The coefficients obtained are similar in magnitude to those obtained from both pressure studies and studies with radioactive carbon dioxide, and indicate that the exchange takes place at sites which are involved in the interaction of carbon dioxide and charcoal.

The results presented are in agreement with the mechanism proposed by earlier workers (3–9) who assumed that the first step was $CO_2 + C \rightarrow CO +$ an oxygenated surface, followed by a slow decomposition of this oxygenated surface to give a second molecule of CO. Under the conditions of the present investigation characterized by the rapid circulation of the CO_2 past the charcoal granules, the first step was very rapid. Consequently, we did not measure either the activation energy of this step nor the inhibiting effect of carbon monoxide. The activation energy for the second step was found to be much lower than that found by the previous workers. However, these workers were not able to separate out experimentally into two distinct stages the process of interaction of carbon dioxide with charcoal. Further work is being carried out at the laboratory on the use of isotopic tracers in the study of the interaction of carbon dioxide, carbon monoxide, steam and charcoal.

We wish to acknowledge assistance of Dr. N. Zwiebel in setting up the apparatus and helpful discussions with Dr. R. W. Dodson.

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[CONTRIBUTION FROM GULF RESEARCH & DEVELOPMENT COMPANY'S MULTIPLE FELLOWSHIP, MELLON INSTITUTE]

Mechanism Studies of the Fischer–Tropsch Synthesis. The Addition of Radioactive Alcohol

BY J. T. KUMMER, H. H. PODGURSKI, W. B. SPENCER AND P. H. EMMETT

To help elucidate the mechanism of Fischer–Tropsch synthesis, methyl-labeled and methylene-labeled radioactive ethyl alcohol have been added to a 1:1 carbon monoxide–hydrogen synthesis gas being passed at 1 atm. pressure over an iron catalyst at about 230°. Measurement of the radioactivity of the hydrocarbon products shows negligibly small activity for all methane formed and an approximately constant activity of 2150 ± 100 counts per minute per cc. S.T.P. for the C_5 to C_{10} hydrocarbons. The C_2, C_3 and C_4 hydrocarbons have activities of about 1825, 1850 and 2000 counts per minute per cc. Degradation experiments on the C_3 hydrocarbons show that about 90% of the added carbon atoms are attached to the α-carbon atom of the alcohol adsorption complex whereas 10% are attached to the β-carbon. These results suggest that either ethyl alcohol or some surface complex formed by the adsorption of ethyl alcohol behaves like an intermediate in hydrocarbon synthesis over iron Fischer–Tropsch catalysts and that at least the first of the added carbon atoms attaches itself principally to the α-carbon atom of the surface complex.

The mechanism of the Fischer–Tropsch synthesis has been the subject of much speculation and experiment since the reaction was first discovered by Fischer and Tropsch in 1926. The original authors endeavored to explain the reaction by proposing[1] that metallic carbides are formed as intermediate products, and that these are reduced by the hydrogen present to form methylene groups which polymerize to give the higher hydrocarbons. The carbide theory, however, was criticized by Elvins and Nash[2] because it did not explain the formation of oxygenated compounds which are found in the synthesis product along with the hydrocarbons. They proposed the other principal mechanism for the synthesis that has thus far been advanced by suggesting that some C–H–O complex on the catalyst surface was the more likely intermediate.

The proposal of Elvins and Nash that carbon–hydrogen–oxygen complexes on the catalyst surface were the true intermediates in the Fischer–Tropsch hydrocarbon synthesis has received considerable indirect support in recent years. Storch and his group at the U. S. Bureau of Mines[3] have called attention to the similarity between the synol process which produces alcohols and the Fischer–Tropsch hydrocarbon synthesis. A. W. Weitkamp,[4] in a very thorough investigation of the products of an operating Fischer–Tropsch unit, has shown that the plot of per cent. branched chain aliphatic hydrocarbons against carbon number (length of chain) gives the same curve as is obtained by plotting the per cent. branched chain alcohols against their carbon number. He pointed out that this strongly suggests that the same mechanism operates in both the formation of alcohols and hydrocarbons.

It occurred to us that speculation relative to the mechanism of hydrocarbon synthesis would be on a much sounder basis if one could trace in the reaction products the disposition of certain simple oxygen-containing organic molecules added to the synthesis gas. In view of the availability of both methyl-labeled and methylene-labeled radioactive ethyl alcohol and in view of the suggestion frequently made that the alcohols may well be intermediate products, we have selected this compound for our first attempt to elucidate the nature of the intermediate complex that may be important in hydrocarbon synthesis.

If ethyl alcohol is either an intermediate or if it becomes modified slightly upon adsorption on the catalyst surface to form an intermediate, one might logically expect in these tracer experiments to find a constant molar radioactivity in all of the hydrocarbon products having three or more carbon atoms. On the other hand, if the alcohol is not an intermediate but is simply degraded to CH_2 groups on the surface or to carbon monoxide, one might expect to find the radioactive carbon distributed as a constant fraction of the carbon atoms in the prod-

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(1) F. Fischer and H. Tropsch, *Brennstoff Chem.*, **7**, 97 (1926).

(2) O. C. Elvins and A. W. Nash, *Nature*, **118**, 154 (1926).

(3) Information Circular 7518, U. S. Bureau of Mines, pp. 77–78.

(4) Paper delivered before the A. A. A. S. Gordon Conferences, New London, New Hampshire, June, 1949.

ucts. We have accordingly added radioactive ethyl alcohol to a 1:1 hydrogen:carbon monoxide synthesis gas being passed over an iron catalyst and have analyzed the hydrocarbon products for radioactivity. The present paper reports results obtained using methylene-labeled radioactive ethyl alcohol as well as those using methyl-labeled alcohol.

Experimental

For these experiments a small bench-scale, one-atmosphere Fischer–Tropsch unit designed to yield in 24 hours sufficient gaseous, liquid and solid hydrocarbons for analysis was used. Two different iron synthetic ammonia catalysts were employed. The one (No. 422) used in the preliminary runs (1 and 2) contained 1.55% Al_2O_3 and 0.58% ZrO_2 as promoters; the one (No. 333) used for the final runs contained 2.82% Al_2O_3 and 1.39% ThO_2 as promoters. In all the experiments approximately 100 g. of the catalyst (about 45 cc.) was placed in a reaction tube 1″ inside diameter and was reduced at 500° in a stream of pure dry hydrogen. The temperature was measured by one thermocouple placed in the furnace and by three placed in a centrally located 0.5″ thermocouple well opposite the center, the top, and the bottom of the catalyst.

The reaction products were caught by passing the effluent gas through an ice-trap, a soda lime tower, and then through a trap cooled in liquid nitrogen. The latter was, at the end of the run, warmed slowly to room temperature. In the final runs, the gas fraction was removed and fractionated in a Podbielniak column; the liquid product was fractionated in a small glass column having a negligibly small holdup.

In the preliminary experiments a temperature of 230 to 243° and a space velocity of 100 were used. In the final runs the temperature was between 210 and 235°.

The methyl-labeled and methylene-labeled ethyl alcohol samples were obtained from Tracerlab, Inc. These were diluted with normal alcohol and introduced into the carbon monoxide–hydrogen stream by bubbling the synthesis gas through the liquefied alcohol in an ice-bath. Since the vapor pressure of alcohol at 0° is 12.2 mm., this procedure gave an alcohol concentration of about 1.6% by volume in the inlet gas.

The gaseous products were counted directly as hydrocarbon gas and also were burned to carbon dioxide and counted again. For counting both the hydrocarbon gas and the carbon dioxide formed by combustion, a Geiger counter tube was used that has been modified by attaching a gas chamber outside the thin mica window.[5] Each liquid sample was allowed to evaporate into a one-liter bulb at room temperature to a pressure of several millimeters which was read accurately; oxygen was then added and the sample burned to carbon dioxide and counted. From the volume of carbon dioxide produced, it was possible to calculate the number of carbon atoms per molecule. The wax was burned completely to carbon dioxide and the molecular weight determined, before combustion, by the Rast method. From the activity of the carbon dioxide and the molecular weight of the hydrocarbon, it was, of course, then possible to calculate the radioactivity per mole of the liquid or solid products.

The water in the ice-trap was analyzed for alcohol by means of a Zeiss immersion refractometer. All hydrocarbon products before being analyzed were washed with water and dried with sodium hydride so as to remove alcohol that may have been present.

Results and Discussion

Preliminary Runs.—In the present paper, results are reported for seven experimental synthesis runs over an iron Fischer–Tropsch catalyst. In three of these runs radioactive ethyl alcohol was added as a tracer. The other four runs were controls.

The results from two preliminary runs, one with ethyl alcohol (run 2) and one without (run 1) are presented in Tables I and II. Perhaps the most striking inference to be drawn from these first experiments is the indication that when the carbon atoms of radioactive ethyl alcohol are incorporated into the higher hydrocarbons, the radioactivity per mole of hydrocarbon formed is approximately constant for the gaseous hydrocarbons, the light liquid hydrocarbons, and the heavy liquid hydrocarbons. Thus the molar activity of the gaseous hydrocarbons can be obtained from Table I as the product[6] of the counts per minute per cc. of CO_2 (column 3), the average number of carbon atoms (column 4) and the constant 22,400. As mentioned in a footnote in Table I, assigning average carbon numbers of 6.8 and 12.5 to the light and the heavy liquid hydrocarbons, respectively, would yield molar activities for the three hydrocarbon fractions that are identical to each other.

TABLE I

ADDITION OF RADIOACTIVE ETHYL ALCOHOL[b] IN A FISCHER–TROPSCH SYNTHESIS EXPERIMENT—RUN 2

		Product analysis		
Product	Amount	Counts per min. per cc. of CO_2 formed by combustion	Average no. of C atoms per molecule	Activity at exit as % of inlet
CO	......	0 ± 5	.....	..
CH_4	150 cc.	14	.....	..
Gas total	1180 cc.	368	2.98	20.8
Satd. content	610 cc.	333	2.34	..
Light liq. hydrocarbon	2.0 g.	162	(6.8)[a]	8.3
Heavy liq. hydrocarbon	0.8 g.	88	(12.5)[a]	1.8
Ethanol				
1. From ice-trap	.5 g.	2040		16.1
2. From liquid N_2 trap	.8 g.	1870		25.8

[a] Values for these molecular weights were not obtained experimentally. They represent the values necessary to give for these two liquid fractions activities per mole equal to those obtained for the gaseous fraction. [b] Nineteen of the twenty-three hours duration of the run were made with added alcohol; four hours were without alcohol. 1430 cc. of alcohol (S.T.P.) were introduced in the experiment. Its activity was 4340 counts per minute per cc. of alcohol (S.T.P.). This is equal to 2170 counts per minute per cc. of CO_2 formed by the combustion of the alcohol. The radioactive carbon was in the methylene position in the alcohol.

A mass balance on the radioactive alcohol used in run 2 shows that about 42% of it was recovered in the ice-trap and the liquid nitrogen trap unchanged, 31% entered into recovered hydrocarbons, and 27% was unaccounted for. It is suspected that a portion of the missing alcohol was probably absorbed by the soda lime tower that was in the recovery train between the trap held at 0° and the one held at −195°. Some of it may have been consumed in partially carbiding the catalyst. From a comparison of the activity of the original alcohol with that obtained from the two traps, it is apparent, therefore, that very little if any additional alcohol was synthesized during the run and passed on into the traps. Additional evidence that the collected alcohol had come through the reactor unchanged was obtained by degrading the alcohol in such a way as to form iodoform from the β-carbon atom. Tests showed that the iodoform from the β-carbon atoms of the recovered alcohol like that from the original alcohol had zero activity.

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(5) J. T. Kummer, *Nucleonics*, **3**, 27 (1948).

(6) For convenience we shall refer to the number of counts per 1/22,400 mole of the various hydrocarbons (1 cc. S.T.P.) rather than to the number of counts per mole of hydrocarbon.

Table I also indicates that very little of the alcohol was converted to either methane or carbon monoxide. The carbon monoxide at the exit of the catalyst had a zero activity and the methane an activity of only 14 counts per minute.

Several other miscellaneous observations on the effect of adding the alcohol to the synthesis gas are of interest. The alcohol appeared to cause the ratio of paraffins to olefins to decrease. Thus in run 1, the ratio of saturated to unsaturated hydrocarbons was 122; in run 2 in which the radioactive alcohol was added the ratio was 1.1. There is definite evidence that the increased olefin yield was not due merely to the dehydration of the ethyl alcohol. In the first place, the olefin content of the gaseous products from run 2 was 570 cc. The activity of the entire gaseous fraction, on the other hand, indicated that only 297 cc. of the alcohol vapor entered the gas phase as hydrocarbons. Clearly, then, the larger yield of olefin relative to paraffins in run 2 in the presence of the alcohol must be attributed to some indirect action. It seems likely that the alcohol itself or the water derived from it slightly lowers the over-all catalytic activity and also tends to decrease the activity of the catalyst for hydrogenating the olefins to paraffins. Additional evidence that this might be the case was obtained in a separate run in which the introduction of 0.6% water vapor into the inlet gas stream was found to increase the olefin content of the gaseous products from 5 to 20%. At the same time the water vapor dropped the percentage contraction during the run from 31 to 24%. The three experimental runs with alcohol reported in Tables I, II, III and IV also showed invariably that the alcohol decreased the activity of the catalyst, higher temperatures being necessary to obtain a given percentage contraction during the synthesis in the presence of the alcohol than in its absence.

TABLE II

SUMMARY OF FISCHER–TROPSCH SYNTHESIS RUNS 1 AND 2

	Run 1, no alcohol	Run 2, 1.6% radioactive[b] C_2H_5OH added to synthesis gas
Duration, hr.	18.8	23.0
Reactor temp., °C.	243[c]	232[c]
Space velocity l./hr.	100	100
Contraction vol. %[a]	47.7	32.3
Gas. hydrocarbons cc. S.T.P.	2350	1180
Gas. hydrocarbons g./m.^{3}	36	18
Liq. hydrocarbons g./m.^{3}	41	26
Water produced g./m.^{3}	12	18
CO_2 produced, g./m.^{3}	360	130
Gas analysis, vol. %		
C_5	1.5	2.8
Butanes	5.4	2.7
Butenes	0.8	7.2
Propane	14.0	11.5
Propylene	0.0	24.9
Ethane	48.1	23.9
Ethylene	0.0	14.2
Methane	30.2	12.8
Mole ratio satd./unsatd.	122	1.1

[a] Calculated from the volume of gas passing the liquid N_2 trap. [b] Labeled on the α-carbon atom. A 1:1 H_2:CO synthesis gas was used throughout. [c] The furnace temperature was 225° in both of these runs. The reactor temperature shown is for the highest thermocouple reading in each bed. The average catalyst temperature was 235° in run 1 and 230° in run 2.

Final Tracer Experiments.—Tables III and IV summarize five experiments that were performed to confirm the constancy of the molal radioactivity of the hydrocarbons obtained in a synthesis run in which radioactive ethyl alcohol was added to the synthesis gas. The two runs in which the alcohol was added as tracer (runs 4 and 6) were carried out with special care. The approximate constancy of the molar radioactivity of the hydrocarbons formed is clearly shown in columns 4 and 7 of Table III and in the plot of the data in Fig. 1.

The values for the activities of the wax as given in Table III require special comment. In run 4 the activity of the wax per cc. S.T.P. calculates out to be in good agreement with that obtained for the lower hydrocarbons if the wax is assumed to contain about 23 carbon atoms per mole. The same is true for the wax obtained in run 6. However, a molecular weight determination on the wax in run 6 indicated that the wax molecule contained 26 carbon atoms. This results in an activity per cc. S.T.P. of 2740 counts per minute compared to the value 2200 obtained for the C_5 to C_{10} hydrocarbons. Unfortunately, the figures for the wax may be in considerable error because of the wax holdup that is known to occur on iron catalysts under the operating conditions used in the present experiments. Thus at the end of run 7, extraction of the catalyst with benzene followed by reduction by hydrogen at 300° yielded a total of 0.8 g. of wax that had presumably been retained by the catalyst at the end of run 7. If the wax holdup from the control runs is considered to reach solution equilibrium with the radioactive wax formed during runs 4 and 6, it is possible to show that the actual activity per cc. S.T.P. of the wax synthesized during a run may have been two or three times as high as the 2200–2740 value shown. This arises from the fact that about 0.5 g. of wax was recovered in the trap at 0° in each run and that dilution by wax from the control runs might have been considerable. It is impossible to calculate the exact amount of dilution since we do not have detailed information as to the amount of wax present in the catalyst at the end of runs 3, 4, 5 or 6. If one assumes a constant retention of 0.8 g. of wax for each of these runs, one obtains a molar activity for the wax being formed about three times as high as for the C_2 to C_{10} hydrocarbons. On the other hand, if the wax builds up by small equal increments in the five runs then the corrected wax figure would be only about twice as high as shown in Table III. Of course the possibility remains that the figures for the wax in Table III are approximately correct as a result of only slight mixing of the wax formed during the run with the wax laid down on the catalyst in previous runs. One indication that there is considerable mixing of the wax content during a run and that the figures for wax in Table III are accordingly low is the fact that the activity per carbon atom for the wax removed at the end of

TABLE III

ADDITION OF RADIOACTIVE ETHYL ALCOHOL[a] IN A FISCHER-TROPSCH SYNTHESIS RUN OVER IRON CATALYSTS—RUNS 4 AND 6

	Using methylene-labeled alcohol—Run 4			Using methyl-labeled alcohol—Run 6		
Products	Average no. of C atoms per molecule	Activity counts per min. per cc. of CO_2	Activity per cc., S.T.P. as vapor	Average no. of C atoms per molecule	Activity counts per min. per cc. of CO_2	Activity per cc. S.T.P. as vapor
CO		0	0		0	0
CH_4	1	20	20	1	143	143
Ethane	2	990	1980	2	1005	2010
Ethylene	2	840	1680	2	875	1750
Propane	3	620	1860	3	656	1970
Propylene	3	590	1770	3	633	1900
Butane	4	498	1990	4	515	2060
Butenes	4	482	1930	...	..	..
Liq. hydrocarbons	4.94	415	2050	5.45	397	2160
Liq. hydrocarbons	5.10	419	2140	5.50	390	2160
Liq. hydrocarbons	6.01	374	2250	6.28	347	2180
Liq. hydrocarbons	6.06	370	2240	6.28	346	2170
Liq. hydrocarbons	6.92	323	2240	6.75	326	2200
Liq. hydrocarbons	7.10	306	2170	6.90	331	2280
Liq. hydrocarbons	8.37	262	2200	7.16	309	2210
Liq. hydrocarbons	8.85	246	2180	7.40	300	2220
Liq. hydrocarbons				8.02	279	2230
				8.49	263	2230
				9.21	247	2280
Wax and oil	23[b]	95	2200	26	105	2740

[a] The partial pressure of alcohol in inlet gas was 12.2 mm. The activity of the methylene-labeled alcohol was 6000 counts per minute per cc. of alcohol (S.T.P.); the activity of the methyl-labeled alcohol was 5500. [b] The molecular weight of this sample was not determined. The value given is the one which would yield a radioactivity per cc. S.T.P. of vaporized wax equal to that obtained for the C_5 to C_9 hydrocarbons. The values for the activity of the wax are probably too low because of dilution of the wax obtained during a run by wax held on the catalyst surface and in tiny capillaries of the catalyst. The wax holdup for runs 3, 4, 5 and 6 was not determined. However, after run 7, 0.5–0.8 g. of wax was removed from the catalyst by extraction.

TABLE IV

SUMMARY OF FISCHER-TROPSCH SYNTHESIS RUNS 3, 4, 5, 6 AND 7

Run no.	3	4[a]	5	6[a]	7
Type of run	Contr.	Alc. added	Contr.	Alc. added	Contr.
Duration, hr.	19.5	19	22.5	25.5	21.5
Reactor temp., °C.[b]	210	222	215	227	210
Space velocity, hr.$^{-1}$	170	137	185	185	170
Contract. vol., % (after liq. N_2 trap)	14.7	22.6	21.0	15.7	19.0
Oil + wax, grams	Approximately 0.5 g. of wax + oil per run				
Liq. hydrocarbons, grams	1.7	3.3	3.0	>3.5	3.6
Gas. hydrocarbons, cc. S.T.P.	1740	1550	1580	>1520	...
Water + alcohol, grams	4.0	6.2	5.9	8.0	3.7
Analysis of gas fraction, vol. %					
C_5		4.4	3.1	1.8	
n-Butane		2.0	1.2	1.4	
Isobutane		0.1	0.3	0.0	
Butenes		13.0	9.9	6.0	
Propane		3.5	3.6	7.5	
Propylene		32.2	30.3	23.7	
Ethane		14.4	16.2	31.0	
Ethylene		25.4	26.4	13.2	
Methane		4.9	8.9	15.3	

[a] In run 4, 1.6 volume per cent. of α-labeled radioactive ethyl alcohol was added; in run 6, the ethyl alcohol was β-labeled. 1:1 H_2:CO synthesis gas was used throughout. [b] Hottest point in the catalyst bed. The furnace temperature was 5 to 7° lower than the temperatures given here.

control run 7 by extraction with benzene was 40% as great as for the wax recovered in the trap at 0° during run 6. For the present, accordingly, we must limit our conclusions to hydrocarbons in the C_2 to C_{10} range.

A comparison of the molar activity of the hydrocarbons produced with the activity in the original alcohol indicates that in run 2 about one molecule out of each four of the hydrocarbons of a given molecular weight contained the carbon atoms from one molecule of the radioactive alcohol; in runs 4 and 6 the corresponding figure is one molecule in three.

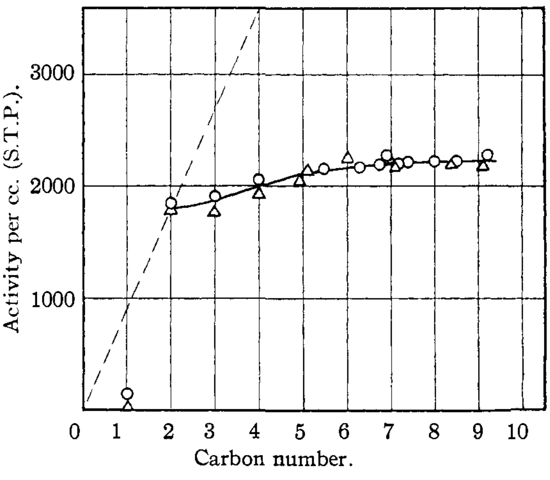

Fig. 1.—Activity per cc. of hydrocarbon vapor formed during synthesis runs using an α-labeled (Δ) and a β-labeled (O) ethyl alcohol. The activity of the α-labeled alcohol was 6000 counts per min. per cc. of vapor; that for the β-labeled alcohol was 5500.

Degradation of Radioactive Propane and Propylene.—Since, as discussed below, runs 2, 4 and 6 indicated that the ethyl alcohol molecule or some complex derived from it during adsorption on the iron catalysts was capable of acting as an intermediate in the Fischer–Tropsch synthesis, it seemed worthwhile to try to obtain some information as to the point at which the added carbon atoms became attached to the initial adsorbed alcohol complex. To this end a number of degradation experiments were carried out on propane and on propylene from runs 4 and 6. The propane from runs 4 and 6 was subjected to partial thermal decomposition (about 10%) at 550 to 575° in a silica tube to give methane and ethylene. If one assumes that the methane is formed exclusively from the end carbon atoms of the propane molecule,[7] then one would expect that for propane obtained in run 4 in which methylene-labeled alcohol was used, the activity of the methane produced by pyrolysis would be zero if the addition of carbon (probably as carbon monoxide) takes place on the methylene carbon atom during synthesis. Furthermore, if one neglects any possible isotope effect (which may be as large as 16%),[7] then the activity of the methane formed by the pyrolysis of propane obtained in a synthesis run using methyl-labeled ethyl alcohol should be one-half the activity per cc. of propane. The activities for the methane actually obtained were 120 and 880 counts per cc. S.T.P. per minute for runs 4 and 6, respectively, rather than the expected values 0 and 985. Nevertheless, these results indicate very definitely that the build-up of alcohol to propane involves addition of carbon primarily to the α-carbon atom of adsorbed alcohol rather than to the β-carbon. This difference between 0 and 120 and between 985 and 880 might be caused by some of the addition (10 to 12%) taking place on the β-carbon of the alcohol complex, or it might be due to slight skeletal isomerization of propane by the Fischer–Tropsch catalyst during the synthesis run.

As an independent check on the point at which carbon monoxide adds to the initial complex, propylene from runs 4 and 6 was treated by a procedure[8] which converted it into acetone. An end carbon atom was then removed as iodoform and tested for radioactivity. The activity of the carbon dioxide produced by combustion of the iodoform was 82 for run 4 and 760 for run 6. These results, like those obtained from propane pyrolysis, indicate that the build-up of alcohol to propylene involves the addition of carbon to the α-carbon atom in the adsorbed alcohol complex. Approximately the same divergence of the activity counts (82 and 760) from the expected values (0 and 950) exists as was found in the pyrolysis of the propane. The possible explanation given for the discrepancy in the propane pyrolysis runs is also applicable to the measurements on propylene. It should be noted in passing that double bond isomerization in the radioactive propylene would not affect the activity of the iodoform obtained by this procedure.

Two attempts[9] were made to determine the activity of the 1-carbon atom of the radioactive propylene formed during synthesis. In both cases propylene from run 6 was used. The first of these analyses gave a value of 427 counts per minute per cc. of carbon dioxide for this end carbon atom, and the second gave an activity of 520. If one assumes that 10 to 12% of the added carbon monoxide goes on the β-carbon rather than on the α-carbon and that, in addition, one has 30 to 35% double bond isomerization, one can account for these observed radioactivity values of the 1-carbon of the propylene.

General Discussion

The tracer experiments here described seem to show quite clearly that ethyl alcohol or the adsorption complex derived from ethyl alcohol when the latter is adsorbed on the surface of the iron catalyst is capable of acting as an intermediate in the synthesis of higher hydrocarbons from a carbon monoxide–hydrogen mixture over an iron catalyst. The results seem definite for the C_2 to C_{10} hydrocarbons but must be considered as somewhat uncertain for the wax fraction. This constancy of the molal radioactivity of the synthesized hydrocarbons argues against any random polymerization process between the alcohol molecules and carbon atoms or CH_2 groups on the catalyst surface. This is true regardless of whether we imagine the alcohol molecules to break up before incorporation into higher hydrocarbon molecules or whether we imagine the molecule or complex as a whole to polymerize randomly with other carbon atoms or CH_2 radicals. If any such random polymerization existed as the sole method of incorporation of the alcohol into hydrocarbons, one would expect the radioactivity per cc. to increase with molecular weight along some such dotted line as given in Fig. 1.

The results seem to be consistent with the several proposed chain growth mechanisms as described by Weller,[10] by Anderson, Friedel and Storch,[11] and by A. W. Weitkamp,[4] provided one assumes that the probability of incorporation of a second alcohol molecule into such a growing chain is negligibly small compared with the probability of adding carbon atoms to the adsorbed alcohol molecules until the hydrocarbons contain at least ten carbon atoms.[12] It is interesting to note too that the estimates of these authors[11,4] as to the percentage (about 10%) of the added carbon going onto the

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[7] D. P. Stevenson, C. D. Wagner, O. Beeck and J. W. Otvos, *J. Chem. Physics*, **16**, 993 (1948).

[8] The propylene from runs 4 and 6 was absorbed in 85% sulfuric acid, hydrolyzed to isopropyl alcohol, and oxidized by chromic acid to acetone. The acetone was then degraded by sodium hypoiodite to iodoform.

[9] In the first attempt the propylene from run 6 reacted with osmium tetroxide in carbon tetrachloride. The osmium tetroxide-propylene complex was refluxed with powdered silicon in alkaline solution to give propylene glycol. The glycol was treated with periodic acid to give formaldehyde and acetaldehyde. The aldehydes were oxidized by alkaline permanganate to acetic acid and carbon dioxide. The carbon dioxide was counted as a gas in the usual way.[5]

The second method used to find the activity of the 1-carbon atoms of propylene involved the absorption of the propylene in concentrated mercuric acetate solution. On addition of sodium hydroxide solution mercuric oxide is precipitated leaving in solution CH_3-CH_2OH-CH_2HgAc [R. Adams, F. L. Roman and W. N. Sperry, THIS JOURNAL, **44**, 1781 (1922)]. Addition of sodium hypoiodite gave a precipitate of iodoform which presumably comes from the 1-carbon atom of the propylene. The iodoform was burned with oxygen to CO_2 over a silver catalyst and counted.

[10] S. Weller, *J. Chem. Physics*, **17**, 801 (1949).

[11] R. B. Anderson, R. A. Friedel and H. H. Storch, to be published.

[12] Since the present experiments do not yield reliable information for the wax, there is no proof that hydrocarbons in the wax range might not be capable of building more than one alcohol complex into their structures.

β-carbon instead of the α-carbon of the adsorption complex agree well with the average value, 13%, deduced from the degradation experiments on propane and propylene.

In conclusion it should be emphasized that the observations reported in the present paper were all made on the products from synthesis runs over a single iron catalyst at one atmosphere pressure for a 1:1 carbon monoxide–hydrogen gas at space velocities in the range 100 to 240 and at temperatures ranging from 210 to 243°. Care must therefore be exercised in extrapolating these data to the higher temperatures and pressures used in commercial or pilot plant operation, though we see no reason to doubt the applicability of this same mechanism to the synthesis at higher pressure, temperature and space velocity.

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[CONTRIBUTION NO. 108 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Solubility of the Rare Earth Oxalates and Complex Ion Formation in Oxalate Solution. II. Neodymium and Cerium(III)[1]

BY CARL E. CROUTHAMEL[2] AND D. S. MARTIN, JR.

The solubilities of cerium(III) and neodymium in buffered oxalate solutions have been determined by means of radiochemical assays. The data have permitted the calculation of equilibrium constants which satisfactorily describe the systems. These constants have been compared with those from earlier work with ytterbium. The results have indicated that neodymium formed the complex ions $Nd(C_2O_4)^+$ and $Nd(C_2O_4)_2^-$ with very nearly the same stability constants as ytterbium, but that it had a minimum solubility of about 1.5×10^{-6} mole/liter compared to 3×10^{-5} mole/liter for ytterbium. Evidence was found for the formation of $Ce(C_2O_4)^+$, $Ce(C_2O_4)_2^-$ and $Ce(C_2O_4)_3^=$; and cerium had a minimum solubility of about 1.7×10^{-6} mole/liter.

Introduction

Previous studies with ytterbium in oxalate solutions[3] have demonstrated that the determination of concentrations by radioassay would permit the evaluation of equilibrium constants for the system. The present paper describes results of similar experiments with neodymium and cerium. Since the lighter rare earths have greater ionic radii,[4] it was expected that the degree of complexing would be less and a lower solubility in oxalate would result. The data presented in this paper for neodymium and cerium confirmed the lower solubility but indicated that the complexes were not substantially weaker. The behavior of cerium was markedly different from that of ytterbium and neodymium in that definite evidence was found for the formation of a trioxalate complex.

We wish to express our appreciation to Dr. F. H. Spedding, and Messrs. T. Butler and J. Powell, who prepared the very pure sample of neodymium oxide, for their assistance, interest and encouragement of this work.

Experimental

Materials.—As source material for cerium, a sample of cerium(IV) ammonium nitrate standard of reference supplied by the G. Frederick Smith Co. was used. This material was analyzed spectroscopically in this Laboratory, and other rare earths were not detected. A sample of cerium(IV) oxide was prepared from this sample and irradiated in the Argonne National Laboratory pile for three months to prepare the Ce^{141} isotope. Ce^{141} has been reported to decay with a half-life of 28–32 days by emission of β^- with a maximum energy of 0.53 mev. and with a partially converted 0.146 mev. gamma ray accompanying 70% of the disintegrations.[5,6,7]. Ce^{139} with a 140 day half life would not have been formed in sufficient quantities to be significant.[8] However, the formation of the 33 hour Ce^{143} which decays to a β-emitting daughter Pr^{143} with a half-life of 13.8 days would be expected to introduce a significant radioactive impurity into the sample.[9] To eliminate the praesodymium fraction, the irradiated sample was reduced to the Ce^{III} state and then incompletely oxidized to Ce^{IV} with sodium bromate. A precipitation of the cerium(IV) iodate according to the procedure of Boldridge and Hume[10] was then effected. Finally, the cerium(IV) iodate was reduced by hydrogen peroxide in sulfuric acid solution and the oxalate precipitated and washed until no barium sulfate test was obtained on the wash solution.

Standard solutions were prepared from samples of 50–100 mg. of CeO_2 weighed on an analytical balance. Aliquots of these solutions withdrawn by means of micro pipets and mounted for counting in the normal procedure yielded specific activities for second shelf geometry of 3×10^6 ct./(min.)(mg. Ce).

Absorption and decay curves indicated no appreciable radioactive impurities.

A sample of the Lindsay Light Co. neodymium carbonate was the neodymium source material. The product was supplied to us after two separations in ion exchange columns[11] and was reported as "spectroscopically pure." It is believed that the upper limit of any rare earth impurity was less than 0.1%.

The neodymium oxide was irradiated with slow neutrons for one month in the Argonne National Laboratory pile to form Nd^{147} which decays by the emission of a 0.9 mev., β^- or a β^- and 0.58 mev. γ with a half-life of 11.0 d.[12,13] The daughter isotope Pm^{147} is also radioactive, decaying by the emission of a 0.2 mev. β^- with a half-life of 3.7 years.

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