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Abstract

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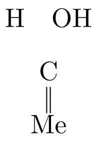
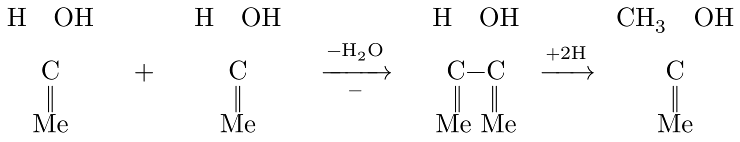
STUDY OF THE ROLE OF FLAT CHAINS IN THE SYNTHESIS OF HYDROCARBONS FROM CO AND H_2

It was shown by Kummer and Emmett (1) and by us (2) that, in the synthesis of hydrocarbons from CO and H_2 on iron and cobalt catalysts, with the addition of labeled alcohols to the initial synthesis gas, the molar radioactivity of the hydrocarbons obtained is constant and does not depend on the number of carbon atoms in the molecule. The constancy of the molar radioactivity found was regarded by the American investigators as confirmation of the dehydration-condensation scheme of synthesis proposed by Storch, Golombic, and Anderson (3). According to this scheme, from CO and H_2 on the surface there is formed a complex,



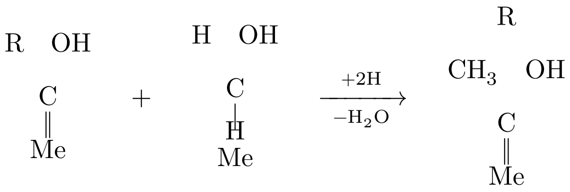
$$\begin{array}{c} \text{H}\quad\text{OH} \\ \text{C} \\ \| \\ \text{Me} \end{array}$$

similar in structure to methyl alcohol. In the comparatively rare reaction of two $CHOH_{ads}$ radicals, chemisorbed radicals CH_3COH are formed, which serve as the initial centers of growth of the hydrocarbon chain. The latter grows as a result of condensation reactions of the dehydration type and hydrogenation:



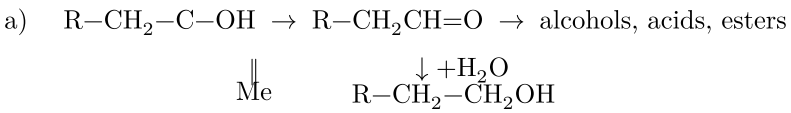
$$\begin{array}{c} \text{H}\quad\text{OH} \\ \text{C} \\ \| \\ \text{Me} \end{array} + \begin{array}{c} \text{H}\quad\text{OH} \\ \text{C} \\ \| \\ \text{Me} \end{array} \xrightarrow[-]{-H_2O} \begin{array}{c} \text{H}\quad\text{OH} \\ \text{C}-\text{C} \\ \|\quad\| \\ \text{Me Me} \end{array} \xrightarrow{+2H} \begin{array}{c} \text{CH}_3\quad\text{OH} \\ \text{C} \\ \| \\ \text{Me} \end{array}$$

which in general form may be represented as

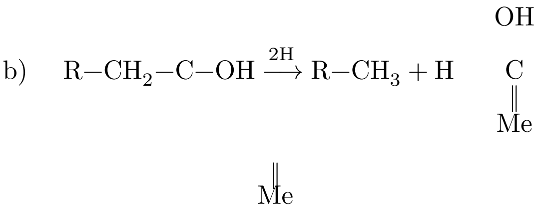


$$\underset{\underset{\text{Me}}{\parallel}}{\overset{\text{R}\quad\text{OH}}{\text{C}}} + \underset{\underset{\text{Me}}{\underset{\text{H}}{|}}}{\overset{\text{H}\quad\text{OH}}{\text{C}}} \xrightarrow[-H_2O]{+2H} \underset{\underset{\text{Me}}{\parallel}}{\overset{\overset{\text{R}}{\text{CH}_3\quad\text{OH}}}{\text{C}}}$$

with termination reactions:



$$\text{a)}\quad R{-}CH_2{-}\underset{\underset{\text{Me}}{\parallel}}{C}{-}OH \rightarrow \underset{\underset{R{-}CH_2{-}CH_2OH}{\downarrow +H_2O}}{R{-}CH_2CH{=}O} \rightarrow \text{alcohols, acids, esters}$$



$$\text{b)}\quad R{-}CH_2{-}\underset{\underset{\text{Me}}{\parallel}}{C}{-}OH \xrightarrow{2H} R{-}CH_3 + H\quad \underset{\underset{\text{Me}}{\parallel}}{\overset{\text{OH}}{\text{C}}}$$

As noted earlier (^{2}), the results of experiments with the addition of labeled alcohols to the initial synthesis gas are not an unambiguous proof of the correctness of the dehydration-condensation scheme, some of whose assumptions appear to us to be of low probability. To substantiate this

of the scheme, it is first of all necessary to prove that the constancy of the molar radioactivity of the hydrocarbons cannot be due to the addition to the synthesis gas of other labeled compounds, besides alcohols—for example, of some products of their conversion. In view of this, in our first experiments, as labeled compounds added to the initial synthesis gas, along with ethyl alcohol we also used acetaldehyde and methyl formate. The present communication gives the results obtained when labeled ethylene was added to the initial synthesis gas.

The study of the behavior of ethylene under the conditions of the synthine process was of special interest in connection with the results obtained in works (4,5) on the hydrocondensation of olefins with CO and the hydropolymerization of olefins in the presence of small amounts of CO. These works show the active participation of olefins in the growth of the hydrocarbon chain in the synthesis of hydrocarbons from CO and H_2 and in chain initiation. According to E. I. Orlov (6), under certain conditions ethylene may be the main product of the catalytic hydrogenation of CO. According to Kummer and Emmett (1), ethylene is formed under synthesis conditions in small amounts from the added ethyl alcohol. Consequently, favorable conditions for initiation by ethylene are present both in ordinary synthesis and in synthesis with the participation of ethyl alcohol. With the aid of labeled ethylene it could be hoped to determine whether ethylene in fact plays this role.

Table 1

Balance of experiments on the synthesis of hydrocarbons with the participation of ethylene

	Experiment No. 1	Experiment No. 2
Taken:		
Initial synthesis gas, l	102	105
Initial synthesis gas, g	48.6	49.7
Labeled ethylene, l	1.54	0.82
Labeled ethylene, vol. %	1.45	0.78
Duration of experiment, hr	39	41
Gas contraction, %	76	76
Obtained:		
Liquid hydrocarbons, g	8.4	7.9
Aqueous layer, g	16.8	18.5
Total radioactivity of hydrocarbons C_8 and higher, % of initial	24.5	26
Total radioactivity of ethane, % of initial	71*	55

	Experiment No. 1	Experiment No. 2
Total radioactivity of aqueous layer, % of initial	–	1.5

* The value given is possibly too high, since the radioactivity of C_2H_6 was calculated as the sum of the radioactivity of C_2H_6 separated from the condensable gases and the total radioactivity of the noncondensable gases, which contained appreciable amounts of gaseous hydrocarbons.

Experiments on the synthesis of hydrocarbons from CO and H_2 with the addition of ethylene labeled with C^{14} were carried out at 195° on a cobalt-thorium catalyst of composition $100Co : 18ThO_2 : 100$ kieselguhr.

The concentration of ethylene in the synthesis gas was 0.78 vol. % in one experiment and 1.45 vol. % in the other. The initial gas, of composition $1CO : 2H_2$, was fed into the reactor at a space velocity of 102–107 l/l • hr. The conditions of the experiments and the results of radiometric analysis of the hydrocarbons obtained are given in Tables 1 and 2. The dependence of the molar radioactivity on the length of the hydrocarbon chain of the hydrocarbon molecules is presented graphically in Fig. 1.

As follows from the data presented, the labeled ethylene in both the first and the second experiments is converted by more than 50% into ethane and enters by 25–26% into the composition of other hydrocarbons formed. Only to a very small extent does the formation of oxygen-containing compounds from ethylene occur, as follows from the insignificant radioactivity found in the aqueous layer in experiment 2 (see Table 1). The molar radioactivity of pentanes and hydrocarbons with a number of C atoms exceed-

Table 2

Specific and molar radioactivity of synthesis products*

Experiment No. 1	Experiment No. 1	Experiment No. 1	Experiment No. 2	Experiment No. 2	Experiment No. 2
reaction products**	sp. activity, counts per 1 mg $BaCO_3$ in 1 min	mol. activity, µCi/mmol	reaction products**	sp. activity, counts per 1 mg $BaCO_3$ in 1 min	mol. activity, µCi/mmol
CO_2	7	0.023	CO_2	6	0.007
CH_4	45	0.15	CH_4	200	0.24
C_2H_6	852	5.5	C_2H_6	3930	9.47

Experiment No. 1	Experiment No. 1	Experiment No. 1	Experiment No. 2	Experiment No. 2	Experiment No. 2
C_3	221	2.15	C_3	460	1.66
C_4	118	1.53	C_4	375	1.80
$C_{6 \cdot 3}$	142	2.92	$C_{5 \cdot 5}$	352	2.32
$C_{6 \cdot 6}$	121	2.58	$C_{6 \cdot 3}$	314	2.38
$C_{7 \cdot 0}$	107	3.00	$C_{7 \cdot 4}$	240	2.15
$C_{7 \cdot 7}$	93	2.32	$C_{7 \cdot 6}$	262	2.39
$C_{9 \cdot 0}$	77	2.25	$C_{9 \cdot 6}$	169	2.29
$C_{11 \cdot 0}$	85	3.02	$C_{10 \cdot 6}$	168	2.14
$C_{11 \cdot 9}$	75	2.92	C_{15}	139	2.50
C_{16}	63	3.25	C_{21}	87	2.19
C_{22}	45	3.20	C_{32}	58	2.23
C_{26}	30	2.53	starting C_2H_4	9120	21.9
starting C_2H_4	–	12.5			

* Radiometric analysis of experiments No. 1 and No. 2 was carried out on different counters with counting efficiencies of 3 and 7%, respectively.

** The number of C atoms was calculated from the molecular weights of the corresponding fractions on the assumption of a 100% paraffin content in them.

also, as in the experiments with labeled alcohols, is practically constant and does not depend on the chain length of the hydrocarbon molecules. This result indicates the participation of ethylene in the initiation of material chains on the catalyst. The possibility that ethylene participates in chain termination, which could likewise lead to constancy of the molar radioactivity, is excluded in view of the intensive participation of ethylene in the growth of material chains, proved by the work of Ya. T. Eidus, N. D. Zelinskii, and others(5), as well as by the data of the present work, which show the absence of a decrease in product yield with increasing ethylene concentration in the initial gas. The specific radioactivity α of the C_3 and C_4 fractions is 1.3–1.8 times lower than α of the heavier fractions. This may indicate a noticeable participation of other reactions in their formation. The high value of α for ethane shows the large role of hydrogenation in its formation. A comparison of the results of the present and previously published works(1,2) leads to the conclusion that, under identical conditions, ethylene participates to a considerably greater extent than ethyl alcohol in the formation of hydrocarbons. At the same space velocity (100 l/l • h) and equal concentrations of the labeled components in the initial synthesis gas (1.45 vol.%), the radioactivity of hydrocarbons C_3 and higher amounted, in the experiment with ethylene, to 24.5%, while in the experiment with ethyl alcohol it was about 6% of the initial radioactivity of the labeled compound. Under identical conditions, ethylene participated in the formation of, on average, one out of every 4–5 molecules of the hydrocarbons formed, whereas ethyl alcohol

Figure 1. Dependence of the molar radioactivity of hydrocarbons on the length of their molecules in an experiment with addition to the initial synthesis gas of 1.45 vol.% $C^{14}CH_4$ (a) and 0.78 vol.% $C^{14}CH_4$ (b)

Figure 1: Figure 1. Dependence of the molar radioactivity of hydrocarbons on the length of their molecules in an experiment with addition to the initial synthesis gas of 1.45 vol.% $C^{14}CH_4$ (a) and 0.78 vol.% $C^{14}CH_4$ (b)

participated in only one out of eighteen. From these data it follows that initiation of chains by ethylene occurs more readily than initiation by ethyl alcohol. This makes probable the assumption that initiation by ethyl alcohol is caused by its preliminary conversion into ethylene. Thus, on the basis of our experiments with ethylene, one may doubt the correctness of the dehydration–condensation scheme of synthesis proposed by Storch, Golumbic, and Anderson, at least for synthesis over a cobalt catalyst.

Let us note that a change in the concentration of ethylene does not lead to substantial deviations from the constancy of the molar radioactivity of the hydrocarbons and practically does not change the ratio between hydrogenation of ethylene to ethane and conversion of ethylene into hydrocarbons C_3 and higher. Only deviations–

the ratio of the molar radioactivity of the initial ethylene to the average molar radioactivity of the hydrocarbons, equal to 9.6 at an ethylene concentration of 0.78 vol.%, fell to 4.5 at a concentration of the latter of 1.45%. Consequently, the participation of ethylene in the formation of heavier hydrocarbons increases in direct proportion to the ethylene concentration. These data, as well as the absence of changes in the yield of reaction products with a change in the ethylene concentration, can be explained by similar rates of formation of the initial center of the hydrocarbon chain along two parallel paths: with the participation of ethylene in the formation of the initial center and without its participation.

Fig. 1. Dependence of the molar radioactivity of hydrocarbons on the length of their molecules in an experiment with addition to the initial synthesis gas of 1.45 vol.% $C^{14}CH_4$ (a) and 0.78 vol.% $C^{14}CH_4$ (b)

The absence of substantial changes in the yield of reaction products with changing ethylene concentration likewise does not permit the ratio of the average molar radioactivity of the hydrocarbons to the molar radioactivity of the initial ethylene to be regarded as the number of material chains arising as a result of chain-transfer processes that began with adsorption of the ethylene molecule.

The results presented cast doubt on the correctness of alcohol-condensation schemes of the synthine process as applied to cobalt catalysts, as well as on the conclusions of American investigators drawn from experiments with labeled alcohols using iron catalysts. There are as yet insufficient data for a complete stepwise scheme of this process; however, the active role of ethylene (and perhaps of other olefins) in the synthine process, and the close similarity of the mechanism of the synthine process to hydrocondensation processes (^{4}), are already evident. It appears interesting to examine from this point of view other types of processes involving $CO + H_2$, and to study, with the aid of labeled compounds, the participation in reactions of this class of other ordinary and labile molecules over both Co and Fe catalysts. It would also be advisable to carry out experiments with labeled ethylene over Fe catalysts in order to determine the applicability of alcohol-condensation schemes of the synthine process to this group of catalysts.

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Note: Figure translations are in progress. See original paper for figures.

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