischer–Tropsch synthesis; (b) however, due to the relative population densities of the various complexes and to the magnitudes of the parameters required to fit the isomer and carbon number distribution data, multiple build-in cannot be distinguished from single carbon stepwise build-in at carbon numbers below C_{12} to C_{16} in the absence of detailed tracer data at higher carbon numbers. The latter is a direct result of the fact that it is only at such high carbon numbers that the number of possible reaction paths becomes sufficiently large to overcome the lower rate constants involved in these condensations (see Appendix II, eq. 13). Thus, the use of the mathematically less complicated stepwise chain growth mechanism in consideration of the reaction kinetics is justified.

Recent work at the U. S. Bureau of Mines[14a] on the kinetics of the Fischer–Tropsch synthesis has shown that the differential rate of consumption of $CO + H_2$ over a wide range of synthesis conditions can be represented by

$$r = \frac{KP_{H_2}}{1 + a_1(P_{H_2O}/P_{CO})} \qquad (12)$$

where K and a_1 are constants. Their data apparently fit this expression for an individual experiment within experimental error, but the constants obtained varied slightly in a systematic manner when the H_2:CO ratio was changed. A suggested interpretation[14a] of this equation was postulated in terms of competitive reactions involving steam oxidation of the iron surface and reduction of the oxide by CO. It is also possible to derive (12) on the basis of the scheme described by (2) to (11). In order to do this, three assumptions about the nature of the synthesis are made. These are: (1) most of the water produced in synthesis [*viz.*, by reactions 2 and 3] reacts with complex to form CO_2; consequently the net yield of water in any differential element of the bed length is small compared to the yield of the other synthesis products. (2) The usage ratio, $\mu = CO/(H_2 + CO)$ consumed, is constant. (3) There is single point attachment of the complexes to the sites on the catalyst and the coverage of the surface with complexes is nearly complete under all conditions of synthesis. The first assumption, while definitely an approximation, is justified by the fact that for moderate conversions the integral yield of CO_2 is much greater than the yield of H_2O presumably because the bulk of the water is reduced (22b) to H_2 by the C_1 complex. The second has also been found to be approximately true for a given experiment,[14b] *viz.*, under given synthesis conditions this ratio varied between 0.40 and 0.47 for conversion of $H_2 + CO$ between 20 and 87%. The third is a postulate, made for convenience, without experimental basis. (It is implicit in the mechanism, as visualized here, that the area/complex is the same for all complexes. This is all that is required.) In the course of the development of (12), further approximations will be made on the basis of the parameters evaluated from the isomer distribution data; it appears that these are relatively independent of the conditions of the synthesis.[14c]

According to (2), in the formation of an n carbon atom complex, n CO molecules are utilized to form the species and $(n - 1)H_2O$ molecules are produced, *i.e.*, one for each C–C bond formed. According to the first assumption, almost all of this water would react with CO (or C_1 complex) to form CO_2. Thus the rate of utilization of CO in the formation of an n carbon product is

$$\left[\frac{-\mathrm{d(CO)}}{\mathrm{d}t}\right]_n = (2n - 1)\frac{\mathrm{d}(C_n)}{\mathrm{d}t} \qquad (13)$$

where $\mathrm{d}(C_n)/\mathrm{d}t$ is the rate of production of n carbon product. Using (9), (13) becomes

$$\left[\frac{\mathrm{d(CO)}}{\mathrm{d}t}\right]_n = (2n - 1)k_sP_n \qquad (14)$$

The over-all rate of usage of CO can be obtained by summation over all carbon numbers, *i.e.*

$$\left[\frac{\mathrm{d(CO)}}{\mathrm{d}t}\right]_{\mathrm{Total}} = \sum_{n=1}^{\infty} k_s(2n - 1)P_n \qquad (15)$$

If the usage ratio is independent of the synthesis variables over the range where (12) is operative, the differential reaction rate r is

$$r = \frac{\mathrm{d}(CO + H_2)}{\mathrm{d}t} = \frac{1}{\mu}\left[\frac{\mathrm{d(CO)}}{\mathrm{d}t}\right]_{\mathrm{Total}} = \frac{k_s}{\mu}\sum_{n=1}^{\infty}(2n - 1)P_n \qquad (16)$$

where μ is the differential usage ratio.[14b] In Appendix I the various required summations are evaluated. Using I-10 from Appendix I, (16) can be rewritten as

$$r = \frac{k_s}{\mu}X_1\left[\frac{1 + f + 3gf}{(1 - f - gf)^2}\right] \qquad (17)$$

Furthermore, from I-8 for one point attachment of the complexes, the total number of adsorption sites utilized by the complexes N_s will be

$$N_s = \sum_{n=1}^{\infty} P_n = \frac{X_1}{1 - f - gf} \qquad (18)$$

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(13) A. W. Weitkamp, H. S. Seelig, N. J. Bowman and W. E. Cody, *Ind. Eng. Chem.*, **45**, 343 (1953); A. W. Weitkamp and C. G. Frye, *ibid.*, **45**, 363 (1953).

(14) R. B Anderson, "Catalysis," Vol. IV, Edited by P. H. Emmett, Reinhold Publ. Corp., New York, N. Y., 1956; (a) p. 297; (b) p. 293; (c) p. 347 ff.

Since it has been postulated that the complexes utilize nearly all the sites under any synthesis conditions, it may be supposed that N_s is roughly constant. Substituting (18) into (17) yields

$$r = \frac{k_s N_s}{\mu} \frac{1 + f + 3gf}{1 - f - gf} \tag{19}$$

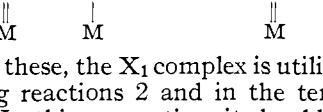
The values of g and f are defined in (7) and (8). Using these definitions, after simplification, (19) becomes

$$r = \frac{2aN_s k_s}{\mu S} X_1 \left\{ 1 + \frac{bX_1}{X_1(a + b) + S} + \frac{S}{2aX_1} \right\} \tag{20}$$

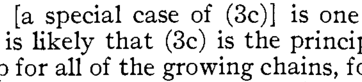
This equation, as it stands, is rather complicated especially when the terms that are included in S [see (4)] are considered. On the basis of the values of the parameters f and g obtained from the isomer and carbon number distribution data, it appears that the second term of the expansion may be neglected with small error (*i.e.*, $\simeq 5\%$). The last term is reasonably large judged on this basis. If this term is dropped, an underestimate of from 20 to 30% may occur, but it still can be said with some justification that an approximate form for (20) will be

$$r \approx \frac{2aN_s k_s}{\mu S} X_1 = k' X_1 \tag{21}$$

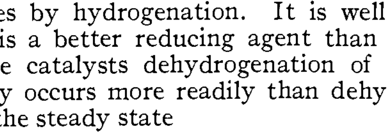
Since in practice the constant k' is chosen as the best value to fit the data, a partial compensation for the errors incurred in going from (20) to (21) will be achieved. It may be assumed that the principal equations governing the formation and destruction of X_1 complex are



$$\underset{\text{M}}{\overset{|}{\text{CO}}} + 2\,\underset{\text{M}}{\overset{|}{\text{H}}} \xrightarrow{k_0} \text{(H)(OH)}\underset{\text{M}}{\overset{\|}{\text{C}}} \tag{22a}$$



$$\text{(H)(OH)}\underset{\text{M}}{\overset{\|}{\text{C}}} + H_2O \xrightarrow{\alpha} CO_2 + 4\,\underset{\text{M}}{\overset{|}{\text{H}}} \tag{22b}$$



$$\text{(H)(OH)}\underset{\text{M}}{\overset{\|}{\text{C}}} + \underset{\text{M}}{\overset{|}{\text{CO}}} \xrightarrow{\beta} CO_2 + \underset{\text{M}}{\overset{\|}{\text{CH}_2}} \tag{22c}$$

In addition to these, the X_1 complex is utilized in the chain building reactions 2 and in the termination reactions 3. In this connection, it should be noted that (22c) [a special case of (3c)] is one of these; actually it is likely that (3c) is the principal termination step for all of the growing chains, followed in some cases by hydrogenation. It is well known that CO is a better reducing agent than H_2 and over these catalysts dehydrogenation of alcohols apparently occurs more readily than dehydration. Thus, in the steady state

$$0 = dX_1/dt = k_0(CO)(H)^2 - \alpha X_1(H_2O) - \beta X_1(CO) - aX_1 \sum_{n=1}^{\infty} P_n - bX_1 \sum_{n=1}^{\infty} X_n - k_1X_1(H_2) - k_2X_1(H_2) - k_4X_1 - BX_1 \tag{23}$$

A similar equation can be written for H_2O. Water is produced by the chain-building steps 2 and also by several of the termination steps 3; it is utilized only in the destruction of the X_1 complex, *i.e.*, (22b) with which we replace the water gas shift reaction. Hence

$$0 \mp dH_2O/dt = aX_1 \sum_{n=1}^{\infty} P_n + bX_1 \sum_{n=1}^{\infty} X_n + k_2X_1(H_2) + k_4(H_2)X_1 - \alpha X_1(H_2O) \tag{24}$$

Combining (23) and (24)

$$X_1 = \frac{k_0(CO)(H)^2 - d(H_2O)/dt}{2\alpha(H_2O) + \beta(CO) + k_1(H_2) + B} \tag{25}$$

is obtained. In view of the fact that under ordinary synthesis conditions essentially all of the oxygen in the products appears as either CO_2 or H_2O, the last two terms of the denominator of (25) can certainly be neglected. Similarly, following the assumption made earlier that net yield of H_2O in any differential element of the bed length is small, the last term in the numerator can also be dropped.

The molecules adsorbed on the surface are principally complexes. Hence, the fraction of the empty surface available for CO, H_2 and H_2O is small and roughly constant. This being the case, the surface concentrations of these species will be proportional to their partial pressures. In this case

$$X_1 = \frac{k_5 P_{H_2}}{1 + a_1(P_{H_2O}/P_{CO})} \tag{26}$$

or using (21)

$$r = \frac{KP_{H_2}}{1 + a_1(P_{H_2O}/P_{CO})} \tag{27}$$

where K and a_1 involve the rate constants and the adsorption equilibrium constants

$$K = 2aN_s k_s k_5/\mu S$$

Equation 27 is identical to that found by Anderson. The two worst approximations in its derivation are probably the assumption that almost all of the H_2O produced reacts with the X_1 complex to form CO_2 and the neglect of the third term of (20). The former tends to make the expression for the rate too high while the latter tends to make it low. Thus, due to the partial compensation of these two sources of error, the expression for the rate may be reasonably reliable. Since K involves the usage ratio and N_s (the number of sites covered with complexes), it would be expected that some systematic variations in the "constants" would occur as the synthesis gas composition and/or total synthesis pressure is changed. This is also observed.

The reactions described by (22) merit some further discussion. According to this picture the C_1 complex is formed directly from CO and H_2; it is assumed that this is the only complex formed. There is reason to believe that H_2O reacts only with the C_1 complex. In the synthesis over the singly promoted catalysts used for the tracer experiments, the yields of alcohols and acids were quite low. Thus, if water had reacted with the alcohol type complexes containing more than one carbon atom, a reaction analogous to (22b) would be expected to produce hydrocarbons containing one less carbon atom. This would lead to the production, in tracer experiments with radioactive ethanol and propanol, of some radioactive methane and ethane, respectively, or else some radioactive CO_2, depending upon where the alcohol was labeled. Since this did not occur, H_2O apparently does not react with these complexes. On the other hand, in methanol tracer experiments highly radioactive CO_2 was produced.[3,6] Under similar conditions, more methanol reacted to form CO_2 than CO, indicating that some of the methanol forming the C_1 complex was converted by (22b). If (22b) were the only source of the CO_2, however, the radioactivity of the CO_2 should be the same as that for the methane (*i.e.*, the same as the activity of the C_1 complex). Since the activity of the CO_2 is about half that of the methane,[6] reactions producing exclusively non-radioactive CO_2 also must be taking place. Reactions of the type (22c) and (4c) allow for this.

The results of Koelbel and Engelhardt[14] support the idea that some CO_2 is formed by a reaction not involving water. Under synthesis conditions at 200°, where the shift reaction has been shown to be quite sluggish,[6,14] even with water removal in 8 steps along the bed by $CaCl_2$, these workers found a yield of CO_2 of 18%. Since, under these definitely less favorable conditions for the water gas shift reaction, or (22b), to operate, CO_2 was still produced in sizable amounts it would appear that some process analogous to that described by (22c) occurs during synthesis. Further evidence supporting these views is to be found in work carried out by the Bureau of Mines.[2b] This work points out that were H_2O the *only* oxygenated product directly produced in the synthesis, only small amounts of CO_2 might be expected to be produced over iron catalysts (as with cobalt catalysts) below 220°, but in spite of extensive testing in the range of 215 to 270°, no appreciable decrease in CO_2 production has been observed, even at the lowest temperatures. Hence, it may be inferred that some CO_2 is produced *directly* in the course of the reaction.

Since a large part of the C_1 complex is removed by (22b) and since this reaction does not appear to destroy complexes of higher carbon number, it would seem that any attempt to fit the relative yield of CH_4 into a simple chain building scheme would be fruitless. Attempts of this sort are probably also hindered by the fact that (22c) can also lead to carbide formation and/or carbon deposition as well as methane. (Were this the case, this reaction would offer an explanation of the fact that whenever an iron catalyst produces principally methane it invariably produces large deposits of carbon.) In view of the many possible side reactions of the C_1 complex, it would appear that its rate of production must be *considerably* greater than that of any other complex. This may explain the fact that the incorporation of radioactive methanol is far lower than the incorporation of any other primary alcohol.[6] Since the amount of radioactive alcohol in the synthesis stream was about the same in all experiments, the crude approximation can be made that in all cases about 10% of the added alcohols became identical with the corresponding complexes. (This is borne out by comparing the radioactivity balances for propanol and methanol.[3]) The complex from methanol according to the present picture would be much more diluted by non-radioactive complex than would be the case with any of the other alcohols, leading to an apparently low incorporation.

One further interesting extension of these ideas can be made. In their studies of the carburization of nitrided iron catalysts with synthesis gas mixtures, Hall, Dieter, Hofer and Anderson[15] found that the rate of carbon deposition was a maximum for a 1:1 H_2:CO mixture. If it is assumed that carbon deposition occurs according to (22c), it is obvious that the rate should be

$$R = k_7(CO)(X_1) \qquad (28)$$

These reactions were carried out under conditions where little if any synthesis was taking place, hence there was no water produced. Thus, using (26), the rate is

$$R = k_7k_5(CO)(H_2)$$

as observed.

It is worth while to note that the mathematical picture developed herein adequately describes such other known generalities of the Fischer–Tropsch synthesis as the shift in product distribution with temperature and/or alkali content and the increase in rate with pressure. In the first instance it is only necessary to suppose that the chain terminating steps, (3), are governed by higher activation energies than chain building steps, (2), so that the product distribution shifts toward the light end with increase of temperature. Similar ideas are applicable to the effects of alkali on the product distribution. The effect of pressure on the rate will arise of course, through an increase in concentration of the single carbon complex, X_1, through the operation of mass action in (2a) and/or (22a).

In conclusion, it might be noted that while the picture presented above does have many shortcomings, it also explains a large number of the experimental facts observed with iron Fischer–Tropsch catalysts. It does not, we feel, apply in the case of cobalt catalysts, since alcohol tracer experiments[7] strongly indicate that here alcohols are not important intermediates.

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Appendix I

The difference equation, (10)

$$\begin{gathered} P_n - fP_{n-1} - gfP_{n-2} = 0,\ n \geqslant 3 \text{ where} \\ P_1 = X_1,\ P_2 = X_2,\ P_3 = (X_3 + Z_3), \text{ etc.} \end{gathered} \qquad \text{(I-1)}$$

can be solved for P_n but for the present purposes it is necessary only to solve for quantities $\sum\limits_{n=1}^{\infty} P_n$ and $\sum\limits_{n=1}^{\infty} P_n$. This can easily be done through the use

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(14) H. Koelbel and F. Engelhardt, *Erdöl und Kohle*, **2**, 52 (1949).

(15) W. K. Hall, W. Dieter, L. J. E. Hofer and R. B. Anderson, This Journal, **75**, 1442 (1953).

of a generating function. The generating function represents an infinite series of equations of the type

$$\text{(a)}\quad P_3 - fP_2 - gfP_1 = 0 \qquad \text{(I-2)}$$
$$\text{(b)}\quad P_4 - fP_3 - gfP_2 = 0$$

Let (a) be multiplied by z, (b) by z^2, etc.; and all of these equations together and collect. Thus

$$P_3z + P_4z^2 + P_5z^3 + \dots - f(P_2z + P_3z^2 + P_4z^3 + \dots) \qquad \text{(I-3)}$$
$$- gf(P_1z + P_2z^2 + P_3z^3 + \dots) = 0$$

Defining the function

$$y(z) \equiv \sum_{n=1}^{\infty} P_nz^n \qquad \text{(I-4)}$$

(I-3) becomes

$$\frac{y(z) - P_1z - P_2z^2}{z^2} - f\,\frac{y(z) - P_1z}{z} - gfy(z) = 0 \qquad \text{(I-5)}$$

Solving (I-5) for $y(z)$, it is found that

$$y(z) = \frac{(P_2 - fP_1)z^2 + P_1z}{1 - fz - gfz^2} \qquad \text{(I-6)}$$

and since $P_2 = fP_1$, this becomes

$$y(z) = \frac{P_1z}{1 - fz - gfz^2} = \frac{X_1z}{1 - fz - gfz^2} \qquad \text{(I-7)}$$

Combining of (I-4) with (I-7) yields

$$\sum_{n=1}^{\infty} P_n = y(z = 1) = \frac{X_1}{1 - f - gf} \qquad \text{(I-8)}$$

and from (I-4)

$$\sum_{n=1}^{\infty} nP_n = \left(\frac{dy}{dz}\right)_{z=1} = \frac{X_1(1 + gf)}{(1 - f - gf)^2} \qquad \text{(I-9)}$$

From (I-8) and (I-9)

$$\sum_{n=1}^{\infty} (2n - 1)P_n = X_1\frac{(1 + f + 3gf)}{(1 - f - gf)^2} \qquad \text{(I-10)}$$

Proof of (11) follows from (I-7); the roots of this denominator are

$$\left.\begin{aligned} z_1 &= \frac{1}{2g}\left(-1 + \sqrt{1 + 4g/f}\right) \\ &\text{and} \\ z_2 &= \frac{1}{2g}\left(-1 - \sqrt{1 + 4g/f}\right) \end{aligned}\right\} \qquad \text{(I-11)}$$

from which it immediately follows that

$$z_1z_2 = -1/gf \qquad \text{(I-12)}$$

and

$$(z_1 + z_2) = -1/g \qquad \text{(I-13)}$$

Substituting (I-12) and (I-13) into (I-7) yields

$$y(z) = \frac{-X_1z}{gf(z_1 - z)(z_2 - z)}$$

which may be separated into

$$y(z) = \frac{X_1}{gf(z_1 - z_2)}\left\{\frac{z/z_1}{1 - z/z_1} - \frac{z/z_2}{1 - z/z_2}\right\} \qquad \text{(I-14)}$$

Expansion of (I-14) yields

$$y(z) = \frac{X_1}{gf(z_1 - z_2)}\,[(z/z_1) + (z/z_1)^2 + (z/z_1)^3 + \dots - (z/z_2) - (z/z_2)^2 - (z/z_2)^3 - \dots]$$

or

$$y(z) = \frac{X_1}{gf(z_1 - z_2)}\left\{\left(\frac{1}{z_1} - \frac{1}{z_2}\right)z + \left(\frac{1}{z_1^2} - \frac{1}{z_2^2}\right)z^2 + \dots\right\} \qquad \text{(I-15)}$$

From (I-15), the coefficient of z^n can be obtained immediately, *i.e.*

$$P_n = \frac{X_1}{gf(z_1 - z_2)}\left\{\left(\frac{1}{z_1}\right)^n - \left(\frac{1}{z_2}\right)^n\right\} = \frac{X_1(z_2^n - z_1^n)}{gf(z_1 - z_2)(z_1z_2)^n}$$

and substituting (I-11) and (I-12) yields the desired relation, *viz.*

$$P_n = f^{n-1}\,X_1\,F_n(g/f) \qquad \text{(I-16)}$$

where

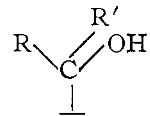
$$F_n(g/f) = \left\{\frac{(1 + \sqrt{1 + 4g/f})^n - (1 - \sqrt{1 + 4g/f})^n}{2^n\sqrt{1 + 4g/f}}\right\} \qquad \text{(I-17)}$$

Equation (I-17) can easily be evaluated by making use of the binomial expansion; thus for $n = 8$, the right-hand member reduces to

$$1 + 6(g/f) + 10(g/f)^2 + 4(g/f)^3$$

Appendix II

The stepwise chain growth theory of the mechanism of the Fischer–Tropsch synthesis[3,4] rests heavily on the observation that it appears to account for both the carbon number and isomer distributions observed for the products. Examination of equations 3 of the text reveals that the chain growth reactions postulated are the simplest of all organic reactions, namely condensation reactions involving the product of H_2O as the primary oxygenated product of the synthesis. There seems to be no "*a priori*" reason why this sort of reaction should be restricted to condensations with C_1 complexes. It must be concluded, then, that either condensations between complexes C_i and C_j do occur or that there is something very specific about the C_1 complex so that reaction with only it can occur. It is the purpose of what follows to show that a multiple build-in scheme, *i.e.*, condensations between C_i and C_j, can operate and still properly describe the isomer and carbon number distributions in the range of carbon numbers for which data are available.

Definitions are provided in the text for complexes of types described by X_n and Z_n. In the development of the present scheme it is also necessary to define another type complex,  by Y_n. In this complex neither R nor R′ is methyl or H; it could, therefore, only have been formed by another reaction than X_{n-1} or Z_{n-1} with X_1. In order to preserve the experimental observation that chain branching, other than methyl branching, does not occur, it is necessary to assume that complexes of the type Y_n can only evaporate (*i.e.*, they cannot enter into the chain building mechanisms). Thus, in the case of the Y_n complex of the lowest carbon number, C_5 can form by condensation of C_2 and nC_3 in two ways, the one yielding a Y_5 complex and the other yielding a Z_5 complex. In this instance, it is assumed that the Z_5 complex can either desorb as product or else continue in the chain building process, but the Y_5 complex must desorb. At first sight, this might appear to be rather artificial but closer inspection reveals that there is ample reason to believe that it is not. Molecular models show that only a few configurations of a Y_n complex will allow a close approach to the surface to form a directional bond and that these few are in such a strained condition that interpenetration of the alkyl radicals is sometimes required. Thus, from the standpoint of both energetics and entropy, these complexes are unstable. Further, the configurations which permit close bonding to the surface severely restrict the rotation of the C–OH bond and bring about a close approach of the alkyl hydrogen to the OH group, making the complex extremely susceptible to dehydration to the olefin and hence to desorption. Within the limitations set forth above, the following may be written

$$\mathrm{X}_n + \mathrm{X}_1 \xrightarrow{a} \mathrm{X}_{n+1} \qquad \text{(II-1)}$$

$$\mathrm{X}_n + \mathrm{X}_1 \xrightarrow{b} \mathrm{Z}_{n+1} \qquad \text{(II-2)}$$

$$\mathrm{X}_n + \mathrm{X}_m \xrightarrow{b} \mathrm{Y}_{n+m} \text{ (OH on } n\text{th carbon; } m,n \geqslant 3) \qquad \text{(II-3a)}$$

$$\mathrm{X}_m + \mathrm{X}_n \xrightarrow{b} \mathrm{Y}_{m+n} \text{ (OH on } m\text{th carbon; } n,m \geqslant 3) \qquad \text{(II-3b)}$$

$$\mathrm{X}_n + \mathrm{X}_n \xrightarrow{b} \mathrm{Y}_{2n} \text{ (OH on } n\text{th carbon; } n \geqslant 3) \qquad \text{(II-4)}$$

$$\mathrm{X}_n + \mathrm{X}_2 \xrightarrow{b} \mathrm{Y}_{n+2} \text{ (OH on 3rd carbon; } n \geqslant 3) \qquad \text{(II-5a)}$$

$$\mathrm{X}_n + \mathrm{X}_2 \xrightarrow{b} \mathrm{Z}_{n+2} \; (n \geqslant 2) \qquad \text{(II-5b)}$$

$$\mathrm{X}_m + \mathrm{Z}_n \xrightarrow{b} \mathrm{Y}_{m+n} \; (m \geqslant 3) \qquad \text{(II-6)}$$

$$\mathrm{X}_2 + \mathrm{Z}_n \xrightarrow{b} \mathrm{Z}_{n+2} \qquad \text{(II-7)}$$

$$\mathrm{X}_1 + \mathrm{Z}_n \xrightarrow{a} \mathrm{X}_{n+1} \qquad \text{(II-8)}$$

where a and b are rate constants as defined in the text; it has been assumed that all reactions not involving X_1 have rate constant b. It may be stated, however, that the same equations would be obtained for the ultimate carbon number and isomer distributions even if reactions involving X_i with X_j proceed at a different rate than reactions involving X_i with Z_j. If more than one reaction occurs for a given pair of reactants, each reaction is counted separately.

Complexes of carbon number n may be destroyed to form a number of possible products by a variety of paths. Thus, equations 4 of the text have their counterparts here and as a result (5) becomes

$$-\left[\frac{\mathrm{d}(\mathrm{X}_n \text{ or } \mathrm{Z}_n)}{\mathrm{d}t}\right] = S(\mathrm{X}_n \text{ or } \mathrm{Z}_n) \qquad \text{(II-9)}$$

and, owing to its lower stability

$$-\left[\frac{\mathrm{d}(\mathrm{Y}_n)}{\mathrm{d}t}\right] = WSY_n \qquad \text{(II-10)}$$

where W is an arbitrary constant and S is a function of the synthesis variables as well as of bed length.

It is now possible to write the material balance equations for the steady-state conditions. Recalling that Y_n and Z_n are zero for n less than 5 and 3, respectively, these are

for $n \geqslant 2$

$$\frac{\mathrm{dX}_n}{\mathrm{d}t} = 0 = a\mathrm{X}_1(\mathrm{X}_{n-1} + \mathrm{Z}_{n-1}) - S\mathrm{X}_n - (a + b)\mathrm{X}_1\mathrm{X}_n - 2b\mathrm{X}_n\left(\sum_{i=2}^{\infty} \mathrm{X}_i\right) - b\mathrm{X}_n\left(\sum_{i=3}^{\infty} \mathrm{Z}_i\right) + b\mathrm{X}_n^2 \qquad \text{(II-11)}$$

and for $n \geqslant 3$

$$\frac{\mathrm{dZ}_n}{\mathrm{d}t} = 0 = b\mathrm{X}_1\mathrm{Z}_{n-1} + b\mathrm{X}_2(\mathrm{X}_{n-2} + \mathrm{Z}_{n-2}) - S\mathrm{Z}_n - a\mathrm{X}_1\mathrm{Z}_n - b\mathrm{Z}_n\left(\sum_{i=2}^{\infty} \mathrm{X}_i\right) \qquad \text{(II-12)}$$

whereas for $n \geqslant 5$

$$\frac{\mathrm{dY}_n}{\mathrm{d}t} = 0 = b\mathrm{X}_2\mathrm{X}_{n-2} + b\left(\sum_{i=3}^{n-3} (\mathrm{X}_i + \mathrm{Z}_i)\mathrm{X}_{n-i}\right) - WS\mathrm{Y}_n \qquad \text{(II-13)}$$

Solving (II-11) for $\mathrm{X}_{,n}$ it is found that

$$\mathrm{X}_n = \frac{a\mathrm{X}_1(\mathrm{X}_{n-1} + \mathrm{Z}_{n-1})}{S + (a + b)\mathrm{X}_1 + 2b\left(\sum\limits_{i=2}^{\infty} \mathrm{X}_i\right) + b\sum\limits_{i=3}^{\infty} \mathrm{Z}_i\Bigg) - b\mathrm{X}_n} \qquad \text{(II-14)}$$

It will be noted that in (II-14), X_n cannot be completely separated; it enters into the denominator of the right-hand member both explicitly and also as part of the summation of X_i. The latter can be circumvented by substitution of the steady-state conditions that

$$u = \sum_{i=1}^{\infty} \mathrm{X}_i; \; v = \sum_{i=3}^{\infty} \mathrm{Z}_i; \text{ and } w = \sum_{i=5}^{\infty} \mathrm{Y}_i$$

where u, v and w are constants. Hence

$$\sum_{i=2}^{\infty} \mathrm{X}_i = u - \mathrm{X}_1$$

Therefore, outside of the explicit $-b\mathrm{X}_n$, the denominator of (II-14) is a function of X_1 only: this factor can probably be ignored with small error with respect to the remainder of the terms summed. This amounts to counting (II-4) twice in the scheme. This comes about due to the fact that when X_n reacts with itself, the OH must always end up on the nth carbon atom and is only counted once in the summations of $\mathrm{X}_n\mathrm{X}_i$ so that the term $b\mathrm{X}_n^2$ must be added to close the summation and is, therefore, subtracted outside the summation. Making this approximation an equation nearly identical to (7) is obtained, *i.e.*

$$\mathrm{X}_n = f'(\mathrm{X}_{n-1} + \mathrm{Z}_{n-1}) \qquad \text{(II-15)}$$

where f' is a function of X_1 and the synthesis variables only. Similarly, but without this complication (II-12) yields

$$\mathrm{Z}_n = \frac{b\mathrm{X}_1\mathrm{X}_{n-1} + b\mathrm{X}_2(\mathrm{X}_{n-2} + \mathrm{Z}_{n-2})}{S + a\mathrm{X}_1 + b(u - \mathrm{X}_1)} \qquad \text{(II-16)}$$

or

$$\mathrm{Z}_n = g'\mathrm{X}_{n-1} + \frac{g'\mathrm{X}_2}{\mathrm{X}_1}(\mathrm{X}_{n-2} + \mathrm{Z}_{n-2}) \qquad \text{(II-17)}$$

where

$$g' = \frac{b\mathrm{X}_1}{S + a\mathrm{X}_1 + b(u - \mathrm{X}_1)} \qquad \text{(II-18)}$$

Further simplification of (II-17) is possible by combination with (II-15), *i.e.*

$$\mathrm{Z}_n = 2g'f'(\mathrm{X}_{n-2} + \mathrm{Z}_{n-2}) \qquad \text{(II-19)}$$

Finally, from (II-13)

$$\mathrm{Y}_n = \frac{b}{WS}\left[\mathrm{X}_2\mathrm{X}_{n-2} + \sum_{i=3}^{n-3} (\mathrm{X}_i + \mathrm{Z}_i)\,\mathrm{X}_{n-i}\right] \qquad \text{(II-20)}$$

The rate of production of products of carbon number, n, will be given by an equation analogous to (9), *viz.*

$$\frac{\mathrm{d}(C_n)}{\mathrm{d}t} = k'_s(X_n + Z_n + WY_n) = k'_sP_n \quad \text{(II-21)}$$

so that

$$P_n = f'(X_{n-1} + Z_{n-1}) + 2g'f'(X_{n-2} + Z_{n-2}) + \\ h'\left(X_2X_{n-2} + \sum_{i=3}^{n-3}(X_i + Z_i)X_{n-i}\right) \quad \text{(II-22)}$$

The isomer and carbon number distributions may be calculated in terms of the parameters f', g' and h' from (II-22), in the same way as indicated in the text for the more simple stepwise scheme, provided the concentration of one complex is fixed. This has been done choosing the concentration of the C_2 complex as unity. These results have been compared to the experimental isomer distribution data of Bruner[12] and to the results of the stepwise schemes in Table III. The "multiple build-in" scheme appears to agree with the experimental data about as well as (or as badly as) the other schemes; similar results are obtained for cobalt catalysts. Considering the experimental difficulties inherent in obtaining such data, it is probable that all the schemes agree with them within experimental error.

As shown by Anderson,[4] given the isomer distribution, only one additional parameter is required to express the distribution of products by carbon number; the same is true of the present development. Although a detailed study of this problem has not been made, a cursory examination of the situation indicates the following:

(a) When the optimum parameters found for the isomer distribution are carried over and used to calculate the carbon number distribution, none of the schemes fit the data as well as if a new choice of all parameters is made. This may reflect the inaccuracies of the data or the approximations made or both; it may, however, be attributable to secondary processes taking place which are unaccounted for, *e.g.*, C_2H_4 build-in.

(b) All schemes tested adequately represented the data, but under the restriction posed above, the "multiple build-in" scheme did not appear to hold quite as well in the region of low carbon number, but perhaps a little better in the region above about C_{12}.

(c) On the basis of the data examined, it is concluded that the theory of "multiple build-in" presented here represents the true state of affairs to at least as good an approximation as the previous stepwise theory. It therefore tends to support the idea that chain growth occurs by simple condensation reactions involving complexes identical to those formed on adsorption of alcohols.

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[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY]

Chemisorption of Carbon Monoxide, Carbon Dioxide and Nitrogen on Nickel Catalysts

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The adsorption of carbon monoxide, carbon dioxide, argon and nitrogen on two types of nickel catalyst have been studied. On one of these catalysts it appears that more than one-third of the nitrogen adsorption at −195° is chemisorption. This complicates the classical procedure for studying carbon monoxide chemisorption. While carbon monoxide chemisorption may still be a useful method of estimating the surface concentration of nickel in promoted catalyst, the surface concentration of alkali promoter cannot be determined simply from carbon dioxide chemisorption.

For two decades the chemisorption of carbon monoxide has been used for estimating the fraction of the surface of iron synthetic ammonia catalyst that is covered with promoter.[1] If the catalyst contained an alkali in the promoter, the surface promoter concentration could be ascertained by measurement of the chemisorption of carbon dioxide at −78°. The carbon monoxide appeared to be chemisorbed on the iron atoms and the carbon dioxide on the alkali promoter molecules. Somewhat later,[2] it was found that similar measurements on nickel catalysts were apparently incapable of measuring the fraction of the surface of a nickel catalyst covered with alkali. The carbon monoxide and the carbon dioxide were each capable of being adsorbed in quantities sufficient to cover nearly the entire surface of the catalyst as measured by nitrogen adsorption at −195°. Very recently,[3] doubt has been thrown on the results for nickel catalysts by the discovery that nitrogen chemisorbs on nickel at −195°. Accordingly, it has seemed worthwhile to reexamine the adsorption of carbon monoxide and carbon dioxide on nickel catalysts.

Experimental

Two types of nickel catalyst were used in the present study. The first of these is designated as SE II and was prepared in the manner described by Emmett and Skau[2] for their Ni II catalyst by precipitation of the hydrous oxide from aqueous $Ni(NO_3)_2$ with NaOH. Two samples of this catalyst were studied, SE II (1) and SE II (2). The other nickel catalyst used in this study was prepared by the method used by Best and Russell.[4] Solid NH_4HCO_3 was added to a solution of $Ni(NO_3)_2$ to precipitate the basic carbonate which was calcined for 6 hr. at about 450° to convert it to NiO. Three samples of this catalyst were studied. These are designated as BR1, BR2 and BR3.

Different reduction procedures were used for the SE II (1) and SE II (2) catalyst. SE II (1) was first reduced with tank hydrogen as the temperature was raised slowly to 340°. Then, the hydrogen was purified by passage through hot copper and through a trap filled with charcoal at −195°. Reduction was continued at a space velocity of about 5000 hr.$^{-1}$ until the amount of water in the effluent gas was less than two parts per million. The catalyst was evacuated for 2 hr. at the reduction temperature prior to the start of an adsorption experiment. After completion of a series of experiments the catalyst was reduced for 2 hr. in the manner described above and evacuated 2 hr. at 340°. This is re-

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[1] P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 310, 1553 (1937).

[2] P. H. Emmett and N. Skau, *ibid.*, **65**, 1029 (1943).

[3] R. J. Kokes and P. H. Emmett, *ibid.*, **80**, 2082 (1958).

[4] R. H. Best and W. W. Russell, *ibid.*, **76**, 838 (1954).