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ON THE UNITY OF THE MECHANISM OF THE SYNTHESIS OF HYDROCARBONS AND OXYGEN-CONTAINING COMPOUNDS FROM CO AND H_2

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Researchers working in the field of synthesis from CO and H_2 have proposed various schemes for the mechanism of synthesis, according to which the formation of hydrocarbons, on the one hand, and oxygen-containing compounds, on the other, proceeds by reaction pathways independent of one another ($^{1-5}$). Experimental data have been obtained, however ($^{1,6-9}$), which lead to the idea that there exists a certain unity of mechanism in the initiation of the synthesis process and in the construction of the carbon chains of aliphatic compounds from CO under the action of hydrogen.

Obtaining direct experimental proof of such unity in the mechanism of formation of hydrocarbons and alcohols from CO and H_2 is of very considerable interest. For this purpose, in the present work the pathways of transformation of alcohols were studied under real synthesis conditions, when the principal synthesis products consisted of a mixture of hydrocarbons and alcohols. The indicators of the behavior of the alcohols formed from CO and H_2 were labeled C^{14} butanol and methanol, added to the synthesis gas in amounts that did not disturb the conditions existing on the catalyst surface.

The experiments were carried out with fused iron catalysts at high pressures (100–150 atm) under conditions ensuring the production of approximately equal amounts of hydrocarbons and oxygen-containing compounds (chiefly alcohols). The reaction products obtained were separated into hydrocarbons and alcohols, and then distilled on a rectification column. Fractions from C_1 to C_9 and the residues were subjected to radiometric analysis by the method used previously (^{10}).

Typical results obtained upon addition of butanol-1-C^{14} to the initial gas mixture are given in Fig. 1.

Fig. 1. Specific activity of hydrocarbons (a) and alcohols (b) as a function of

Fig. 1

Figure 1: Fig. 1

carbon number (experiments with butanol of specific activity 780 imp/min per 1 mg $BaCO_3$).
1—concentration of butanol 0.04 vol.%; synthesis conditions: 150 atm, 200°, space velocity of $1CO + 2H_2$ equal to 2000 hr^{-1}; specific activity at the reactor outlet: butanol 386 imp/min, CO_2 3.8 imp/min, CO 0 imp/min;
2—concentration of butanol 0.1 vol.%; synthesis conditions: 90 atm, 160-180°, space velocity of $1CO + 4H_2$ equal to 500 hr^{-1}; specific activity at the reactor outlet: butanol 460 imp/min, CO_2 4.9 imp/min, CO 0 imp/min; butylene 0.15 imp/min.

Under the conditions employed, butyl alcohol possesses low reactivity. The bulk of the introduced labeled butanol (90-95%)

passes through the reaction zone unchanged. At the same time, it is clearly found that the labeled (and consequently also the unlabeled) butyl alcohol can, to a certain extent, take part in the formation both of higher alcohols and of the corresponding hydrocarbons. However, the specific activity of butanol at the reactor outlet in this case is about 400 pulses/min per 1 mg of $BaCO_3$, whereas the specific activities of the subsequent fractions are only units of pulses. These data show that less than one-hundredth of the hydrocarbons above C_4 and of the C_6-C_9 alcohols could have been formed with the participation of butanol.

Thus, the overall radioactivity balance and comparison of the specific activities lead to the unambiguous conclusion that butanol is not an intermediate product in the synthesis of hydrocarbons and oxygen-containing compounds from carbon monoxide and hydrogen on fused iron catalysts. Under these circumstances, the presence of radioactivity both in the hydrocarbons and in the alcohols (which moreover have specific activities of the same order) can be explained by the intermediate participation of a certain oxygen-containing complex, formed, although only to a small extent, from butyl alcohol upon interaction with the catalyst surface. This complex is apparently similar to the complex formed during synthesis on the catalyst surface from CO and H_2 and responsible for growth of the carbon chain. From this complex both hydrocarbons and alcohols are formed; moreover, as the carbon chain grows, the activity must naturally decrease owing to the successive addition of inactive carbon atoms, which is in fact observed.

From the positions set forth above, the anomalously high values of the specific activity of amyl and hexyl alcohols indicate the existence of an independent branch of alcohol transformations, not dependent on the main synthesis pathway. These transformations are evidently similar to the known reaction of alcohol homologation. The radioactivity caused by this series of transformations naturally falls sharply on passing from the lower alcohol to the higher one and, already beginning with heptyl alcohol, is practically no longer detected.

The activity observed in the C_7-C_9 alcohols, as well as the activity in the hydrocarbons, is due to growth of the oxygen-containing complex, which is the common progenitor for hydrocarbons and alcohols.

In experiment 2, when the concentration of radioactive butanol in the reaction mixture was increased by a factor of 2.5 (as compared with experiment 1), the specific activities naturally increased in all the fractions obtained, and the side reactions of the alcohols appeared to a greater extent (see Fig. 1). A maximum of specific activity appeared in the chain with 8 carbon atoms, which indicates the possibility, under favorable conditions, of intermolecular condensation of alcohols, in particular butanol, or else condensation of two surface C_4 complexes.

Dehydration of butanol under the conditions studied proceeds only to an insignificant extent, and therefore the observed distribution of radioactivity cannot be explained by reactions of butylene, which is confirmed by the results of studying the behavior of butylene under analogous conditions ([11]).

Of particular interest, from the point of view of the unity of the mechanism, was the study of the behavior of methanol under synthesis conditions from CO and H_2, since the latter, upon interaction with the catalyst, can give a formation containing only one C atom.

From the data obtained in this case it is seen (Fig. 2) that methanol under synthesis conditions undergoes various transformations much more readily than butanol: it decomposes to a considerable extent with formation of carbon monoxide and hydrogen, is oxidized to carbon dioxide, and takes part in the synthesis of alcohols and hydrocarbons. More than 1/10 of all hydrocarbons and alcohols could have been formed with the participation of methanol. The specific radioactivity of hydrocarbons and alcohols with the same chain length practically coincides, which proves their common origin.

However, there is not only a quantitative but also a qualitative difference in the behavior of methanol and butanol: the character of the participation of the alcohol in the formation of carbon chains differs in principle. The specific radioactivity in the synthesis products remains constant independently of the chain length. The molar radioactivity increases linearly as the length of the molecule increases. This means that methanol participates not only in the initiation of growth of the carbon chain, but also in its very growth, being included many times and regularly in the growing chain. However, comparison of the specific activity of methanol (300 imp/min per 1 mg of $BaCO_3$) and the other synthesis products (on the average 44 imp/min) shows that it is not methanol itself that is the intermediate product, but rather some surface compound comparatively easily formed from methanol. This surface complex, apparently, is analogous or even identical to the primary complex formed on the catalyst surface during synthesis from CO and H_2 and responsible for growth of the carbon chain.

Figure 2

Figure 2: Figure 2

Fig. 2. Specific (1) and molar (2) radioactivity of hydrocarbons (*a*) and alcohols (*b*) as a function of the carbon number (experiment with methanol of specific activity 3000 imp/min per 1 mg of $BaCO_3$; experimental conditions: 90 atm., 210–220°; space velocity of $CO + H_2$ equal to 1600 h^{-1}; specific activity at the reactor outlet: methanol 300 imp/min, CO_2 75 imp/min, CO 12 imp/min)

From the totality of the data obtained it follows that the processes of synthesis from CO and H_2 of hydrocarbons and oxygen-containing compounds are interrelated. Hydrocarbons and alcohols, when synthesized from CO and H_2 on fused iron catalysts, have a common progenitor. The latter is an unstable intermediate complex on the surface of the catalyst, obtained in the primary act of interaction of CO and H_2 and containing C, H, and O atoms. This intermediate complex (C_1) can condense with one like itself, providing formation of a carbon–carbon bond and of a new oxygen-containing intermediate compound with two carbon atoms, C_2. Further growth occurs through successive addition of the primary intermediate formation C_1 to the growing complexes C_2, C_3, C_4, etc.

$$\mathrm{CO{+}H_2}\,leftarrows\,\mathrm{C_1}\quad \begin{array}{c}\uparrow\ \mathrm{CH_4}\\ +\mathrm{H_2}\\ \downarrow\ \mathrm{CH_3OH}\end{array} \xrightarrow{-\mathrm{H_2O}} \mathrm{C_2}\quad \begin{array}{c}\nearrow\ \mathrm{C_2H_6}\quad \mathrm{C_2H_4}\ \nwarrow\\ \downarrow\\ \mathrm{C_2H_5OH}\end{array} \xrightarrow{-\mathrm{H_2O}} \mathrm{C_3}\quad \begin{array}{c}\nearrow\ \mathrm{C_3H_8}\quad \mathrm{C_3H_6}\ \nwarrow\\ \downarrow\\ \mathrm{C_3H_7OH}\end{array} \xrightarrow{-\mathrm{H_2O}}$$

It should be pointed out that, alongside the proposed mechanism of growth of the carbon chain, which follows directly from the experimental data obtained, the possibility is also not excluded of incorporation into the growing chain of CO and H_2 molecules reacting with the growing complex but not yet bound into the primary complex. Probably, combination of larger aggregates C_2, C_3, C_4, etc. with one another is also possible, although under the conditions studied this growth path plays a subordinate role. Growth of a given chain proceeds continuously on the surface of the catalyst until, as a result of more or less complete hydrogenation of the growing complex or its rearrangement and desorption, a stable compound is formed—an aldehyde, alcohol, olefin

or paraffin. An alcohol or hydrocarbon (olefin or paraffin) that has already formed cannot serve as an intermediate product. But they can, upon again coming into contact with the surface of the catalyst, undergo the secondary transformations indicated above, the extent of which will depend on the properties of the catalyst and the synthesis conditions. In this case alcohols may also partially pass into that intermediate complex from which they were formed during synthesis from CO and H_2. To the extent that alcohols can generate this intermediate complex, they will be incorporated into the chains growing on the catalyst surface.

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