

directly to CO₂. 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).

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

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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 C¹⁴-labeled primary alcohols containing 2, 3 or 4 carbon atoms are added to a 1:1 H₂: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 C₁₀) 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 shown² 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 H₂ 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 C₁ complex should be derivable from either adsorbed methanol or adsorbed formaldehyde (enol form). The present authors⁸ 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-

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

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

(3) 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, p. 592.

(4) S. Weller and R. A. Friedel, *J. Chem. Phys.*, **17**, 801 (1949).

(5) R. B. Anderson, R. A. Friedel and H. H. Storch, *ibid.*, **19**, 331 (1951).

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

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

(8) W. K. Hall, R. J. Kokes and P. H. Emmett, *THIS JOURNAL*, **79**, 2983 (1957).

TABLE I
 SUMMARY OF SYNTHESIS VARIABLES FOR TRACER RUNS

Run no.	H7 ^d Fe	H19 ^c Fe	H15 ^e Fe	K20 ^c Fe	K10 ^d Fe	K16 ^c Co	K13 ^c Co
Catalyst ^a	D3001[R]	D3001[R]	D3001[R]	614[R]	D3001[N]	108B[R]	108B[R]
SVH	247	100	300	200	100	150	150
Temp., °C.	245-275 ^b	241	242	239	215	190	187
% Contraction	15-7	62-63	68	29	70	52	53
Duration, hr.	37	27.5	8	26	~240	11	9
Pressure, atm.	1	7.5	21.5	1	7.5	1	1
% ethanol in syn. gas	1.5	1.0	1.3	.06	1.0	1.5	.04
Activity ethanol, c./min. cc.	6940	7000	5965	75000	7260	6030	75000
Total liq., g.	12.3	10.7	..	18.8	15.4
Total CO ₂ , g.	47.7	25.5	..	1.7	1.4
Gaseous products	Composition of gaseous products (vol. %)						
CH ₄	5.1	54.7	39.1	16.7	48.6	64.6	72.9
C ₂ H ₄	44.6	8.1	16.8	14.1	6.3	0.0	0.5
C ₂ H ₆	5.8	10.7	12.6	22.1	15.4	9.4	8.1
C ₃ H ₆	29.0	13.4	19.0	26.3	14.9	6.2	3.0
C ₃ H ₈	2.0	3.9	4.7	6.0	4.9	11.0	8.8
C ₄ H ₈	10.6	5.7	5.0	10.2	5.2	3.2	1.9
C ₄ H ₁₀	1.0	1.5	1.7	1.8	2.3	3.8	3.2
C ₅ H ₁₀	1.8	1.3	0.7	2.3	1.4	0.6	0.5
C ₅ H ₁₂	0.1	0.6	0.2	0.5	1.0	1.1	1.0

^a The symbols [R] and [N] mean reduced and nitrated. ^b The temperature was continuously raised during the run to maintain the same contraction. ^c In this run the methyl carbon atom was radioactive. ^d In this run the methylene carbon atom was radioactive.

ments contained about 1-1.5% radioactive ethanol. Also made were two experiments in which the synthesis gas contained about 0.05% strongly radioactive ethanol in the synthesis gas. These two runs, both at atmospheric pressure, were carried out over a singly promoted iron catalyst and over a cobalt catalyst.

Experimental

The experimental procedures are only outlined below, since detailed accounts of the equipment and the procedures used have been given in earlier publications.^{1,2,3,9}

Syntheses at one atmosphere were performed in the fixed bed Fischer-Tropsch unit described in the first paper of this series. The runs at higher pressures were carried out in cooperation with the U. S. Bureau of Mines at Bruceton, Pennsylvania.

Gaseous synthesis products were separated into C₁, C₂, C₃, C₄ and C₅ cuts in a Podbielniak column. The individual cuts were analyzed for radioactivity, after which the olefins were removed in a scrubber and the residual gas was again analyzed for radioactivity. Subsequent mass spectrographic analysis made it possible to calculate the activity of olefins and paraffins as a function of carbon number.

Except for one instance, the liquid products were first washed with water, separated and then distilled from sodium hydride to remove the residual water, unreacted alcohol and other products containing oxygen. The liquids were then fractionated by low temperature distillation in high vacuum and burned to CO₂. From the volumes of the gaseous cut and the CO₂ produced, and the activity of the CO₂, the radioactivity of the cut could be calculated on a molar basis.

In run no. K10 over the nitrated catalyst, the procedure for handling the liquids was modified to permit separation of the alcohols from the hydrocarbons. The liquid products were first distilled to remove the waxes, and then refluxed with alkali to remove the acids and to saponify the esters. This step probably also removed aldehydes and/or ketones. The oil layer was then chromatographed using Davison silica gel No. 923 (inactive to olefins) as an adsorbent and methanol as a displacement agent. The alcoholic fraction obtained was then cut on a spinning band column into eight fractions, the last four of which were found to be substantially

free of ethanol and methanol by mass spectrographic analysis. Except in the one case in which appreciable water was present, the carbon number was determined by a vaporometric method. From these data and the activity of the CO₂ formed on combustion, the radioactivity of the cuts could be calculated on a molar basis. Results of infrared analyses on these cuts showed that in spite of appreciable losses in the separation procedures, the cuts were substantially free of non-alcoholic organic contaminants and were 97 ± 2% pure on a molar basis. The hydrocarbon fraction from this run was analyzed in the standard fashion.

Three catalysts were used in this study. The singly promoted iron catalyst, no. 614, contained 0.64% Al₂O₃ and 2.00% ZrO₂ in addition to iron oxide. The doubly promoted iron catalyst, D3001, and the cobalt catalyst, 108B, are standard catalysts used by the U. S. Bureau of Mines at Bruceton, Pennsylvania.³ Catalyst D3001 contains Fe₃O₄ + 4.6% MgO, 0.6% K₂O, 0.6% SiO₂ and 0.6% Cr₂O₃. The cobalt catalyst, 108B, has the composition Co:ThO₂:kieselguhr, 100:18:100. For the sake of completeness, the catalyst used by Kummer, *et al.*,² in run J4 was No. 333; in addition to iron oxide, it contained 2.82% Al₂O₃ and 1.39% ThO₂.

Results

The experimental conditions are summarized in Table I along with the product distributions for the various tracer runs. In Table II, the radioactivities per cc. are listed for the products of each of these runs. Previous^{1,2} data have shown that a complete balance of inlet and exit radioactivity is not feasible owing to carbiding and wax retention on the catalyst; hence no attempts were made to effect a radioactive material balance.

In synthesis over the doubly promoted iron catalyst D3001, the gaseous product distribution is not strongly affected by increasing the pressure. The product distribution for a singly promoted catalyst was different from that for a doubly promoted catalyst. In the *control* runs at one atmosphere (not shown in Table I), it was found that the C₂ product from the singly promoted iron catalyst was about 85% paraffinic, whereas for the doubly

(9) R. B. Anderson, "Catalysis," ed. by P. H. Emmett, Vol. IV, Reinhold Publ. Corp., New York, N. Y., 1956, p. 40.

TABLE II
 SUMMARY OF RADIOACTIVITY

Run no. Catalyst	H7		H19		H15		K20		K10 ^a Nitrided		K16 ^{a,b,c}		K13 ^{a,c}	
	FeD3001		FeD3001		Fe614		Fe614		Fe D3001		Co108B		Co108B	
	C no.	Activ- ity ^d	C no.	Activ- ity ^d	C no.	Activ- ity ^d	C no.	Activ- ity ^d	C no.	Activ- ity ^d	C no.	Activ- ity ^d	C no.	Activ- ity ^d
Pressure, atm.	1		7		21		1		7.5		1		1	
Ethanol activity	6940		7000		5965		75,000		7260		6000		75,000	
Gaseous product														
CH ₄	1	0	1	18	1	5	1	367	1	0	1	53	1	40
C ₂ H ₄	2	918	2	332	2	56	2	2130	2	107	2	..	2	..
C ₂ H ₆	2	1580	2	505	2	113	2	4330	2	107	2	120	2	72
C ₂ as a whole	2	980	2	470	2	75	2	3475	2	107	2	120	2	72
C ₃ H ₆	3	1285	3	700	3	138	3	3685	3	103	3	93	3	25
C ₃ H ₈	3	1110	3	644	3	166	3	4760	3	107	3	69	3	69
C ₃ as a whole	3	1260	3	680	3	144	3	3893	3	105	3	79	3	56
C ₄ H ₆	4	992	4	603	4	145	4	3560	4	150	4	60	4	43
C ₄ H ₁₀	4	1215	4	562	4	147	4	4500	4	110	4	75	4	57
C ₄ as a whole	4	1010	4	585	4	145	4	3720	4	135	4	69	4	53
C ₅ H ₁₀	5	..	5	467	5	104	5	3210	5	123	5	..	5	..
C ₅ H ₁₂	5	..	5	417	5	152	5	3790	5	69	5	..	5	..
C ₅ as a whole	5	940	5	460	5	124	5	3310	5	109	5	54	5	..
CO	~0		~0		~0		~0		~0		~0		~0	
CO ₂	~0		~0		~0		~0		~0		~0		~0	
Liquid products	5.24	1225	5.10	530	5.42	131	5.04	3166	5.21	82	5.30	89	5.57	62
	6.24	1227	5.41	463	5.56	143	5.25	3274	7.06	97	6.31	110	5.83	49
	6.55	1265	6.40	489	5.78	124	5.57	3415	7.54	90	6.24	47
	6.69	1333	7.24	438	5.93	124	6.25	3570	6.60	86	6.78	105	6.80	53
	6.82	1329	8.23	415	6.74	131	5.90	3300	7.72	95	7.66	112	7.42	51
	7.76	1375			6.70	176	6.86	3600	8.00	99	7.53	108	7.73	50
	8.15	1328			6.65	159	6.42	3280	7.54	96				
					6.97	211	8.20	3670						

^a The precision of these data is about ± 7 c./m./cc. hydrocarbon. ^b In this run the activities of the olefins and paraffins of a given cut were calculated on the basis of the amount absorbed by an olefin scrubber rather than by a subsequent mass spectrographic analysis. ^c In these two runs the yield of C₅ products was so low only the activity of the total C₅ cut could be determined. The yield of ethylene was also quite low ($\sim 1\%$ of the C₂ cut); hence, the activity of the ethylene could not be determined. ^d Activity in c./min./cc.

promoted catalyst it was 85% olefinic. This may be a consequence of the known lower hydrogenation activity of the doubly promoted iron catalyst compared to those containing no alkali.¹⁰ Furthermore, although it had been previously noted² that ethanol addition definitely retarded the synthesis reaction over singly promoted catalysts at one atmosphere, this effect was not found in the present studies.

The gross results of these experiments are summarized in Table III, which gives the fraction of the products formed from the alcohol (per cent. incorporation) *vs.* synthesis variables for all the experiments herein reported. For the sake of comparison, a representative run reported by Kummer, *et al.*,² has been included. Runs H7, H19 and H15 yielded data for the same catalyst under different synthesis conditions. In these runs, the temperature, contraction and synthesis pressure vary. There does not appear to be a clear relation between the per cent. incorporation and either the temperature or the contraction; on the other hand, it does appear that the per cent. incorporation decreases with increasing pressure.

The variation of the molar radioactivities with carbon number for runs over the doubly promoted catalyst is illustrated by the curves in Fig. 1.

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

Their qualitative features are quite similar, even though they were carried out at different pressures. The plots all show a maximum in the C₃-C₄ region and a trend toward a local minimum in the curves at about C₅.

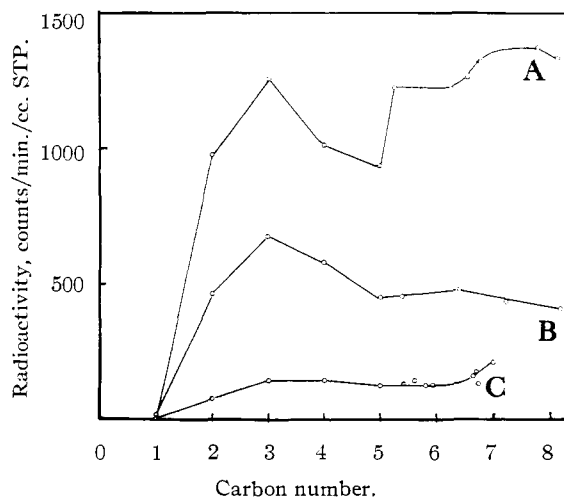


Fig. 1.—Influence of pressure in ethanol tracer runs over doubly promoted iron catalysts, D3001: A, H7, 1 atm 245–275°; B, H19, 7.5 atm., 241°; C, H15, 21 atm., 242°.

TABLE III
 ETHANOL INCORPORATION

Run no.	Catalyst ^a	t, °C.	Pressure, atm.	% Contraction ^b	% Ethanol ^c	% Incorp. ^d
J4 R Fe	Singly promoted	225	1.0	23	1.5	35
K20 R Fe	Singly promoted	239	1.0	29	0.46	5
H7 R Fe	Doubly promoted ^e	245-275	1.0	7-15	1.5	18
H19 R Fe	Doubly promoted	241	7.5	63	1.0	7.2
H15 R Fe	Doubly promoted	242	21.0	68.70	1.33	2.7
K10 RN Fe	Doubly promoted	215	7.5	70	1.0	1.4
K13 R Co	On kieselguhr	187	1.0	53	0.04	0.07
K16 R Co	On kieselguhr	190°C.	1.0	52	1.5	1.6

^a The symbols R and N refer to reduction and nitriding, respectively. ^b This is an average value for the whole run.

^c This is the volume % ethanol in the synthesis gas. ^d % incorporation = $\frac{\text{activity products (C}_2^+ \text{) c./m./cc.}}{\text{activity of added ethanol c./m./cc.}} \times 100$. ^e This doubly promoted catalyst was inferior to the singly promoted catalyst for synthesis at one atmosphere. In order to maintain even the low level of contraction the temperature was increased continuously throughout the run.

The effect of increased pressure on ethanol incorporation is clearly evident from Fig. 1. The average incorporation falls from 18 to 7 to 2.2% as the pressure is increased from 1 to 7.5 to 21 atm. In the case of one of these runs (H7), the catalyst was so unstable (see footnote *e* of Table III) that the *detailed* features of the plot of radioactivity *vs.* carbon number are questionable. For this reason, any general remarks made in the discussion pertaining to the shape of the activity *vs.* carbon number curves of all the tracer runs herein reported need not necessarily apply to run H7. In spite of this difficulty, it is clear that in this run as well as in runs H19 and H15 the ethanol is acting primarily as a chain initiator.

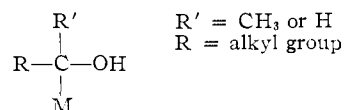
The effect of alkali on the incorporation of ethanol can be deduced from the data in Table III, where data obtained with the singly promoted iron catalyst at one atmosphere, run J4 previously reported by Kummer, *et al.*,² are compared with those obtained from run H7. In run H7, insofar as it was possible, the conditions were similar to those used in run J4, except that the doubly promoted catalyst was used. Incorporation in these two runs was found to differ by a factor of 2, with the run over the doubly promoted catalyst showing the lower incorporation.

In the standard tracer experiments carried out previously,² the concentration of ethanol in the synthesis gas was always about 1 to 1.5% by volume. In such runs at one atmosphere over singly promoted catalysts, about 35% of the products were formed from the radioactive ethanol. Since in these runs, $\frac{1}{3}$ of the products originate from a C₂ chain initiator rather than the normal C₁ chain initiator, the net effect must be to skew the product distribution from that typical of normal synthesis. How much this will tend to obscure the normal mechanism of the synthesis can only be determined by experiment. In run no. K20, conditions were similar to the other one atmosphere tracer experiments over singly promoted iron catalysts, except that the ethanol activity was much higher and the concentration of alcohol in the synthesis stream was lower, *i.e.*, about $\frac{1}{25}$ that in the standard tracer runs. The data obtained (Table III) show that the synthesis details for this experiment were quite similar to those for run no. J4. The incorporation, however, was only about

5% or $\frac{1}{7}$ th that of J4; consequently, the effect of alcohol addition on the product distribution was relatively small. In Fig. 2, activity *vs.* carbon number curves are given for runs K20 and J4. The qualitative differences in these two curves are striking; in fact, the curve for run K20 more closely resembles the runs over doubly promoted catalysts (Fig. 1) than it does J4. These results suggest that the qualitative differences between run J4 and all the runs herein reported for iron catalysts are principally a result of the higher incorporation in run J4 and the concomitant skewing of the product distribution rather than any fundamental difference brought about by changes in synthesis pressure or catalyst composition.

In runs J4 and K20, the over-all reaction rate is comparable. Thus, the incorporation divided by the per cent. alcohol in the synthesis stream is roughly proportional to the fraction of the alcohol that reacts. These values turn out to be about 23 and 83 for runs J4 and K20, respectively. If the reasonable assumption is made that the rate of build-in of the alcohol is proportional to the surface concentration of alcohol, θ , the fact that the fraction of alcohol reacting falls off with increasing alcohol partial pressure indicates that the adsorption of ethanol is medium strong.

In the chain building scheme put forward by Kummer, *et al.*,² adsorbed alcohol complexes of the type



are presumed to be the chain initiators and the complex where both R and R' are H may also act as a build-in unit. Hydrocarbons may be produced by a variety of reactions.³ Alcohol production could most simply be allowed for by hydrogenation of the carbon-metal bond, *i.e.*, reversal of the adsorption process. In any case, if this proposed mechanism is correct, the alcohol products (C₃ and higher) from tracer experiments wherein the synthesis gas contains labeled ethanol should give the same molar activity *vs.* carbon number plot as the hydrocarbons, as these alcohols stem from common intermediates. Unfortunately, such an experiment is ordinarily difficult in the usual synthesis over iron catalysts because the yield of oxygen-containing or-

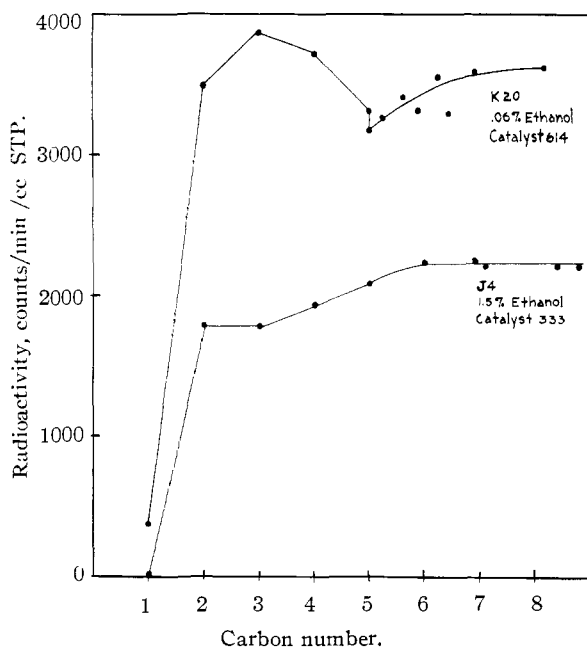


Fig. 2.—Concentration on incorporation over singly promoted catalysts. In run K20 the activity of the ethanol was 75,000 counts/min./cc. STP; in run J4, 6000 counts/min./cc. STP.

ganic products is so low. Recently,¹¹ however, it has been shown that nitrated iron catalysts yield a much higher percentage of alcohols than the reduced catalysts. This increased yield of alcohols does not require that the above discussed mechanism be discarded; it only requires that the relative rates of the various (particularly the chain termination) reactions involved be different on the nitrated catalyst. Tracer experiment No. K10 substantiates this view. In this experiment, the activities of the alcoholic products from C₃ through C_{5,4} were determined. Synthesis details for this experiment are given in Table I, where it may be noted that it was considerably longer than any of the others. This was necessary in order to obtain a sufficient yield to permit an efficient separation of the alcohols. The activity data for the hydrocarbon products from this experiment are summarized in Table II, while results for the alcohol fractions are given in Table IV. These same data are also illustrated in Fig. 3. Qualitatively, the plots are similar to those obtained for the reduced doubly promoted catalyst at the same pressure. Quantitatively, there is a significant difference in the magnitude of the incorporation. That for the reduced catalyst is almost five times greater than that for the nitrated catalyst. This difference, together with the qualitative similarity of the curves, lends support to the contention that the mechanism of synthesis is similar over the two catalysts, but that the various rates involved are different. Although the activity data for the alcohols are subject to larger errors than those obtained from the hydrocarbons, it is quite evident that the *average* activities of the alcohols and hydrocarbons are the same within experimental

(11) J. F. Shultz, E. Seligman, L. Shaw and R. B. Anderson. *Ind. Eng. Chem.*, **44**, 397 (1952).

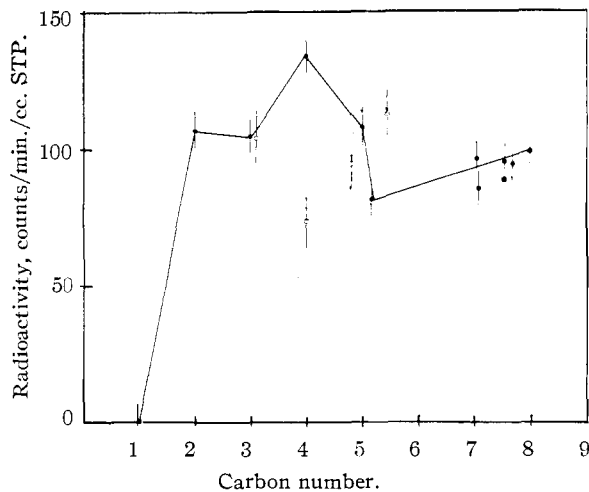


Fig. 3.—Ethanol tracer runs over a nitrated iron catalyst at 7.5 atm. and 215°. The assumed precision of the data is indicated by the length of the vertical lines: O, alcohols; ●, hydrocarbons.

error. This agreement would be expected on the basis of a mechanism which presumes that the alcoholic and hydrocarbon products both arise from the same complex. Qualitatively, the variation of alcohol activity with carbon number appears as if it might be different from that for the hydrocarbons insofar as it shows a minimum at C₄ rather than a maximum (Fig. 3).

TABLE IV
ACTIVITY OF ALCOHOL FRACTION OF LIQUID PRODUCTS FOR RUN NO. K10

Fraction ^a	Mol. wt. ^b	Carbon no. ^b	CO ₂	Activity, c./min./cc. Alcohol
5	62.4 (60.4)	3.1	33.5	104
6	59.4 (62.0)	4.0 ^c	18.6 ^c	74 ^c
7	85	4.8	19.8	95
8	93.5	5.4	21.1	113
				Av. 96 ± 10
				Av. for hydrocarbons in this range 110

^a These four samples were ethanol-free according to mass spectrographic analysis. ^b Molecular weights were determined vaporometrically. Check results are given in parentheses. Except for cut no. 6 carbon numbers were calculated using the data in column 2. ^c Mass spectrographic analysis showed this cut to be pure butanol plus some water. Distillation data also indicated this. Since small amounts of water would affect considerably the vaporometric molecular weight, the data in column 2 were ignored and those in columns 3, 4 and 5 were calculated assuming the cut was pure butanol.

In addition to the runs on iron catalysts, two runs were made on cobalt catalysts (K13 and K16). In these experiments, the H₂:CO ratio was 2:1 and, of course, the operating temperature was lower. In runs K16 and K13, the synthesis stream contained 1.5 and 0.04% ethanol, respectively. The plots of radioactivity vs. carbon number, constructed from the data obtained, are presented in Fig. 4. In contrast to the results with iron, the incorporation is quite low (~2%). The shape of the curves is such as to indicate that ethanol, on adsorption, forms a complex which acts primarily as a chain initiator. In striking contrast to *all* the re-

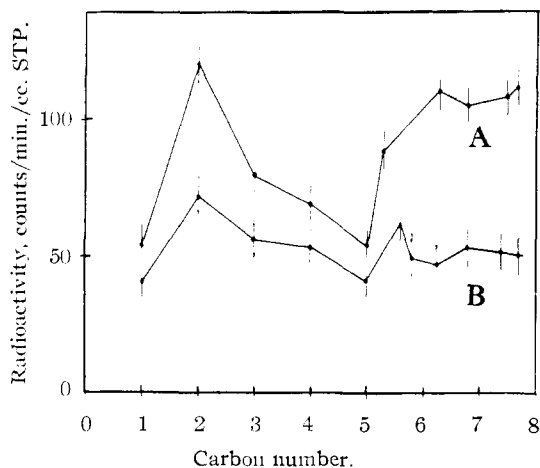


Fig. 4.—Ethanol tracer runs over a cobalt catalyst. The assumed precision of the data is as indicated by vertical lines. The activity of the ethanol in K13 was 75,000 counts/min./cc. STP; in run K16, it was 6030: A, K16, ethanol 1.5%; B, K13, ethanol 0.04%.

sults for ethanol tracer experiments with iron catalyst, however, the C_2 products had the highest activity. One possible explanation of this behavior is that the ethanol itself does not build-in, but that it does dehydrate to ethylene which will build-in over cobalt catalysts.¹² Since Co is an excellent hydrogenation catalyst, it would be expected that proportionately more ethylene would hydrogenate to ethane than would build-in, so that the C_2 products would have the highest radioactivity. An attempt was made to check this hypothesis by cracking the propane fraction. The results of this experiment were expected to show whether or not addition always took place preferentially on the carbinol carbon atom; unfortunately, the activities of the cracked products were so low that the experiment was inconclusive.

The activity of the methane fraction was quite high, indicating that appreciable cracking took place. If all of this came from the C_2 fraction, roughly one ethanol molecule cracked for every one that reacted to form higher molecular weight products. These results are definitely different from those obtained with iron catalysts. Even in the run in which cracking occurred to the greatest extent (K20), only about one ethanol molecule cracked to methane for every 10 or 15 that built in. It seems likely, therefore, that the same mechanism is not operative over iron and cobalt catalysts. This supposition finds some support in the available data on the product distributions and conditions required for synthesis over cobalt catalysts; these are quite different from similar data on iron catalysts.³

The effect of the ethanol concentration on its incorporation over cobalt catalysts is made evident by comparing runs K13 and K16 in Table III. Use of the same arguments here as for iron, shows that the fraction of the ethanol that undergoes build-in changes by less than a factor of 2 for an approximate 40-fold change in concentration, whereas in

the case of iron the change was ~ 3.5 for a 25-fold concentration change. This, too, is in approximate accord with the suggestion that the mechanism is not the same over iron and cobalt catalysts.

Discussion

Many features of the ethanol incorporation with iron catalysts can be explained in a crude way on the basis of competitive Langmuir adsorption, if it is assumed that the rate of build-in of ethanol is proportional to the fraction of the surface covered with adsorbed ethanol, θ_2 . For competitive Langmuir adsorption

$$\theta_2 = \frac{K_2 X_2 P}{1 + P \sum K_i X_i} \quad (1)$$

where K_i and X_i are the equilibrium constant and mole fraction, respectively, of the i th species, and P is the total pressure. If the rate of synthesis is proportional to the total pressure,¹² then, to a first approximation the per cent. incorporation, I , will be proportional to the ratio of the rate of ethanol build-in to the rate of normal synthesis, *i.e.*

$$I = k' \frac{K_2 X_2}{1 + P \sum K_i X_i} = k' \frac{K_2 X_2}{1 + PK_2 X_2 + \sum' PK_i X_i} \quad (2)$$

where k' is a ratio of rate constants and where the \sum' excludes the term for ethanol. Table III contains data for runs (K20 and J4) at $P = 1$, which differed only in the concentration of ethanol in the synthesis stream. The ratio of the incorporation (7/1 is the ratio of the incorporation for J4 to that for K20) can be used to obtain estimates of the θ_2 in these runs. Equation 2 (assuming $\sum' K_i X_i$ is about the same for both runs) yields

$$\frac{7}{1} = \frac{0.015 K_2}{1 + 0.015 K_2 + \sum' K_i X_i} \times \frac{1 + 0.0006 K_2 + \sum' K_i X_i}{0.0006 K_2} \quad (3)$$

which reduces to $1 + \sum' K_i X_i = 5 \times 10^{-3} K_2$. Insertion of this admittedly crude estimate back into (1), reveals that in run J4 about 80% of the surface is covered with the ethanolic complex, while in run K20 the corresponding value is 12%.^{12a}

The above estimates readily can be extended to the variation of incorporation with synthesis pressure for a fixed amount of alcohol in the synthesis gas. The data in Table III show that the incorporation at atmospheric pressure with a doubly promoted catalyst (run H7) is only about $1/2$ that observed for the singly promoted catalyst. Provided that k' of (2) is independent of the alkali promoter, then θ_2 on the doubly promoted catalyst is about $1/2$ that on a singly promoted catalyst, *viz.*, about 0.4, as with the singly promoted catalyst it was concluded above that in the neighborhood of 80% of the available surface was covered with ad-

(12a) The calculations based on equations (1), (2), (3) and (4) are admittedly speculative and involve numerous assumptions. They should probably be considered as more qualitative than quantitative. A typical difficulty that arises from a quantitative interpretation is illustrated by the figure "80%" for the percentage of the surface covered by "adsorbed ethanol complex" in run J4. If this adsorbed complex were identical to that formed from carbon monoxide and hydrogen during synthesis, then most of the hydrocarbon products would have been radioactive. Actually only one molecule in three of the hydrocarbon products in run J4 was radioactive. Presumably one must therefore conclude that only a fraction of the adsorbed ethanol complex is of the type that participates in the actual synthesis of higher hydrocarbons.

(12) R. B. Anderson, "Catalysis," ed. P. H. Emmett, Vol. IV, 288, Reinhold Publ. Corp., New York, N. Y., 1955.

sorbed ethanol. Within the framework of the present discussion, all precursors to hydrocarbon products may be viewed as adsorbed alcohols, so that in this instance there can be little bare surface. With the doubly promoted catalyst, if the same ratio exists between adsorbed ethanol and remaining alcoholic complexes, an upper limit for the coverage of the rest of the surface can be set, which cannot exceed 0.2. The total surface coverage then becomes ≈ 0.6 with the doubly promoted catalyst. Thus

$$1 - \theta = \frac{1}{1 + \sum K_i X_i} = 0.4 \quad (4)$$

and $\sum K_i X_i = 1.5$. Using this value in (2), the incorporation at 21 atm. can be calculated to be about $1/13$ th the incorporation at one atm. The actually observed value is about $1/8$, but in view of the crudeness of the approximations this may be taken as in fair agreement with the calculated value.¹³ It is implicit in the solution of (4) that the relatively large uncovered fraction comes about through small values of the K_i , rather than mechanical blockage with alkali. This appears to be justifiable, since $\theta = \sum \theta_i$ may be taken as the fractional coverage of available surface, without altering the result.

This picture can be used to explain the fact that Kummer, *et al.*,⁴ found that the addition of ethanol retards the synthesis, whereas in the present experiments, this was not found to be the case. Kummer found that when 1.5% ethanol was added to a synthesis gas stream, which was subsequently passed over a singly promoted iron catalyst, it was necessary to raise the temperature about 12° over that used for the control run with no ethanol added. Use of the experimentally determined activation energy (~ 20 kcal./mole)¹⁴ indicates that the normal rate of synthesis should increase by a factor of 1.7 for such an increase in temperature. Moreover, since 35% of the products originate from the ethanol, the rate increase should be even greater (*i.e.*, ≈ 2.3). Thus, if the temperature were kept constant, the rate of synthesis from the normal C₁ complex would be reduced to about 40% of its value when the alcohol is introduced. Estimates presented above indicate that in the tracer runs of Kummer, *et al.*² (*e.g.*, J4, Table III), the adsorbed ethanol covered about 80% of the surface. Thus, at most, only about 20% of the surface was available for normal synthesis in those runs. Under the conditions where the ethanol build-in is small (run K20), only $\approx 12\%$ of the surface is covered with the ethanolic complex. In normal synthesis, therefore, as much as 85 to 90% of the surface is available for formation of the C₁ complex. Since it is likely that the rate of normal synthesis is proportional to the concentration of the C₁ complex,⁷ a decided poisoning on ethanol addition would be expected for the former situation (*e.g.*, J4). This poisoning would be correspondingly less for runs in which the incorporation was small. In fact, in all

the runs reported in Table III except for J4 and H7 it would not be experimentally observable. Unfortunately, in run H7 conditions were such that the poisoning could not be observed (see footnote *e* in Table III).

In normal synthesis the production of alcohols is generally smaller with reduced singly promoted catalyst than with reduced doubly promoted catalysts. The yield of alcohols can be further increased when using the latter catalysts by an increase in pressure.³ Lastly, nitrided doubly promoted catalysts yield much more alcohol than the corresponding reduced catalysts at the same pressure.¹¹ It is interesting to note in Table III that as the synthesis conditions are altered in such a direction to make alcohol production more favorable, the percentage of tracer ethanol incorporated falls off. Examination of (2) reveals that such a fall off in *I* is most likely to be brought about by a decrease in K_2 . Since presumably the adsorption of the alcohol-type complex is one point adsorption at the carbinol carbon atom,² this decrease in K_2 would indicate a similar decrease in the adsorption equilibrium constants for all the alcohols. This can be viewed as a relative increase in the desorption rate of the alcohols. This prediction, based on (2), would lead to the conclusion that in normal synthesis the alcoholic complex is more likely to evaporate from the surface and increase the yield of alcohols under the synthesis conditions which lead to a relatively low incorporation of ethanol in a tracer run.

It is interesting to note that whereas cobalt catalysts show a relatively low incorporation of ethanol it is also well-known that cobalt catalysts produce very low yields of alcohols. This discrepancy with the predictions of (2) in addition to the differences noted earlier between cobalt and iron catalysts, tend to support the suggestion that the predominant synthesis mechanism is not identical over the two metals.

In the discussion thus far, the qualitative differences in ethanol incorporation for different runs over iron catalysts under different synthesis conditions have been ignored. Figures 1, 2 and 3 illustrate the various types of behavior observed. In run J4 the incorporation was large ($\sim 35\%$). The activity per cc. was the same for the C₂ and C₃ products, but increased slightly between C₃ and C₆ ($\approx 20\%$); it again became constant for the C₆⁺ hydrocarbons. In run K20, which like run J4 was carried out at one atmosphere over a singly promoted catalyst, the incorporation was low. This plot of radioactivity per cc. *vs.* carbon number shows a maximum in activity in the C₃-C₄ region and a local minimum at C₅ followed by a small increase in activity for C₆⁺ products. The total variation in activity is about 20%. The curves for the reduced and nitrided doubly promoted catalysts all show the maximum in the C₃-C₄ region, although not all of them show the minimum at C₅. As already mentioned it appears that the maximum occurs whenever the incorporation is low, and is independent of the catalyst composition or the synthesis pressure.

In terms of the simple chain building picture mentioned earlier the molar activity should be independent of carbon number. The observed varia-

(13) In order to obtain a numerical estimate of the fall off in *I* with synthesis pressure, it is necessary to make some assumption regarding the surface coverage at one atmosphere, *i.e.*, that the surface was 60% covered. Even without this assumption, however, eq. 2 predicts, qualitatively, the fall off in incorporation as the pressure is increased.

(14) R. B. Anderson, "Catalysis," ed. by P. H. Emmett, Vol. IV, Reinhold Publ. Corp., New York, N. Y., 1956, p. 285.

tion with carbon number appears to increase as the incorporation decreases. For example, the ratio of the peak activity to the C_2 activity (a measure of the variation) is 1.29 and 1.45, in runs H7 and H19, whereas the incorporation is 18 and 7.2%, respectively. This suggests that when the normal synthesis is least disturbed by the added alcohol the variation of radioactivity with carbon number is most pronounced. For the most part, however, the activity is fairly constant ($\sim \pm 20\%$) so that the simple hypothesis advanced by Kummer and Emmett¹ is probably close to the truth. These shortcomings of the theory do suggest, however, that even though the alcohol-type complexes are the principal chain initiators, some other species are also capable of acting in a similar capacity.

The nature of the chain initiator is indicated by the results obtained by Kummer, *et al.*² They found that 90% of the propane formed in ethanol tracer runs appeared to be obtained by addition to the α carbon atom of the methylene-labeled ethanol, and the remainder by the addition to the β -carbon atom. It was also established that the hydroxyl group of the unreacted ethanol had not migrated to the unlabeled carbon atom. Thus, it appears that a small fraction of the ethanol reacted to form some species in which the two carbons were indistinguishable and which could also build-in to form higher hydrocarbons. Clearly, this suggests that ethylene formed by the dehydration of ethanol is

capable of build-in over iron catalysts to form higher hydrocarbons. This has been known to be the case with cobalt catalysts for some time¹⁵ and the present authors have shown that when radioactive ethylene is introduced into the synthesis stream some build-in occurs.⁷ Thus, the results with propane suggest that 80% of the propane comes from ethanol with all the addition taking place on the labeled (methylene) carbon atom and 20% of the propane comes from radioactive ethylene with the addition to the labeled carbon occurring only 50% of the time. It seems probable that this effect contributes heavily to the above-mentioned skewing of the radioactivity *vs.* carbon number curves.

In conclusion, it should be emphasized that the mechanism of synthesis appears to be complex, with two or more intermediates functioning as chain initiators. In spite of this, however, the mechanism suggested by Storch, *et al.*,³ and Kummer, *et al.*,¹ is probably the predominant one operating in the synthesis over iron catalysts and is capable of explaining many of the observed facts.

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(15) R. B. Anderson, *ref. 14*, p. 317.

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The Free Radical Initiated Polymerization of Gaseous Unsaturated Hydrocarbons¹

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Methyl radicals from thermally decomposing di-*t*-butyl peroxide were found to initiate the polymerization of gaseous acetylene, 1,3-butadiene, ethylene and propene in the temperature range 130–165°. The rate of polymerization of each unsaturated hydrocarbon was proportional to the first power of the concentration of monomer and to the square root of the concentration of di-*t*-butyl peroxide. This is consistent with a three-step polymerization mechanism consisting of initiation by a unimolecular split of the peroxide into free radicals, propagation by addition of radicals to a multiple bond and termination by radical combination. From a consideration of the relationship between the activation energies of chain initiation, propagation and termination, and of the known values of the activation energies for initiation and termination, the activation energies for propagation of polymerization of acetylene, butadiene, ethylene and propene were determined to be 5.1, 4.9, 8.2 and 5.6 kcal./mole, respectively.

Introduction

Few of the studies of the polymerization of the simpler unsaturated hydrocarbons in the gas phase have been concerned with obtaining values of the activation energies for the chain propagation reactions or, alternatively, for the addition of atoms or radicals to the multiple bond. Raal and Danby² reported 6.8 kcal./mole as the activation energy for propagation of ethylene polymerization initiated in the gas phase by methyl radicals. James and Steacie³ give a preliminary value of 6–8 kcal./mole as the activation energy for the addition of ethyl

radical to heptene-1. Volman⁴ initiated the polymerization of butadiene by the thermal decomposition of di-*t*-butyl peroxide and reported 2.6 kcal./mole for the propagation activation energy. Volman and Graven⁵ later initiated butadiene polymerization by the photolysis of di-*t*-butyl peroxide and acetone and reported 5.4 kcal./mole for the propagation activation energy, in good agreement with Gee's value of 5.5 kcal./mole for the propagation step in the gas phase mercury-photo-sensitized polymerization of butadiene,⁶ and the estimate of White and Winkler⁷ of 5 kcal./mole for the addition of a hydrogen atom to butadiene. More recently,

(1) Based on a portion of a thesis presented by L. C. Landers in partial satisfaction of the requirements for the degree of Doctor of Philosophy in the University of California.

(2) F. A. Raal and C. J. Danby, *J. Chem. Soc.*, 2219 (1949).

(3) D. G. L. James and E. W. R. Steacie, unpublished work cited in E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1954, p. 581.

(4) D. H. Volman, *J. Chem. Phys.*, **19**, 668 (1951).

(5) D. H. Volman and W. M. Graven, *THIS JOURNAL*, **75**, 3111 (1953).

(6) G. Gee, *Trans. Faraday Soc.*, **34**, 712 (1938).

(7) W. H. White and C. A. Winkler, *Can. J. Research*, **26B**, 3 (1948).