JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 79 JUNE 26, 1957 NUMBER 12

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF GULF RESEARCH & DEVELOPMENT COMPANY, MELLON INSTITUTE]

Mechanism Studies of the Fischer–Tropsch Synthesis. The Addition of Radioactive Methanol, Carbon Dioxide and Gaseous Formaldehyde

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RECEIVED JANUARY 26, 1957

When a gas mixture containing 1.4% radioactive carbon dioxide in a 50:50 H_2:CO synthesis gas is passed over an iron catalyst at 240°, very little carbon dioxide is converted to carbon monoxide or to hydrocarbons. Apparently the water gas conversion reaction under these conditions is very slow. Methanol can act as a chain initiator in hydrocarbon synthesis and to a slight extent can build into the chain to form higher hydrocarbons. It also forms considerable carbon dioxide by direct decomposition on the catalyst. Similar results were obtained with gaseous formaldehyde, except that it decomposes rapidly on the iron catalyst in the presence of synthesis gas to form carbon monoxide and carbon dioxide having activities almost as great as for complete equilibration between these two gases and the formaldehyde. Hence, in this instance, the slope of the activity *vs.* carbon number plot for the hydrocarbons formed can be accounted for by the radioactivity of the carbon monoxide. Apparently neither formaldehyde nor methanol forms on adsorption the type of C_1 complex identical to that occurring in actual synthesis.

Tracer studies reported in two previous communications[1,2] from this Laboratory have shown that when small amounts of radioactive primary alcohols are added to a 1:1 carbon monoxide–hydrogen synthesis gas mixture which is being passed over a reduced iron catalyst at about 235°, the hydrocarbon synthesis products of carbon number greater than that of the added alcohol have an approximately constant radioactivity per cc. This has been interpreted as indicating that the complex formed by the adsorption of the alcohol on the iron catalyst is capable of acting as an intermediate (a chain initiator) in the synthesis of higher hydrocarbons.

Of all the primary alcohols studied only radioactive methanol yielded hydrocarbon products, the radioactivity of which per cc. increased appreciably with increasing carbon number. Apparently the complex formed on addition of methanol not only initiates chains but also enters into chain building.

With a view to investigating further the behavior of radioactive complexes containing a single carbon atom, the methanol experiments have now been extended into the higher pressure range of commercial synthesis. These are reported in the present paper together with experiments at one atmosphere pressure in which radioactive formaldehyde and radioactive carbon dioxide were used as tracers. Gaseous formaldehyde was used with a view to testing it as a possible source of a single carbon complex both for chain building and chain initiation.

Several other facts, pertinent to the discussion of the present paper, had also been established in the earlier work. Pyrolysis of the propane formed in experiments,[1] where methyl-labeled and methylene-labeled ethanol were added to the synthesis gas, showed that carbon atoms attach themselves preferentially to the methylene carbon atom of the alcohol complex. Further, all results obtained were in agreement with the pattern of build-up of hydrocarbon on the surface of the catalyst suggested by Weller and Friedel,[3] by Anderson, Friedel and Storch,[4] and by Weitkamp, *et al.*[5] In addition, it was possible to suggest[2] a modification of one of these reaction schemes[4] to allow for the enhanced reactivity of the carbon attached to the hydroxyl group; the result was a somewhat more descriptive picture of these surface processes than had previously been available.

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

(2) J. T. Kummer and P. H. Emmett, *ibid.*, **75**, 5177 (1953).

(3) S. Weller and R. A. Friedel, *J. Chem. Phys.*, **17**, 801 (1949); **18**, 157 (1950).

(4) R. B. Anderson, R. A. Friedel and H. H. Storch, *ibid.*, **19**, 313 (1951)

(5) A. W. Weitkamp, H. S. Seelig, N. J. Bowman and W. E. Cady, *Ind. Eng. Chem.*, **45**, 343 (1953).

The experiments with carbon dioxide were designed to ascertain whether or not the slope of the curves representing plots of radioactivity of the products as a function of carbon number obtained in the methanol and formaldehyde tracer runs could be explained as due to the incorporation of the moderately active carbon dioxide obtained as a reaction product.

Experimental

Most of the techniques involved in the radioactive analysis of the products had previously been standardized.[1,2] A description of these will not be repeated here. A few remarks are in order, however, relative to the analysis of the carbon monoxide and carbon dioxide in the tail gas for radioactivity. For measurements on the carbon monoxide, the tail gas was passed through a liquid nitrogen trap and over copper oxide heated to 360°. The exit gas containing water vapor, CH_4 and CO_2 was passed into a second trap where the CO_2 and water vapor were condensed and the methane was removed by pumping. The carbon dioxide was then evaporated from the trap at $-78°$ and counted. Carbon dioxide in the tail gas was collected by passing a portion of the tail gas through barium hydroxide for about five minutes. Such pairs of samples were obtained from two to three times during a run.

In the methanol run, it was thought to be important to establish whether or not the activity of the olefin and paraffin fractions behaved similarly as a function of carbon number. Since the activity of the gaseous olefins and paraffins alone could not decide this point, an attempt was made to extend these measurements to the liquid product. This entailed a separation of the olefins and paraffins. To this end the liquids were passed through a chromatographic column packed with Davison code 923 silica gel (inactive toward the polymerization of olefins); ethanol was used as the eluting developer. The oil product was thus cut into 13 approximately equal cuts of about 2 cc. each. Refractive index measurements showed a sharp rise after the fourth cut and another after the twelfth cut. In the region between these points, there was a gradual decrease in refractive index with an increase in cut number indicating a small fractionation according to molecular weight. The thirteenth cut contained the entire colored band and was presumed to contain most of the oxygenated product obtained in synthesis. Beyond cut 13, the refractive index fell rapidly to that of the eluting ethanol. On the basis of these results, it could be inferred that the liquid had been at least partially fractionated into olefins and paraffins.

Since preliminary examination of the infrared spectrum of these fractions indicated that a major portion of the olefins present consisted of α-olefins, a group type analysis was set up for this species. The results of this analysis are contained in Table I, where the concentration of the $-HC{=}CH_2$ radical is expressed in moles per liter of liquid.

TABLE I

Fraction no.	Concn. α-olefin, moles/l. of liq.	Fraction no.	Concn. α-olefin, moles/l. of liq.
1	0.31	8	3.3
2	.23	9	3.4
3	.18	10	3.5
4	.16	11	3.7
5	1.9	12	3.5
6	2.8	13	1.1
7	3.1		

These data indicated that at least a semi-quantitative separation of olefins and paraffins occurred between cuts four and five. None of the fractions was found to be completely free of olefin, but since the concentration of α-olefin in fraction 10 was nearly 20 times that of fraction 3, an upper limit of about 5% α-olefin could be put on the latter fraction. The other question of interest is the purity of the olefin fractions with respect to paraffins; this may be defined as C/C_0, where C is the observed olefin concentration and C_0 is the concentration in moles per liter of the pure olefin of the same molecular weight. A minimum average molecular weight could be determined for fraction 10; this turned out to be greater than octane, the uncertainty existing because it was not possible to distil a small residual portion of the material in high vacuum at room temperature. On this basis, the purity of the predominant α-olefin turns out to be 55%. The spectra, however, showed also the presence of both *cis*- and *trans*-olefins of the type $R_1CH{=}CHR_2$. There is some uncertainty in treating the spectral data for these species, because the 965 cm.$^{-1}$ band of the *trans*-olefin overlaps the 990 cm.$^{-1}$ band of the α-olefin. In fraction 10, however, it was possible to establish that these species amounted to a total of 2.4 ± 0.3 mole/liter. Making this correction leads to a purity value for the olefin in this cut of 92%. Cuts 3 and 10 were used for the analysis of the radioactivity of the liquid paraffins and olefins, respectively. It is apparent from the above that these cuts were $90^{+}\%$ pure paraffin and olefin, respectively.

The runs with the gaseous formaldehyde and the carbon dioxide additions were made in our one atmosphere all-glass reactor previously described;[1,2] the run in which the radioactive methanol was added to the synthesis at 100 p.s.i.g. was made in the bench scale reactors[6] of the catalyst testing laboratories of the U. S. Bureau of Mines, Bruceton, Pennsylvania.

In the glass reactor several thermocouples were buried in the catalyst bed. The reduced catalyst was brought into synthesis at about 200° the gradual addition of carbon monoxide to the gas stream so as not to locally overheat the catalyst. Then, the temperature was slowly increased until a contraction of from 20 to 35% was reached. When these steady state conditions were attained, traps were put on and the run commenced. After a period comparable to that to be used in the radioactive run, the products were collected for analysis, and the synthesis was continued with the radioactive additive in the gas stream. Similarly, after the collection of the radioactive products, another non-radioactive test run was made. In the run in the pressure reactor, a similar procedure was followed, except that the catalyst was put on stream using the Bureau's standard test procedure,[7] and the radioactive run was started in the fourth week of operation. In all instances, the presence of the radioactive additive in the synthesis gas appeared to have no large effect on the catalytic activity or on the product distribution. Therefore, the data collected in Table II are representative not only of the tracer runs but also the control runs.

The catalysts used in the individual runs are noted in Table II. All were reduced fused iron oxides. Catalyst number 955 contained 7.95% Al_2O_3 and number 614, 2.0% ZrO_2 and 0.64% Al_2O_3 in addition to Fe_3O_4. Catalyst D-3001 is the standard doubly promoted catalyst of the Bureau of Mines; it contains 0.6% SiO_2, 0.6% Cr_2O_3. 4.6% MgO and 0.6% K_2O; its properties and behavior have been extensively described elsewhere.[8-11] It should be noted that catalyst 955 was used in the earlier[2] methanol run, so that the carbon dioxide addition experiment reported herein pertains more directly to the earlier than to the present methanol experiment. Since, however, the behavior of the methanol in both experiments is qualitatively similar, this makes little difference.

One millicurie lots each of carbon dioxide (as $BaCO_3$) and formaldehyde (as a dilute aqueous solution) were secured from the Atomic Energy Commission's laboratory at Oak Ridge, and two millicuries of methanol were obtained from Tracerlab, Inc., Boston.

The methanol was appropriately diluted with non-radioactive methanol to a volume of 35 cc. The carbon dioxide was liberated from the $BaCO_3$ with concentrated H_2SO_4 in a vacuum system and subsequently diluted to about 7.5 liters. This was transferred into a small (approximately 12 l.) steel cylinder where it was blended with

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(6) R. B. Anderson, A. Krieg, B. Seligman and W. E. O'Neill, *Ind. Eng. Chem.*, **39**, 1548 (1947).

(7) R. B. Anderson, B. Seligman, J. F. Shultz, R. E. Kelly and M. A. Elliott, *ibid.*, **44**, 391 (1952).

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

(9) W. K. Hall, W. H. Tarn and R. B. Anderson, *J. Phys. Chem.*, **56**, 688 (1952).

(10) R. B. Anderson, L. J. E. Hofer, E. M. Cohn and B. Seligman, THIS JOURNAL, **73**, 944 (1951).

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

TABLE II

SYNTHESIS VARIABLES AND PRODUCT DISTRIBUTION OF TRACER RUNS[a]

Radioactive additive	1.0% CH_3OH	1.4% HCHO	1.3% CO_2
Catalyst no.	D-3001	614	955
Space velocity[b]	100	244	228
Av. operating temp., °C.	237	227	230
Av. contraction, %	62	25	30
Duration of expt., hr.	73	25.4	22.5
Pressure, atm.	7.8	1	1
Total gas production, cc. gas, STP	51,000	4400	11,750[c]
Specific radioactivity of additive, c./min./cc.	6950	5010	9450
Liquid products, g.		14.8	
CO_2, g.		34.2	

PRODUCT DISTRIBUTION, % OF GAS

CH_4	49.9	25.3	17.6
C_2H_4	6.4	12.9	5.1
C_2H_6	15.8	19.9	27.8
C_3H_6	14.8	24.6	22.3
C_3H_8	4.2	5.0	12.5
C_4H_8	4.9	8.5	8.6
C_4H_{10}	1.8	1.5	3.0
C_5H_{10}	1.1	1.8	2.1
C_5H_{12}	0.5	0.4	1.0

[a] In all runs herein reported a 1:1 H_2:CO synthesis gas was used. [b] Space velocity is here defined as volume of entering gas per volume of catalyst space per hour; the catalyst volume was 100 cc. in the radioactive methanol addition experiment and 50 cc. in all others. [c] Contains an estimated 15% CO_2; exact figures are not available.

enough carbon monoxide to bring the final pressure up to about 285 p.s.i. Under these conditions, the tank was found to contain 2.6% radioactive CO_2. This gas, after passing through a Dry Ice trap, was blended with a separate stream of pure dry hydrogen to obtain a 1:1 H_2:CO synthesis gas.

The radioactive formaldehyde was mixed with an appropriate amount of a concentrated (40%) solution of formaldehyde. From this, paraformaldehyde was prepared by vacuum distillation of the water from the solution. This polymer was thoroughly dried over anhydrous magnesium perchlorate in a vacuum desiccator. Production of the formaldehyde gas was carried out in a vacuum system, which prior to the actual synthesis was baked out with a torch under vacuum to remove adsorbed water from the glass. The gas was generated when the paraformaldehyde was heated to 120° *in vacuo* and was passed through a line heated to the same temperature followed by a five-stage trap, the top stages of which were kept at 120° and the bottom stages at −78°; it was then collected in a receiver at liquid nitrogen temperature. This procedure is similar to that used by Spence and Wild.[12] Further purification was achieved by several distillations. The over-all yield of purified formaldehyde was better than 80%. A stream of hydrogen was passed through the liquid formaldehyde at −78° where it picked up approximately 2.8% gaseous formaldehyde. This was blended with an equal amount of CO to yield about 1.4% formaldehyde in the 1:1 synthesis gas. The concentration of formaldehyde in the synthesis stream was continuously monitored with a thermal conductivity gage. In spite of all the precautions taken in drying the hydrogen, after two to three hours the clear formaldehyde would become a stiff gel. It was discovered, however, that this gel would maintain the vapor pressure of pure formaldehyde for periods up to 20 hours; at the end of this period the vapor pressure would fall suddenly. It was found, furthermore, that a good percentage of the original liquid could be regenerated by a simple distillation. For these reasons, the addition to the synthesis was interrupted after about 18 hours for a few minutes to heat up the gel and regenerate the formaldehyde.

In the methanol experiment, the liquid was injected into the top of the reactor under pressure by a small single-stroke pump run by a synchronous motor. This pump, which operated much like a hypodermic syringe, was developed by the Bureau of Mines engineers and was found capable of delivering as little as 1/4 cc. per hour, accurately and reproducibly, under pressure up to 300 p.s.i. Under the conditions of the present experiment, this amounted to 1% of the synthesis gas.

Results

(a) Methanol.—The data collected from the hydrocarbon products of the methanol run are plotted in Fig. 1, where they are compared to those obtained earlier at lower pressure by Kummer and Emmett.[2] In the earlier run, the olefins and paraffins were determined separately only on the gaseous products (C_2 to C_4); the liquid products were fractionated by distillation and the activities of the individual cuts, which contained both olefins and paraffins, were determined. These data fall on a straight line indicating the "build-in" of at least enough of the complex formed on the adsorption of methanol to account for the difference between the observed slope of 70 counts/min./cc./carbon number and the activity increment due to the radioactivity of the carbon monoxide (32 counts/min./cc. in the exit gas). In the new runs, on catalyst D-300 under pressure, the data do not fall on a straight line, although the over-all trend indicates a similar "build-in" corresponding to about 38 counts/min./cc./carbon number, of which at most 23 counts/min./cc./carbon number may be attributed to the radioactivity contained in the carbon monoxide. These newer data were obtained with nearly pure fractions of olefins and paraffins; it should be noted that the olefin curve more or less parallels that of the paraffins, though it falls slightly

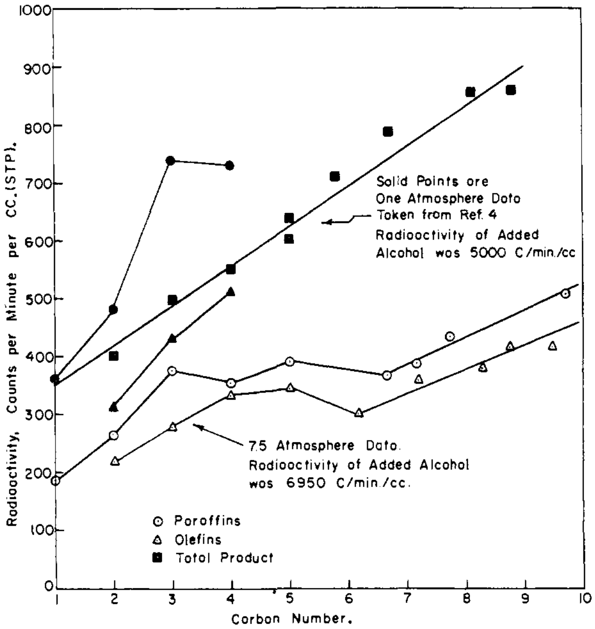

Fig. 1.—Radioactivity of hydrocarbons obtained in the experiment in which 1% radioactive methanol was added to the synthesis at 7.5 atmospheres. These data are compared to the earlier one atmosphere results of ref. 4.

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[12] R. Spence and W. Wild, *J. Chem. Soc.*, 338 (1935).

Table III

Radioactivity of Tail Gas and of the Methane of Synthesis Runs (counts/min./cc. (STP))

Radioactive additive	CO		CO_2		CH_4	CH_4/CO_2
Methanol, 1 atm.[a]	32		175		360	2.06
Methanol, 7.5 atm.[b]					186	
Sample no. 1	22	Av. = 23.5 ± 1.5	82	Av. = 83.5 ± 1.5		2.27
Sample no. 2	25		85			2.19
Formaldehyde, 1 atm.[c]						
Sample no. 1	150	Av. = 138 ± 12	128	Av. = 132 ± 10		1.73
Sample no. 2	129		126		221	1.75
Sample no. 3	135		142			1.55

[a] Taken from data of ref. 2: radioactivity of added alcohol was 5000 counts/min./cc. [b] Radioactivity of added alcohol was 6950 counts/min./cc. [c] Radioactivity of added formaldehyde was 5010 counts/min./cc.

below it. Further, both curves show an amazing similarity in the region of lower carbon number where the comparison can be made to the shape of the same curves obtained earlier. This similarity was rechecked and confirmed in a separate run. Thus, although the present data do not afford an unique explanation of this behavior, the rapid rise in activity from methane to propane or from ethylene to butylene followed by a range of relatively constant activity before the molar radioactivity increases further seems well established. For the present, it can only be concluded that the present work confirms the older[2] in showing that there is a tendency for the complex resulting from adsorbed methanol to enter the chain building step as well as to function (principally) as a "chain initiator."

In the older work on the basis of the data from C_2 to C_8, about one molecule in from 10 to 15 appeared to originate from the complex formed from methanol on the catalyst surface; in the present work, the ratio is found to be closer to one in 35. This decrease in the relative amount of methanol incorporated on increasing the pressure of the synthesis appears to be perfectly general and applicable also to other alcohols; it will be discussed by the present authors in a paper to be published shortly.[13] It will suffice here to point out that it may be explained by the simple assumption that methanol must compete for adsorption sites with the complex formed from carbon monoxide and hydrogen, and that the fraction of the adsorbed layer consisting of radioactive methanol is smaller at 7.5 atmospheres than at one atmosphere pressure.

Further data of interest are collected in Table III. The activity of the carbon monoxide is low in both methanol runs, indicating that the amount of methanol which decomposes to carbon monoxide is a small but definite amount.

Had all the methanol entering the pressure reactor been decomposed at the entrance, the radioactivity of the emerging carbon monoxide would have been some six times higher (*i.e.*, 138 counts/min./cc). In the present instance in which 1% methanol was added, the activity is about $^2/_3$ that found in the earlier one atmosphere run in which 1.5% methanol was added.

The presence of the high activity carbon dioxide observed earlier[2] was confirmed by the present work; as before, the activity indicates that at least part of the radioactive CO_2 was not formed *via* CO. It is of interest to note that the radioactivity observed in the pressure run (83.5 c./min./cc.) has decreased with an increase in total pressure in almost exactly the same ratio as the fractional incorporation into hydrocarbons, suggesting that the reaction responsible is one involving a common intermediate on the catalyst surface.

(b) **Carbon Dioxide.**—The general trend of increasing radioactivity per cc. of hydrocarbon as a function of increase in carbon number observed in the methanol runs, might conceivably be attributed to the radioactive carbon dioxide formed in these runs. Thus, for example, the slope of 70 counts/minute/cc/carbon number observed by Kummer and Emmett[2] could easily be accounted for if a sufficient amount of the radioactive carbon dioxide (175 counts/min./cc.) were to enter into the chain building reaction. The present data appear to rule out this possibility.

In this experiment, a blend of 97.4% non-radioactive CO +2.6% radioactive CO_2 (9,450 counts/min./cc. of CO_2) was metered into the reactor along with an equal amount of hydrogen. The data collected are listed in Table IV. Since background on our tube ran from 40 to 46 counts/min., and since many observations (obtained by subtracting the background reading from the total reading) were only a fraction of this, the data obtained are admittedly crude; they are, however, adequate to show that the amount of carbon dioxide incorporated into the product (corresponding to about 2 atoms of carbon incorporated per 1000 carbon atoms) is much too small to account for the increasing activity as a function of carbon number found in the methanol runs. The activity of the carbon monoxide in the tail gas is found to be about 14 counts per minute per cc. This level of activity is high enough within our experimental error (probably ± 6 counts/min./cc.) to account for all of the activity found in the products. Thus the major portion of the entering carbon dioxide passes through the bed unchanged, but diluted with that formed in synthesis.

The low but detectable activity observed in the carbon monoxide could arise from either an exchange of an oxygen atom with the carbon monoxide, *viz.*

$$C^{14}O_2 + CO \rightleftarrows CO_2 + C^{14}O \qquad (1)$$

or by a reversal of the water gas shift reaction on the catalyst surface

$$C^{14}O_2 + H_2 \rightleftarrows C^{14}O + H_2O \qquad (2)$$

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(13) R. J. Kokes, W. K. Hall and P. H. Emmett, This Journal, **79**, 2989 (1957).

TABLE IV

RADIOACTIVITY OF TAIL GAS AND HYDROCARBONS FROM CARBON DIOXIDE EXPERIMENT[a] (COUNTS/MIN./CC. (STP))

Compound		Activity	Activity/C atom
Carbon monoxide, sample no. 1		13	13
Carbon monoxide, sample no. 2		14	14
Carbon dioxide, sample no. 1		532[b]	532[b]
Carbon dioxide, sample no. 2		1760[c]	1760[c]
Methane		22	22
Ethane		33	17
Ethylene		13	7
Propane		81	27
Propylene		21	7
Butanes		64	16
Butylenes		54	14
Liquid of av. carbon no.	5.00	65	13
	5.38	103	19
	5.73	120	21
	6.69	76	12
	7.16	118	16
	8.28	120	15
Av. of hydrocarbons =			16

[a] Radioactivity of the 1.3% carbon dioxide in synthesis gas was 9450 counts/min./cc. STP of gas. [b] Sample taken at ~38% contraction. [c] Sample taken at about 32% contraction.

Had complete radioactive equilibrium been reached by either of these reactions, the observed level of activity in the exit carbon monoxide would have been raised to 246 counts/min./cc. It is particularly interesting to note that reaction 2 is shown by these data to be quite sluggish over a Fischer–Tropsch synthesis catalyst operating under the conditions used. It is equally true, however, that these results do not preclude the possibility that such a reversal may be less sluggish with the higher contractions and the somewhat higher temperatures usually employed in a commercial synthesis.

(c) **Formaldehyde.**—As noted in an earlier communication,[1] if it were possible to add to the synthesis a radioactive organic compound which on adsorption became identical with the C_1 complex formed from carbon monoxide and hydrogen on the surface and responsible for building into the hydrocarbon chains, the molar activity *vs.* carbon number curve would necessarily be a straight line passing through the origin (at zero carbon number). Since current theories[2,4,5] of the mechanism of the synthesis lead to the inference that this "chain-building" complex contains oxygen, the number of possibilities of radioactive additives is severely limited. It was for this reason that formaldehyde addition was studied.

The data obtained from the hydrocarbon product of the synthesis are plotted in Fig. 2. The solid line shows that a reasonably good linear relation exists between the molar radioactivity and the carbon number of the total product (our most accurate data). These data, like those for methanol, cannot conceivably be interpreted as being due to the formation of a single complex identical with that obtained from carbon monoxide and hydrogen. If such a complex were formed, the data would fall on a straight line passing through the origin. Since the left hand margin of Fig. 2 corresponds to unit carbon number (rather than zero carbon number), the corresponding requirement is that the data would have to fall around one of a family of lines having the same slope as intercept, such as the dashed line shown. For the same reason, the data show that complete decomposition of the formaldehyde could not have taken place before an appreciable fraction of the bed length had been passed. Otherwise, all hydrocarbon activities would be the same per C atom as for CO, namely, 138 counts/min./cc. The data do not preclude but are actually consistent with the formation by the formaldehyde of a chain-initiating complex with or without a chain-building complex.

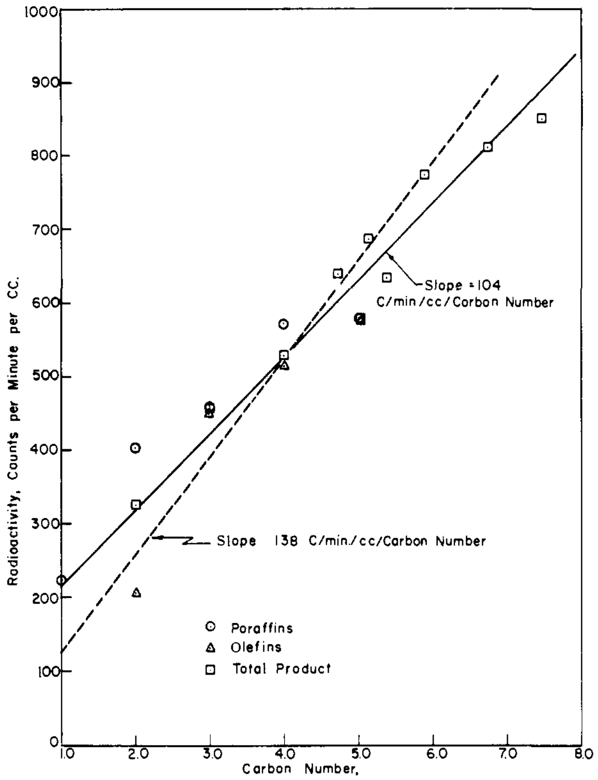

Fig. 2.—Radioactivity of hydrocarbons obtained in the experiment in which 1.4% radioactive gaseous formaldehyde was added to the synthesis at 1 atmosphere.

Data obtained for the pairs of carbon monoxide and carbon dioxide samples of the tail gases from the converter are shown in Table III. The average activity of 138 counts/min./cc. found for the carbon monoxide together with the observed activities for CO_2 and for the C_1—C_8 hydrocarbons show that the formaldehyde, in contrast to methanol, must have been nearly completely decomposed before the gases emerged from the reactor. (For complete decomposition outside the reactor, the activity of the carbon monoxide would have reached only 140 counts/min./cc.) In separate experiments, it was shown that

a. The expected amount of formaldehyde was delivered to the top of the reactor, undecomposed and unhydrogenated by the hydrogen carrying gas.

b. No appreciable decomposition of pure formaldehyde gas occurs in glass at temperatures up to 285° for periods of circulation up to 45 minutes.

c. Exchange between or decomposition of 27% formaldehyde in 73% carbon monoxide is negligibly small in glass in 45 minutes at 285°.

These results show that the source of the activity in the carbon monoxide must be attributed to some reaction in the catalyst bed rather than in the hollow glass preheater section of the reactor.

In contrast to the results obtained in the methanol run, the activity of the carbon monoxide found in the tail gas is more than adequate to account for the observed slope (104 counts/min./cc./carbon number) of the solid line of Fig. 2. The activity of the carbon dioxide produced in the run (132 c./min./cc.) is, within the experimental error, equal to that of the carbon monoxide. These high values for carbon monoxide and carbon dioxide activities would have been expected if all the formaldehyde had decomposed in the preheater before reaching the catalyst, but would not necessarily be observed for the decomposition of formaldehyde over the catalyst. As noted above, however, the data obtained for the hydrocarbons indicate that the formaldehyde must have passed over an appreciable length of the catalyst bed before decomposition was complete.

A brief analysis will show that if carbon dioxide is formed exclusively from the carbon monoxide and always by consecutive reactions, one of which is nonreversible, the activity of the carbon dioxide will be less than that of the carbon monoxide at any given point in the catalyst bed. However, carbon dioxide *produced* in any increment of the catalyst bed will, of course, have the same molar activity as the carbon monoxide in the same increment.

If x is the distance along a catalyst bed, and l is the total bed length

$$A_{CO_2}(l) = \frac{\int_0^l A_{CO} \frac{dV_{CO_2}}{dx}\, dx}{V_{CO_2}(l)} \quad (3a)$$

where A_{CO} is the activity of CO (counts/min./cc.) at point x in the bed, l is the length of the bed, $A_{CO_2}(l)$ is the activity of CO_2 in the tail gas and V_{CO_2} is the total amount of CO_2 present at x. Integration by parts yields

$$A_{CO_2}(l) = A_{CO}(l) - \frac{1}{V_{CO_2}(l)}\int_0^l V_{CO_2} \frac{dA_{CO}}{dx}\, dx \quad (3b)$$

Thus, it is apparent that $A_{CO_2}(l)$ can approach $A_{CO}(l)$ only if the integral term in 3b is small compared with $A_{CO}(l)$. This could most reasonably be realized if the activity of the CO increases rapidly at first (and in this region $V_{CO_2}/V_{CO_2}(l)$ is very small) and rapidly attains its final value. This would mean that the integrand is essentially zero over most of the bed length. Thus, A_{CO} would have to reach its final value much faster than V_{CO_2} if the second term in eq. 3b is to be small.

The above analysis would require that the decomposition of formaldehyde to CO occurs before appreciable synthesis and concomitant production of CO_2 can take place. The data in Fig. 2 show that synthesis is occurring before the decomposition of formaldehyde is complete. Thus, it would be closer to the truth to assume that the production of radioactive CO from formaldehyde follows the same functional dependence on x as the formation of CO_2 from CO. In this case, according to eq. 3, the activity of the CO_2 would be only one-half as great at the exit as the activity of the carbon monoxide. Since the activity of the CO_2 in the exit gas is roughly the same as the activity of the CO, it appears that at least some of the CO_2 is formed *directly* from the adsorbed formaldehyde. Similar conclusions were reached regarding the CO_2 produced in methanol tracer experiments.

The calculations that are made on the basis of eq. 3a and 3b for the increase in the radioactivity of carbon dioxide with bed length are equally applicable to the consideration of the slope of the line in Fig. 2 for the activity of the hydrocarbon products as a function of carbon number. A nonreversible transformation of CO into hydrocarbons along the bed would, on the basis of the arguments given in connection with eq. 3a and 3b, result in the activity increment per added carbon in the hydrocarbon being always less than the activity of the CO. The exit values of 138 counts/min./cc. for the carbon monoxide and a slope of 104 counts/min./added carbon for the plot in Fig. 2 conform to expectation if the build-in step in forming the hydrocarbons is mostly from a complex formed from carbon monoxide but not directly from formaldehyde.

Discussion

A detailed evaluation of the present data in terms of an over-all synthesis picture will be deferred until data are presented relative to the incorporation of propionaldehyde and ethylene in experiments at one atmosphere[14] and ethanol in high pressure experiments.[13] It will suffice, therefore, to summarize here the firm conclusions that can be drawn from these data without reference to subsequent runs. The conclusions to which the present experiments lead may be summarized as follows.

(1) Carbon dioxide does not build into hydrocarbons appreciably during their synthesis from carbon monoxide and hydrogen over a singly promoted iron catalyst at one atmosphere pressure and 240°.

(2) The water–gas conversion reaction is extremely sluggish over a singly promoted iron catalyst at 240° at one atmosphere, as judged by the very small conversion of radioactive CO_2 to carbon monoxide.

(3) Methanol adsorbs on iron catalysts to form a complex capable of initiating hydrocarbon synthesis chains on the catalyst surface, though as a chain initiator it is only about $^{1}/_{5}$ as effective as ethanol; furthermore, its effectiveness decreases by a factor of two when the pressure is raised from one to 7.8 atm. This or a different complex formed by methanol builds into the hydrocarbon chain and also forms CO_2, as evidenced by the fact that the slope of the activity *vs.* carbon number curve and the absolute activity of the carbon dioxide are both too high to be accounted for by the radioactivity of the carbon monoxide.

(4) Formaldehyde appears to decompose almost completely into carbon monoxide and hydrogen, though a portion of the decomposition must be

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(14) W. K. Hall, R. J. Kokes and P. H. Emmett, to be published.

directly to CO_2. To a small but finite extent formaldehyde forms a complex capable of initiating hydrocarbon chains. The mechanism by which formaldehyde builds into the hydrocarbon chain involves either the carbon monoxide formed by decomposition or a second complex. The carbon monoxide at the exit has ample radioactivity (138 counts/min./cc.) to account for the observed slope of the activity *vs.* carbon number plot (104 counts/min./cc/carbon number).

Acknowledgment.—The authors are indebted to Dr. R. B. Anderson and his capable staff at the U. S. Bureau of Mines, Bruceton, Pa., for use of their facilities and for assistance rendered in carrying out the pressure experiments.

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[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF GULF RESEARCH & DEVELOPMENT COMPANY, MELLON INSTITUTE]

Fischer–Tropsch Synthesis Mechanism Studies. The Addition of Radioactive Ethanol to the Synthesis Gas

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RECEIVED JANUARY 26, 1957

The incorporation of radioactive ethanol in the Fischer–Tropsch synthesis has been studied over reduced singly promoted iron catalysts, a reduced doubly promoted iron catalyst, a nitrided doubly promoted iron catalyst and a reduced cobalt catalyst. Most of the experiments were carried out with the synthesis gas containing about 1.5% ethanol, but in some runs the concentration was as low as 0.04%. At one atmosphere the incorporation is greatest for the reduced singly promoted iron catalyst, less for the reduced doubly promoted iron catalyst, and least by far for the cobalt catalyst. The incorporation over the reduced doubly promoted iron catalyst falls off with increasing pressure and also at 7.5 atm. the incorporation is lower for the nitrided catalyst than it is for the reduced catalyst. The average of the molar radioactivities of the alcohols produced over the nitrided catalyst is the same as for the hydrocarbons from the same run. Experiments with varying ethanol concentrations indicate that the ethanol adsorption is medium strong at concentrations between 1.5 and 0.04%. The results are discussed on the basis of Langmuir adsorption and stepwise growth of hydrocarbon chains involving an adsorbed alcohol as the principal intermediate.

It has been shown that when small amounts of C^{14}-labeled primary alcohols containing 2, 3 or 4 carbon atoms are added to a 1:1 H_2:CO synthesis gas at one atmosphere and passed over a singly promoted iron catalyst at about 235°, the resulting Fischer–Tropsch hydrocarbon products (at least up to C_{10}) have an approximately constant radioactivity per mole.[1,2,3] Thus it appears that these alcohols are acting as chain initiators. In the experiments involving ethanol, moreover, it has been shown[2] that the chain initiation occurred preferentially (90% of the time) at the methylene carbon atom. These results, together with the fact that $^1/_3$ to $^1/_2$ of the synthesis products originate from the added alcohols, which constitute only 1.5% by volume of the synthesis gas, clearly suggest that the complex formed from the adsorbed alcohol may well be an intermediate in the normal synthesis.

According to the picture put forward by Storch, Golumbic and Anderson,[3] the formation of hydrocarbons from CO and H_2 occurs in a stepwise fashion. Various schemes have been advanced on the basis of such a mechanism, several of which predict both the isomer and carbon number distributions in the products.[4–6] The best agreement with the experimental data is obtained using scheme A of ref. 5. This scheme is similar but not identical to the one which would be obtained if the single carbon chain building unit, as well as the chain initiation units, were adsorbed alcohols with a carbon–hydrogen bond of the carbinol carbon atom replaced by a carbon–metal bond.[1–3,7]

Tracer experiments[1,2] over singly promoted iron catalysts at one atmosphere are, by and large, consistent with this picture. Perhaps its most significant shortcoming is the suggestion that the single carbon chain building complex is an adsorbed alcohol. This, of course, suggests that the C_1 complex should be derivable from either adsorbed methanol or adsorbed formaldehyde (enol form). The present authors[8] have shown that neither of these acts as the primary build-in unit although they both function as chain initiators. In spite of the difficulty, the over-all success of the mechanism justifies additional tracer experiments to further test its applicability.

The alcohol tracer experiments reported previously[1,2,8] with the exception of one of the methanol experiments,[8] have all been carried out at atmospheric pressure on reduced, singly promoted, iron catalysts. Of these experiments, those in which primary alcohols having 2, 3 or 4 carbon atoms were used yielded results which lend themselves most easily to interpretation in terms of a simple chain building scheme. In order to test more completely this simple picture, some additional ethanol tracer experiments were made. These were carried out over a reduced, doubly promoted, iron catalyst at 1, 7.5 and 21 atmospheres; over a nitrided, doubly promoted, iron catalyst at 7.5 atmospheres; and over a cobalt catalyst at 1 atmosphere. The synthesis gas for these experi-

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