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THE MECHANISM OF THE FISCHER–TROPSCH REACTION AND THE INITIATED HYDROPOLYMERISATION OF ALKENES, FROM RADIOCHEMICAL AND KINETIC DATA

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I. INTRODUCTION

In the last ten years, the mechanism of the formation of hydrocarbons and their derivatives from CO and H_2 by the Fischer–Tropsch process has been discussed[1-4] in connection with the mechanism of the hydropolymerisation of alkenes under the influence of small quantities of CO in the presence of H_2.[5,6] This relates chiefly to processes on Co catalysts, since it is only on these catalysts that the hydropolymerisation of alkenes takes place[7-9]. This group of reactions based on CO is of general interest for the theory of heterogeneous catalysis, since in this field data have been obtained indicating the existence of planar chains and also the important part played by intermediate surface compounds of the radical type in various heterogeneous catalytic reactions. It is therefore convenient to combine the examination of the mechanism of the hydropolymerisation of alkenes with a discussion of new data on the mechanism of the Fischer–Tropsch reaction, particularly since they are associated with a number of common unresolved or partially resolved theoretical problems.

Among the fundamental more or less completely solved problems in the mechanism of the Fischer–Tropsch reaction we can include first of all the carbide hypothesis[10] and the Rideal–Craxford *neocarbide theory*[11-13], according to which bulk carbides or surface carbides respectively, formed from CO and the metal of the catalyst, are intermediate products. These views were subjected to well-founded criticism as early as the nineteen forties[14-18]. Of the later data refuting these hypotheses, we may mention the results of work by Roginskii and coworkers[19] on the exchange of carbides, labelled with ^{14}C, with carbon monoxide on a Co catalyst and of work by Indian authors[20], who showed that under the normal conditions of the preparation of hydrocarbons on a Co catalyst, the CO is present on the surface chiefly as the chemisorbed gas and is not fixed to any significant extent in the form of carbides; a single treatment in a vacuum at 200° removes the CO from three-quarters of the surface.

Another hypothesis which has been refuted is the theory[11-13] of a "giant" molecule, formed by the polymerisation of methylene radicals and undergoing hydro-cracking under the influence of atomic hydrogen to give the final products. The justified[21] rejection of this hypothesis, however, had to some extent an undesirable effect, since it led to an underestimation of the part played by degradation processes in the reaction and the part played by hydrocarbon radicals in the formation of the chains.

The most important, continuously discussed theoretical problems related to the mechanism of the two reactions being considered are: (1) the part played by oxygen compounds as intermediate products; (2) the part played by heterogeneous hydrocarbon and oxygen-containing radicals at the start of chain formation and in the process of chain growth; (3) the chemistry of the formation of C–C bonds between the units of the chains — the choice between polymerisation and condensation schemes, and (4) the part played by degradation processes in the formation of the final reaction products.

II. THE THEORY OF INTERMEDIATE FORMATION OF ALCOHOLS IN THE FISCHER–TROPSCH REACTION

The theories of intermediate alcohol formation in the Fischer–Tropsch reaction are held chiefly by American (Storch and Emmett) and English (Gibson) workers, who have made extensive studies of the reactions of alcohols under the conditions of the preparation of hydrocarbons from CO and H_2. Since it was initially assumed[22] that methanol is formed from CO and H_2 on the catalyst surface, the transformations of this alcohol were studied first. The starting point was provided by the results of our work[23], according to which the rate of formation of hydrocarbons from methanol in the presence of a catalyst consisting of $Co–ThO_2$ on kieselguhr at 200° is less than that for the reaction from CO and H_2, so that the formation of hydrocarbons from this alcohol is preceded by its decomposition to CO and $2H_2$. These results, in the opinion of Storch and coworkers[24], do not necessarily indicate that the methanol decomposes; the authors considered it possible that a primary complex is formed from the alcohol on the catalyst. Shortly afterwards, Kummer and Emmett[25] reached the same conclusion with reference to the transformation of methanol on an Fe catalyst, on the basis of their radiochemical studies. Our results were confirmed, however, by Gibson and coworkers[26], who pointed out that the primary reaction in the presence of a Co catalyst is the decomposition of methanol to CO and $2H_2$, from which the hydrocarbons are formed in a secondary reaction. These contradictions led Darby and Kemball[27] to make a detailed study of the transformation of methanol on a $100Co : 6ThO_2 : 3MgO : 200$ kieselguhr catalyst at various points along the catalyst layer. It was found that at 192° methanol reacted to the extent of 53%, of which only 1% was converted into reaction products. Analogous results were obtained over a wide range of temperatures (163–210°). The reaction was of first order with respect to alcohol, the reaction rate was decreased by carbon monoxide, and when allowance was made for the side reaction of methane formation from CO and H_2, it was found that the addition of H_2 has little influence on the kinetics, which is given by the equation:

$$-\frac{dp_{CH_3OH}}{dt} = k\frac{p_{CH_3OH}}{1+bp_{CO}}.$$

Hydrogen is adsorbed less strongly than methanol; its adsorption possibly takes place on different centres. The rate-limiting stage of the process might be the adsorption of the alcohol, which takes place less extensively than the adsorption of CO, or the decomposition of the adsorbed methanol. It was concluded that methanol is not converted directly into the reaction products but undergoes preliminary decomposition to CO and H_2, in agreement with published results[23,26].

On the basis of data on the transformations of methanol, ethanol, and formic acid on a Co–ThO_2–kieselguhr catalyst, Eidus[23] suggested that when the catalytic reduction of CO by hydrogen is incomplete, the formation of the methylene radical is preceded by the formation of an oxymethylene radical on the surface. It was later shown[28] that a CH_2O complex is formed during the successive adsorption of CO and H_2 on a catalyst of this type. The fact that methanol is not converted directly into hydrocarbons on a Co catalyst was attributed[27] to the fact that the methanol adsorption complex, inactive in the hydrocarbon synthesis, is isomeric with the active oxymethylene and is slowly converted into the latter; this explains the too low concentration of oxymethylene radicals formed from methanol:

$$\underline{\mathrm{CH_2{-}O}} \longrightarrow \underline{\mathrm{CH{-}OH}}.$$

Taking into account published data[29], it was concluded[27] that the reaction of methanol takes place in different ways on Co and Fe catalysts. Emmett and coworkers[30] found that when 1.4% methanol labelled with ^{14}C is added to the original $CO:H_2$ mixture in the presence of an Fe catalyst at 240° and 1–7.8 atm, the growth of the hydrocarbon chains can begin with the alcohol; the alcohol can take part to a slight extent in chain growth. Analogous results were obtained with formaldehyde, which, however, decomposes rapidly and completely on the catalyst surface with the formation of CO and CO_2, whose radioactivity is equal to that of the original formaldehyde. The molar radioactivity of the final reaction products increases linearly with increase in the number of carbon atoms in the molecule (the C number). The addition of 1.4% CO_2, labelled with ^{14}C, to the original mixture of CO and H_2 showed that at atmospheric pressure, other conditions being equal, CO_2 undergoes little conversion into CO or hydrocarbons, evidently due to the low rate of reaction of water gas. It was concluded[30] that neither methanol nor formaldehyde, on adsorption, form a complex identical to the primary complex from which growth of the carbon chain begins in the preparation of hydrocarbons from CO and H_2.

Evidence put forward in support of the intermediate formation of alcohols in the preparation of compounds from CO and H_2 includes the similarity in the structures of the alcohols and hydrocarbons in the Synthol process on an Fe catalyst (p. 474 of Ref. 24) and also the similarity in the curves giving the distribution of the branched alcohols and hydrocarbons formed on this catalyst with respect to C number[31]. Weitkamp[31] considers that the formation of alcohols and hydrocarbons on Fe catalysts takes place by a single mechanism with the primary formation of both alcohols and alkenes, and also that the alcohols do not undergo dehydration and are not precursors of the alkenes.

Studies on the correlation of the rates of decomposition of alcohols in mixtures with CO and H_2 with the rates of their formation from CO and H_2 on Co catalysts were carried out by Gibson and coworkers[26,32,33]. Under the usual conditions of preparation (190°, 10 atm) from a $CO:2H_2$ mixture on a standard catalyst (100Co : $5ThO_2$: 8MgO : 200 kieselguhr), the final product contains only 1% of alcohols and aliphatic acids. If, however, the reaction temperature is lowered and the duration of contact decreased, the concentration of normal primary alcohols may increase to 60%. These results are also taken as evidence for the intermediate formation of alcohols. The alcohol-enriched reaction product obtained at 10 atm and 160–170° from a 37.5 g m^{-3} $CO:2H_2$ mixture with a degree of conversion equal to 10–20% was studied[26] to determine the distribution of the alcohols with respect to C number. The distribution was compared with the relative stability of the normal primary alcohols under the conditions of preparation in a mixture with H_2 or $CO + H_2$. It was concluded that ethanol and higher primary alcohols are converted directly into hydrocarbon products without intermediate decomposition with the formation of CO. Slightly different results were obtained[23] for ethanol, which decomposes on a Co–ThO_2–kieselguhr catalyst at 200° with the formation of a gas with composition: 48.3% H_2, 27.7% CH_4, 9.6% CO, 9.0% C_2H_6, 2.9% unsaturated hydrocarbons, and 2.5% CO_2. It was assumed that the initial product is acetaldehyde, which subsequently decomposes to CH_4 and CO. Hydrocarbons are formed in 6% yield in a secondary reaction from CO and H_2. According to Gibson's data[32], ethanol was found to be the most stable of the alcohols studied under the reaction conditions; at 150° it is converted into saturated gaseous hydrocarbons and water; at 185° it forms gases, containing 9% CO, and liquid hydrocarbons, whose yield, however, was 21% greater (relative to the ethanol used up in the reaction) than could have been obtained in the normal preparation from CO and H_2. The alcohol is apparently dehydrated to form ethylene, which reacts with CO and H_2, undergoing hydropolymerisation[5,6]. Homologues of ethanol decomposed in the mixture with $CO + H_2$ at 150° at a rate comparable with the rate of preparation from CO and H_2. The chief reaction was dehydration. In accordance with its stability, ethanol was obtained in the preparation from CO and H_2 in relatively high yields: 8.6% of the total liquid products and more than 50% of the total alcohols in the aqueous layer. Decrease in the temperature of the reaction and increase in the pressure and volume rate of the original gas led to a decrease in the rate of decomposition of the alcohols and a simultaneous increase in their concentration in the product of the preparation from CO and H_2. The yield of alcohols also increased with decrease in the degree of conversion of the original mixture and increase in the $CO:H_2$ ratio in this mixture. Decrease in the temperature of the reaction and in the $CO:H_2$ ratio, and increase in the degree of conversion of CO and in the activity of the catalyst led to an increase in the average molecular weight of the final product. At a low degree of conversion of about 20–30%, increase in pressure from 1 atm to 11 atm led to a decrease in the average molecular weight, whereas at degrees of conversion greater than 50% an increase in the average molecular weight was observed[33]. The alcohols are not formed from alkenes by an oxo-synthesis scheme via the aldehydes, but are most probably formed directly from CO and H_2 by a mechanism involving the stepwise growth of the carbon chain on the catalyst[34–38]. The most probable process[32] is the stepwise attachment of methylene radicals to the end of the growing chain, which terminates in an oxymethylene group[23]. The chains are desorbed by hydrogen with the formation of saturated alcohols. If the desorption does not depend on the C number and a definite fraction (α) of chains with any C number are desorbed before further growth, the curve giving the distribution with respect to C number for the alcohols formed at the start of the reaction is given by the formula

$$Y_n = K \cdot \alpha (1-\alpha)^{n-1},$$

where Y_n is the molar quantity of alcohol with C number equal to n, and K a constant. With a correction for stability, the calculated curve coincides with the experimental curve, the maximum corresponding to ethanol, in agreement with the experimental data.

Comparison of the curves giving the distribution of the alcohols with respect to C number with the distribution

curve for the hydrocarbons obtained on a Co catalyst by Martin[39] under ordinary conditions shows some discrepancies. The curve giving the yield of hydrocarbons, unlike the curve giving the yield of alcohols, which shows a maximum at C_2 in the range C_2–C_5, showed a minimum. This difference might be contradictory to the theory of intermediate alcohol formation. It was suggested that in the preparation, ethanol undergoes dehydration to ethylene, which subsequently undergoes hydrocondensation with CO [40] and hydropolymerisation[5,6]. Since the rates of these reactions decrease on going from ethylene to propene and butene[41,42], the maximum on the curve should be displaced towards C_5. It is not excluded that ethanol reacts with CO and H_2 without decomposition, as is the case on an Fe catalyst[25,29].

The results of the correlation of the rates of formation and decomposition of the alcohols and the influence of the process conditions on these rates were taken[32,33] as confirming the theory of intermediate alcohol formation, although it is possible that alkenes are also primary products. The reaction mechanism changes to some extent with change in the conditions: if these are favourable for the preparation of hydrocarbons, the formation of the chains involves methylene radicals, into which the oxymethylene radicals, which are unstable under these conditions, are converted; if, however, the conditions are favourable for the preparation of alcohols, there is an increase in the stability and concentration of the oxymethylene radicals, and these play a predominant part in the growth of the chains. It is possible that a decrease in the length of the carbon chains takes place as a result of secondary hydro-cracking reactions.

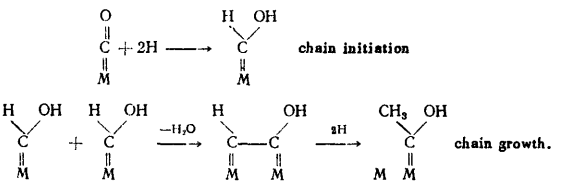
In Gibson's opinion[32], the results of Eidus and coworkers[5] indicate that the growth of the hydrocarbon chains begins only in the presence of radicals containing oxygen, since ethylene and hydrogen are converted into into ethane, and the addition of less than 1% CO leads to the formation of higher hydrocarbons. The appreciable yields of hydrocarbons with odd C number indicates dissociation of the ethylene molecule into two methylene radicals.

III. START OF FORMATION AND GROWTH OF CARBON CHAINS

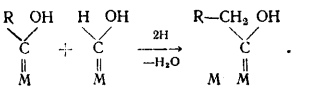
1. Radiochemical Studies of the Formation of Hydrocarbons from CO and H_2 Using Labelled Alcohols

Important radiochemical studies on the mechanism of the Fischer–Tropsch reaction were carried out by Emmett and coworkers, who studied the reactions of the original gaseous mixtures with added alcohols labelled with ^{14}C. The reaction was first carried out on an Fe catalyst promoted with Al, Zn, and Th oxides, at atmospheric pressure and 230° with a $1CO : 1H_2$ gas mixture containing 1.6 vol.% ethanol labelled with ^{14}C in the methyl or methylene group. It was found that the molar radioactivity of the methane was negligible, that of the C_5–C_{10} hydrocarbon fraction appreciable and independent of the C number, and that of the C_2–C_4 fractions slightly less than that of the liquid hydrocarbons. These results show that ethanol does not decompose before taking part in chain growth and that its adsorption complex plays the part of intermediate product in the preparation. The radioactivity of the C_2 fraction indicates successive dehydration and hydrogenation of the alcohol. Experiments on the stepwise splitting of the propane molecule showed that ~90% of the attached C atoms combine with the α-C atom of the adsorbed alcohol complex and only ~10% with the β-C atom.

Experiments under the same conditions with the addition of 1.5% labelled propanol or isobutyl alcohol to the original gas gave C_2–C_{10}, C_3–C_{10}, and C_4–C_{10} fractions which had an almost constant molar radioactivity, equal to between one-third and one-half the radioactivity of the original alcohol. Isopropyl alcohol underwent intensive conversion into isobutane and isobutene. Only one C_7 molecule out of 15 and one C_9 molecule out of 27 were formed with the participation of labelled isopropyl alcohol. t-Butyl alcohol apparently did not take part in the formation of hydrocarbons under these conditions. Experiments with labelled propanol gave n-butane containing ^{14}C, and isobutane containing no ^{14}C. In experiments with labelled isopropyl alcohol, on the other hand, the isobutane was radioactive and the butane was not. Adsorbed methanol also took part in the formation of carbon chains, but with an efficiency which was only one-quarter of that for the other alcohols used. These results led to the conclusion that in the Fischer–Tropsch synthesis on Fe catalysts the CO and H_2 form primary complexes similar to the adsorbed complexes of primary alcohols. Kummer and Emmett[29] put forward a scheme for the growth of the carbon chains, similar to the schemes advanced by others[31,35,38]. In this scheme the chief part in the formation of the carbon chains is played by the CHOH radical. This takes part in the formation of C–C bonds by condensation with the liberation of water from the hydroxyl of one oxymethylene group and the hydrogen of another:



In general:



Chain termination takes place by desorption of aldehydes, hydrogenation to alcohols, decomposition to alkenes, etc.

Subsequent experiments with the addition of labelled ethanol[43,44] showed that it is included in the reaction products more intensively in the preparation on a once-promoted Fe catalyst than on a twice-promoted catalyst, and more intensively on a catalyst which had not been treated with nitrogen than on a catalyst treated with nitrogen. The radioactivity of the reaction products decreased with increase in pressure in the range 1–21 atm. The radioactivity of the alcohols formed on a catalyst treated with nitrogen was approximately the same as that of the hydrocarbons in the range of C numbers C_3–C_6. With the addition of 0.04 vol.% strongly radioactive ethanol, it was shown that the increase in the extent to which the alcohol is included is slower than the increase in the partial pressure of alcohol in the original gas.

In experiments with an Fe catalyst at 224°, with the addition of 1.5% propanol or propanal to the original gas, almost half of the final products were formed with the participation of these compounds; the butane and butenes had the normal structure.

Soviet workers [45] published the results of experiments on the preparation on a 100Co : 18ThO_2 : 100 kieselguhr catalyst with a CO : 2H_2 mixture containing added labelled ethanol at 195°. The molar radioactivity of the C_6–C_{29} hydrocarbons was constant and independent of the C number. An average of one molecule out of 18 was formed with the participation of the alcohol. The molar radioactivity of the methane and C_2–C_4 hydrocarbons was slightly less than the molar radioactivity of the liquid hydrocarbons. In analogous experiments by American workers [43], one hydrocarbon molecule out of 60 was formed with the participation of labelled ethanol with the same concentration in the original gas, that is, the quantity was much less than that in the presence of any Fe catalyst. The methane had approximately the same radioactivity as the higher hydrocarbons, whereas on Fe catalysts it had a radioactivity which was 10–100 times less than that of the higher hydrocarbons. In the product of the reaction with a Co catalyst, the greatest molar radioactivity was shown by the C_2 fraction; this was attributed to the fact that the species included in the chain was not ethanol, but its dehydration product, ethylene, which undergoes partial hydrogenation to form ethane. When 1.5% ethanol is added, it is included in the chain to a greater extent than when 0.04% is added, but the increase is less than the increase in the concentration. Emmett and coworkers [43] concluded that on Fe catalysts, alcohols are intermediate products in the preparation of hydrocarbons from CO and H_2, but that the mechanism of the preparation on Co catalysts differs from that on Fe catalysts.

Soviet workers [45] consider that these and other data [25,29] indicate that transfer of the chain, which begins with the adsorption of alcohol molecules, produces material chains with a number of units up to n - 1, where n is the C number of the hydrocarbons. The observed coefficient 1 : 18 may express the ratio of the units in the reaction and material chains. Thus one unit in the reaction chain corresponds to one material chain. The fact that the molar radioactivity of the liquid hydrocarbons is constant with change in C number reflects the single mechanism of chain formation with the direct participation of the labelled alcohol or its adsorption complex. This participation, however, may be manifested not only in the initiation of chain growth, as assumed by Emmett and coworkers [25,29], but also in the termination of the material chains, which leads to the same results. The Soviet workers [45] point out that neither their results nor the results of Emmett and coworkers [25,29] provide a basis for rejecting the methylene-polymerisation scheme, since it has not been proved that CH_2 radicals cannot take part in chain growth initiated by alcohol. A parallel reaction without inclusion of alcohol also does not exclude the participation of CH_2 radicals. Moreover, a stage involving the polymerisation of CH_2 radicals on a Co catalyst is confirmed by the hydropolymerisation of alkenes [5,6]. The oxymethylene-condensation scheme for the formation of carbon chains is more probable for the mechanism of the iso-synthesis in the presence of oxide catalysts, in view of the semi-contact character of the hydrogenation of CO under these conditions [46].

The fact that the adsorption complexes of alcohols tend to bring about the growth of carbon chains in the presence of CO and H_2 on Co and Fe catalysts still does not prove that the true primary complex formed from CO and H_2 is an alcohol-like product. It was therefore of interest to add compounds of other classes to the original gas.

Experiments on a Co catalyst were carried out with gas containing added acetaldehyde or ethanol labelled with ^{14}C in both carbon atoms, and with methyl formate labelled in the methoxycarbonyl group [47]. The products of the reaction with ethanol and acetaldehyde showed a constant molar radioactivity with increase in C number, whereas the products of the reaction with methyl formate showed a linear increase in the molar radioactivity with increase in C number, the molar radioactivity in the first two reactions amounting to 5–6%, and that in the last reaction to 63% of the radioactivity of the original labelled compound. This shows that methyl formate, like formic acid [23], decomposes on the catalyst surface with the formation of CO, which, however, reacts at the moment of formation, since the radioactivity of carbon monoxide in the gas is low. The similarity in the results of the experiments with ethanol and acetaldehyde indicates that the aldehyde is reduced to the alcohol. Chain growth is due to an adsorption complex of alcohol, but it has not been proved that it contains oxygen.

2. Radiochemical Studies of the Formation of Hydrocarbons from CO and H_2 Using Labelled Alkenes

Experiments carried out at 195° on a Co catalyst with an original mixture of CO and H_2 containing ethylene labelled with ^{14}C are of particular interest in the investigation of the mechanism of the hydropolymerisation of alkenes [5,6]. Under these conditions, ethylene is converted into higher hydrocarbons to the extent of 25% and into ethane to the extent of 50%. The molar radioactivity of the liquid hydrocarbons remained constant with change in C number and at concentrations of ethylene in the original gas equal to 0.78% and 1.48% it amounted to 10% or 22% respectively of the radioactivity of the added ethylene. Thus under these conditions the extent to which the labelled compound took part in chain formation increased in proportion to its concentration. The results obtained show that ethylene is present in the primary complex bringing about the growth of the material chains on the catalyst. Chain termination by ethylene must be excluded, since increase in its concentration in the original gas does not lead to a decrease in the yields of the higher hydrocarbons. The hydropolymerisation of ethylene [5,6] also provides evidence against chain termination by ethylene.

Comparison of published data [45,47,48] indicates that ethylene takes part to a greater extent than ethanol in the formation of hydrocarbons on a Co catalyst. One molecule out of 4–5 is formed with the participation of the labelled compound when using ethylene, compared with the figure of one molecule out of 18 for ethanol. It is possible that the alcohol is first dehydrated to form ethylene, which then enters the complex initiating chain growth. This casts doubt on the applicability of the condensation scheme. All these facts taken together leave no doubt that the growth of hydrocarbon molecules on the catalyst surface takes place by a chain mechanism.

Experiments [19] on a Co catalyst at 195° with an original mixture containing 1.5% labelled propene showed that the molar radioactivity of the liquid products remained constant with change in the C number, but that propene took part in the formation of products to a smaller extent than ethylene: only one out of 12 hydrocarbon molecules was produced with its participation. The lower reactivity of propene compared with ethylene was previously observed in hydropolymerisation under the influence of CO. [41,49] An interesting feature is that increase in the concentration of labelled alkene in the original mixture of CO and H_2 above a definite limit may lead not only to participation of the alkene in the

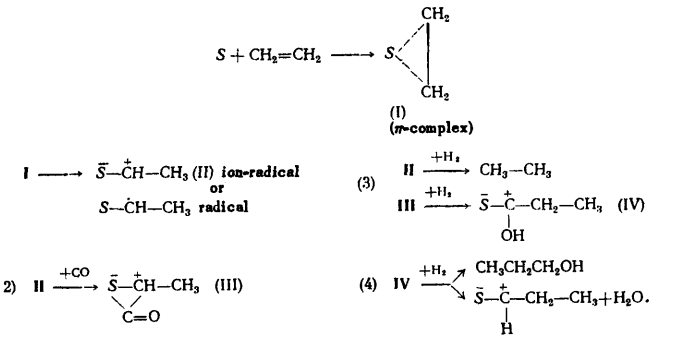
formation of the primary complex, but also to its participation in chain growth. This was observed[19] by the addition of 4.8% ethylene, when the molar radioactivity remained unchanged with change in the C number of the hydrocarbons in the range 5–9, but increased for hydrocarbons above C_9. This phenomenon can be regarded as an intermediate stage between the Fischer–Tropsch reaction and the hydropolymerisation of the alkene. Under these conditions one out of 1–2 molecules of C_5–C_9 hydrocarbons was formed with the participation of the labelled carbon of ethylene.

In the reaction on an Fe catalyst at 224° with a $CO:H_2$ mixture containing 1.25% labelled ethylene, the quantities of hydrocarbons formed with its participation amounted to 12% at 1 atm and 6% at 6.5 atm. These results show that ethylene may initiate chain growth, but not to the same extent as primary alcohols[44].

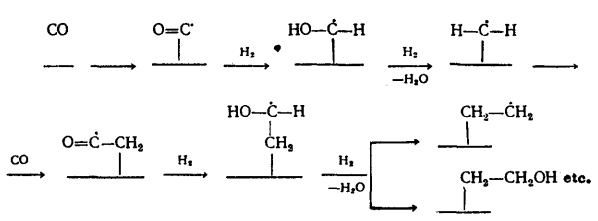
A very interesting series of studies has been carried out by Kryukov, Bashkirov, Kagan, and their coworkers on the mechanism of the preparation of alcohols and hydrocarbons on fused Fe catalysts at 160–300° and 20–150 atm at a volume rate of gas equal to 500–2000 h^{-1}, using the tracer method[50–55].

Under these conditions, butanol labelled with ^{14}C and added in quantities of 0.04–0.1% to an original $1CO:2H_2$ mixture remained 90–95% unchanged. Less than a hundredth of the resulting hydrocarbons above C_4 and of C_6–C_9 alcohols could have been formed with its participation[51]. Thus butanol is not an intermediate product of the preparation. The slight radioactivity of the pentanol and hexanol formed, however, indicated the formation of a radioactive complex containing oxygen. Labelled butene added to the original gas (90 atm and 220°) underwent hydrogenation, oxidation, and hydro-cracking, took part to some extent in the formation of C_5 products, but took no part in the formation of alcohols and hydrocarbons above C_9.[52] As expected, methanol was less stable than butanol under these conditions and underwent various transformations, particularly decomposition to CO and H_2.[51] It took part not only in chain formation, but also in chain growth, as indicated by the increase in the molar radioactivity of the product with increase in the C number. The fact that the radioactivities of alcohols and hydrocarbons with equal C numbers were the same was attributed to their formation from the same "precursor", that is, from the same primary complex, formed from CO and H_2 and containing oxygen in addition to carbon and hydrogen[50,51]. The primary complex bringing about growth of the carbon chain is formed by the reaction of CO, activated on an Fe atom dissolved in iron carbide, with hydrogen, physically adsorbed on neighbouring carbide atoms[54]. An interesting feature is that in the study of the part played by iron carbides using CO labelled with ^{14}C in experiments on fused catalysts (300° and 20 atm) it was found[53] that in this instance they cannot be regarded as intermediate products. The carbides were hydrogenated to form methane and exchanged carbon with CO. Both of these processes took place very slowly. Only one out of 3000 CO molecules underwent exchange and five out of 3000 CH_4 molecules were formed from the labelled carbide. Hydrocarbons could have been formed via the carbides to the extent of only 0.03%. Even from this low degree of conversion of carbides into reaction products it is possible to estimate the part played by methylene radicals in chain formation. On the basis of data obtained in a study of ethylene added to the original gas and iron carbides labelled with ^{14}C, it was concluded[55] that the chains may grow simultaneously in two main ways: by condensation of intermediate oxygen-containing compounds with the liberation of water, and by polymerisation of surface compounds which may or may not contain oxygen. In the polymerisation scheme, growth of the carbon chain takes place at the end of the molecule which does not contain the hydroxyl group. An analogous dual mechanism for the growth of carbon chains in the iso-synthesis[56–59] was proposed by Eidus[46]. A slight difference was that Eidus[46] assumed stepwise growth not only by groups containing one C atom but also groups containing several C atoms. Some of the stages in the two schemes, particularly in the initial stages, are similar or even identical.

To explain the participation of ethylene in chain initiation, Roginskii and coworkers[19] proposed a step scheme in which ethylene, after formation of a π-complex with the catalyst and conversion into an ion-radical or ethylidene radical, combines with an adsorbed CO molecule, forming successively, and with the participation of hydrogen, ion-radicals or α-hydroxypropylidene radicals and then α-propylidene, with regeneration of the unsaturated carbon atom in the α-position to the catalyst:



Voevodskii and coworkers[60] put forward a chain scheme for the preparation of organic compounds from CO and H_2, involving the gradual growth of a univalent surface radical:

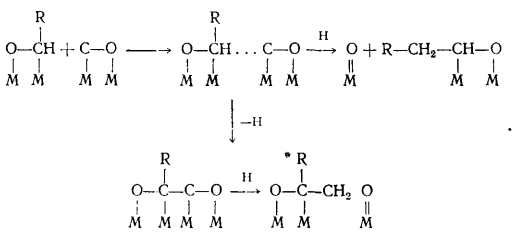


3. Radiochemical Studies of the Formation of Hydrocarbons from CO and H_2 Using Labelled Keten

Blyholder and Emmett[61] used keten labelled with radioactive ^{14}C in the methylene group. The experiments were carried out on an Fe catalyst at atmospheric pressure and 247° with the addition of 2% keten to a $CO:H_2$ mixture. The hydrocarbon product had an almost constant molar radioactivity, which was independent of the C number and equal to the radioactivity of the original keten. Analogous experiments were made with the addition of 0.25% labelled keten to a $1CO:2H_2$ mixture (Co–ThO_2–MgO–kieselguhr catalyst) at 185°. The molar radioactivity of the hydrocarbons was approximately independent of the C number and amounted to one-third of the radioactivity of the keten. The methane formed was not radioactive. Since the adsorbed keten

underwent intensive introduction into the reaction products, it was concluded that its adsorption complex is similar to the primary complex of the Fischer–Tropsch reaction. It was assumed that the keten molecule is joined to the catalyst surface by metal–carbon and metal–oxygen bonds. The following three possible results from the introduction into the reaction of a keten labelled in the methylene group were examined: (1) for dissociation of the keten into methylene and CO, assuming the applicability of the methylene–polymerisation scheme, the reaction product should have a molar radioactivity directly proportional to the C number; (2) with dissociation of the keten into CH_2 and CO, if polymerisation of the methylene radicals or their inclusion in the preparation by another mechanism do not take place, the reaction product should not be radioactive, whereas the methane should be radioactive; and (3) if the keten does not dissociate, but initiates chain growth, the reaction product should have a radioactivity which is independent of the C number. The experimental data appear to confirm the third possibility.

The results obtained show that on Co and Fe catalysts the keten is converted almost completely into reaction products, indicating that it is strongly adsorbed and possibly that an oxygen–catalyst bond is formed. The possibility of formation of such a bond is indicated[62] by the exchange of O atoms between $^{12}C^{16}O$ and $^{13}C^{18}O$ on an Fe catalyst, which shows that the CO is joined to the surface through the C and O atoms. In accordance with this, Blyholder and Emmett[61] proposed a reaction scheme in which the keten and CO are adsorbed through the C and O atoms, and new C–C bonds are produced between the carbon of the carbon monoxide and the carbon of the carbonyl group of the keten without condensation with the liberation of water. Oxygen is liberated in the form of atoms adsorbed on the catalyst:



The keten is adsorbed more strongly than saturated alcohols, so that it is more effective at the start of chain growth. According to Blyholder and Emmett[61], alcohols should undergo preliminary dehydration before forming the initial complex. This is indicated by the ability of ethylene to form a complex which brings about chain growth. Ethane does not exhibit these properties.

Blyholder and Emmett[61] considered three possible results of the use of keten, but they did not consider the fourth, most probable possibility: dissociation of the keten with the subsequent participation of the methylene radical in chain initiation. New conclusions were reached in subsequent work[63]. The reaction was carried out on a once-promoted Fe catalyst at 256° with the addition of 0.7% keten, labelled in the carbonyl group, to the original gas, and on a Co catalyst at 189° with the addition of 0.5% of the same keten. Hydrocarbons with molar radioactivity directly proportional to the C number were formed on both catalysts. Thus the keten undergoes preliminary dissociation on the catalyst with the formation of a methylene radical, which initiates the chain, and carbon monoxide, which takes continuous part in the chain growth. The exchange of carbon between CO and the keten under these conditions is slight and is not reflected in the results. Convincing confirmation was thus obtained for the initiation by heterogeneous methylene radicals of the growth of chains in the Fischer–Tropsch synthesis on Co and Fe catalysts. This shows that not only oxygen-containing but also hydrocarbon radicals exhibit these properties. The results obtained, however, did not touch on the polymerisation of CH_2 radicals. It would be of interest to use higher concentrations of keten, labelled in the methylene group, to study this process. The CH_2 radicals would then take part in chain growth in a fashion analogous to that of ethylene at higher concentrations[19]. An interesting feature is that the addition of 0.5–0.7% keten to the original gas led to an increase in the yield of lighter products.

4. Radiochemical Studies of the Hydropolymerisation of Ethylene Using Labelled CO

Gibson and Fletcher[64] described a study of the mechanism of the hydropolymerisation of ethylene under the influence of CO. The chief aim of this work was to investigate the part played by two types of radical: hydrocarbon radicals and oxygen-containing radicals. It was assumed that an oxygen-containing radical initiates chain growth, since hydropolymerisation does not take place in the absence of CO but takes place to an appreciable extent at a concentration of 0.1% CO in the original gas[5]. The reaction was carried out on a $100Co : 5ThO_2 : 8MgO : 200$ kieselguhr catalyst at 185° with a $C_2H_4 : H_2$ mixture containing 5% CO labelled with ^{14}C. 50–60% of the CO and almost all the ethylene, 50% of which was hydrogenated to form ethane, took part in the reaction. The molar radioactivity of the C_4–C_{10} hydrocarbons increased regularly with increase in the C number. Approximately one out of 6–7 carbon atoms was produced from CO. The molar radioactivities of the methane and ethane were low. Side-products of the Fischer–Tropsch reaction were formed in small quantities. With the exception of appreciable yields of C_4 hydrocarbons, the formation of large quantities of other true polymeric forms was not observed. Gibson and Fletcher[64] consider that this confirms the earlier conclusion (see p. 341) that ethylene dissociates into two methylene radicals, forming hydrocarbons and methane. Comparison of the radioactivity of the hydrocarbons with the radioactivity of the original CO shows that some of the molecules formed do not contain C atoms originating from the CO. This means that after initiation of the reaction, chain growth can continue and be renewed to some extent without the participation of CO. Gibson and Fletcher[64] quote the results of Eidus and coworkers[65], according to which, after the reaction of a mixture of CO, H_2, and C_2H_4, it is possible to obtain liquid hydrocarbons for some time by passing a mixture of C_2H_4 and H_2 containing no CO over the Co catalyst. These experiments were repeated[66] using ^{14}CO; the same results were obtained, and both the volatile and high-boiling fractions of the reaction product contained ^{14}C. These data[64,65] show that the formation of hydrocarbon chains is also possible even when the original C_2H_4–H_2 mixture does not contain CO. Chain growth is initiated by radicals on the catalyst surface, for which CO is necessary at the start of the reaction. These heterogeneous radicals can apparently be subsequently regenerated from ethylene even in the absence of CO. This explains the absence of ^{14}C in a fraction of the reaction products, and their formation from a mixture of C_2H_4 and H_2.

Determination of the radioactivities of each of the three C atoms in the molecule of the propene liberated[64] gave the following radioactivity ratio:

$$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_3}$$
$$304 : 26.5 : 220 .$$

The low radioactivity of the central C atom shows that it comes chiefly from the ethylene. The radioactivity may provide a measure of the quantity of propene formed by the Fischer–Tropsch reaction from CO and H_2. If the propene were formed by the direct attachment of a C atom from CO to an ethylene molecule by hydrocondensation[40,67,68], one of the terminal C atoms should show a high radioactivity. The high radioactivity of both terminal C atoms is apparently due to migration of the double bond, which takes place readily on a Co catalyst; this has been shown many times[69-76]. The propene formed from CO and H_2 then exhibits radioactivity:

$$CH_2=CH-CH_3$$
$$26.5 : 26.5 : 26.5.$$

The initial distribution of the radioactivity in the propene formed by the hydropolymerisation of ethylene is as follows:

$$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_3}$$
$$471 : 0 : 0 .$$

A study was made[77] of the distribution of the radioactivity in propanol, whose yield amounted to 4% of the liquid products of the reaction. The propanol was converted into propene by a method which prevented movement of the double bond. The following radioactivity distribution was observed:

$$\underset{15}{\overset{3}{CH_3}-\overset{2}{CH_2}}-\underset{85}{\overset{1}{CH_2OH}}$$

The molar radioactivity of the propanol was 11 times the radioactivity of the propane and more than one-third of the radioactivity of the original carbon monoxide. All the propanol was formed according to the reaction

$$CH_2=CH_2 + {}^{14}CO \longrightarrow CH_3CH_2{}^{14}CH_2OH.$$

Less than 10% of the C_3 products was formed with the participation of ^{14}CO, and the greater part was formed from the carbon of the ethylene. It was therefore concluded that the ethylene dissociates into two methylene radicals. The distribution of the radioactivity is of the same type for propene and propanol, as a result of the fact that the ^{14}C is attached to the ethylene in the form of CH_2 or oxygen-containing radicals with one ^{14}C atom in each instance; it is possible that propene is formed from propanol. Since the original gas contains a large quantity of ethylene, the hydropolymerisation is not identical with the Fischer–Tropsch reaction, but the fact that the radioactivity distribution is the same for propanol and propene was taken[77] as confirming the previous suggestion that in the Fischer–Tropsch reaction on a Co catalyst the primary products are alcohols, from which alkenes and alkanes are produced by dehydration and hydrogenation.

The characteristics of the liquid product of the hydropolymerisation of ethylene, obtained from an equimolar mixture of ethylene and hydrogen containing ~5% CO are given in the Table. The slight discrepancies in the data must be attributed to slight differences in the composition of the Co catalysts used in the experiments.

The reaction products are forms with odd and even C numbers (see Table). Gibson and Clarke[78] confirmed the data of Eidus and coworkers[5], who showed that the yield of C_4 and higher hydrocarbons increases with increase in the CO concentration in the range 0.3–5%. The yield of methane does not increase, and the quantity of ethylene converted into ethane decreases from 90% to 35% with increase in the CO concentration from 0.3% to 6.1%.

TABLE. Characteristics of the liquid product of the hydropolymerisation of ethylene.

Fraction	Concentration, wt. %	Concentration of unsaturated compounds, %	Concentration, wt. %	Concentration of unsaturated compounds, %
	according to Ref. 78		according to Ref. 79	
C_5	20	73	11	100
C_6	28	62	18	68
C_7	8	54	17	65
C_8	13	53	13	60
C_9	10	52	9	51
$>C_9$	21	—	32	—

The distribution of the radioactivity over the individual atoms in the hexene and heptene molecules was determined[78] by a specially developed method for the stepwise degradation of these molecules. The following radioactivity ratios were obtained:

$$\overset{6}{C}-\overset{5}{C}-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$
$$2.3 : 6.2 : 40.7 : 41.8 : 7.9 : 1.1$$

$$\overset{7}{C}-\overset{6}{C}-\overset{5}{C}-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$
$$0.6 : 13.1 : 22.4 : 30.9 : 31.8 : 0.9 : 0.3.$$

The accuracy of these figures increases with increase in the actual figures, from ±30–50% for the values 0.6–2.3 to ±1–5% for the values 30–42. Thus in hexene and heptene the central two or three C atoms respectively have a high radioactivity and the terminal atoms have a low radioactivity. The double bonds lie chiefly between atoms 2 and 3 in hexene and between atoms 2 and 3 or 3 and 4 in heptene.

Gibson and Clarke[78] consider that the mechanisms of chain growth in hydropolymerisation and the formation of hydrocarbons from CO and H_2 are similar. Stepwise attachment of species containing one C atom to the growing chain takes place. The distribution of the radioactivity in the final product is the same as that in the chain with the same C number on the surface. The radioactivities of each C atom 3 and 4 in hexene and heptene correspond to the increase in radioactivity for the attachment of one atom from ^{14}CO. The properties of the radicals produced from CO and from C_2H_4 are different, in agreement with the conclusions reached by Blyholder and Emmett[63].

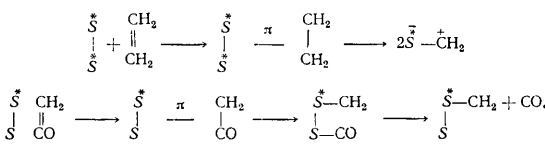
In a study of the radioactivity distribution in propanol, hexene, and heptene, with the assumption that the reactive group (hydroxyl or multiple bond) is the growing end of the chain, Gibson and Clarke[78] reached the following conclusions: (1) chain growth is initiated by the reaction of CO, or an oxygen-containing radical formed from it, with an adsorbed radical produced from ethylene, to give a chain of three C atoms; (2) chain growth involves the attachment, to this radical of three C atoms (or its derivative), of radicals each containing one C atom, and also of oxygen and radicals produced from CO or ethylene. Chain growth does not take place in the absence of oxygen-containing radicals. These radicals, which are produced from ethylene, may be formed from hydrocarbon radicals, if their concentration on the

surface is high, by reaction with adsorbed oxygen, produced according to the scheme proposed by Blyholder and Emmett[63] (see p. 344). The formation, from hydrocarbon radicals, of oxygen-containing radicals active in chain growth apparently explains two observations: firstly, the presence of non-labelled C atoms in the centre of the chains, and secondly the formation of higher hydrocarbons from a mixture of ethylene and hydrogen on a catalyst which has taken part in the reaction of a ternary mixture of C_2H_4, H_2, and CO;[65,66] and (3) chain termination takes place by the reaction of the growing chain with radicals produced from ethylene and containing one or two C atoms.

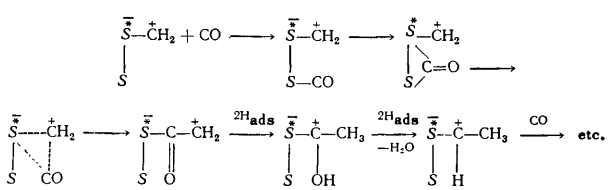
A considerable difference is observed in the influence of the concentration of CO in the original gas in the Fischer–Tropsch reaction and in hydropolymerisation. The latter takes place more slowly with increase in the CO concentration above 5%, apparently due to the adsorptive displacement of the alkene from the catalyst surface, as a result of which the rate of the process is determined by the conversion of carbon monoxide into methylene radicals. The adsorptive displacement of the alkene by carbon monoxide also explains the lower rate of hydropolymerisation of propene[49] and butenes[80,81] at CO concentrations of 10–15%.

On the basis of new radiochemical data, Ronginskii[82] developed his scheme[19] of chain growth (see p. 343) to include methylene radicals or ion-radicals in the primary stage. It is assumed that there exist on the surface unique active centres S, on which the growing chains are fixed. The centres differ in their structure and in the concentration of modifying additives from the other active centres S on which other processes take place, for example, the adsorption of CO and H_2.

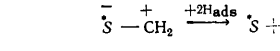
The primary active forms with the properties of chain growth initiators are assumed to be heterogeneous radicals or the simplest carbonium ions $S-CH_2$ or $S-CH_2$, which are formed in particular by the dissociation of ethylene or keten:



The growth of the carbon chains takes place with the participation of CO and H_2 by a number of successive processes of the same type: CO and the methylene ion radical combine on the surface to form a keten molecule which is adsorbed by two C atoms and which is converted into a different adsorbed state — a keten molecule adsorbed only by the C atom of the carbonyl group. Under the influence of hydrogen, the carbonyl group is converted successively into a hydroxymethine group and then into a methine group with the liberation of a molecule of water. Chain growth continues with the attachment of CO, adsorbed on the surface, to the ethylidene ion-radical (see p. 343).



Chain termination takes place by hydrogenation to saturated hydrocarbons:



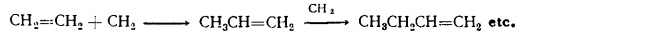
On the basis of the fact that the isotopic effect α_i (H_2, D_2) for the Fischer–Tropsch reaction is 0.77,[83] it was concluded that any stage in which the transition state is formed with the participation of free hydrogen molecules cannot be the rate-determining stage; the same is true of the diffusion, adsorption, and desorption of hydrogen. According to Roginskii[82], the kinetics of the reaction[43] and the fact that the isotopic effect α_i is < 1 show that the limiting stage must be one of the stages in the formation of additional methylene radicals, involving the participation of carbon monoxide and hydrogen in the adsorbed state.

IV. DEGRADATION OF CARBON CHAINS

All the above schemes consider only growing chains. Degradation processes, apart from the dissociation of ethylene into two methylene radicals, which unlike the dissociation of keten into CH_2 and CO has not been experimentally proved, is not considered in these schemes. Experiment shows, however, that degradation processes play an extremely important part in hydropolymerisation[84–86]. It is assumed that the species undergoing decomposition are semi-hydrogenated forms of alkenes consisting of heterogeneous hydrocarbon radicals, and that this decomposition takes place intensively in the presence of CO; this can probably be attributed to the action of radicals containing one carbon atom[87,88]. The formation of radicals with a smaller C number from chains with a large C number is observed particularly clearly in the hydropolymerisation of isobutene[89–98] and higher alkenes such as hex-1-ene[99,100] and oct-1-ene[101]. These processes take place with the participation of hydrogen, the concentration of the latter in the original gas influencing the reaction rate and the composition of the final products[102,103].

It has been noted that the products of the hydropolymerisation of alkenes, in addition to polymeric forms, contain compounds with C numbers which are not multiples of that of the original alkene. Their concentration in the high-boiling fraction of the condensate, which contains hydrocarbons with a C number greater than that of the original alkene, increases with increase in the C number of the latter and has the values (wt.%): 34, 44, 73, 80, and 85 for ethylene, propene, but-1-ene, pent-1-ene, and oct-1-ene respectively[74,104]. This is attributed to the fact that the greater the C number of the original alkenes, the greater the number of "non-multiple" hydrocarbons which can exist; this number is equal to n - 1 when the C number of alkene is equal to n.

Examination of the methods by which higher hydrocarbons with a non-multiple C number can be formed leads to the conclusions that they cannot be formed in such large quantities entirely by hydrocondensation of the original alkene with CO according to the scheme:



Non-multiple hydrocarbons are formed chiefly by rupture of the C–C bonds in the course of the process with the subsequent reaction of the resulting radicals with adsorbed alkene molecules.

The number of molecules of the original normal α-alkene taking part in the formation of higher hydrocarbons and corresponding to one CO molecule taking part in the same reaction (yield with respect to initiator) is usually greater than unity, indicating [105,106] a chain mechanism for the reaction, in good agreement with the radiochemical data examined above. The yield with respect to the initiator decreases with increase in the C number of the original alkene, other conditions being equal. At ratios in the original gas $H_2 : CO \simeq 8$ and $C_nH_{2n} : H_2 \simeq 1$, the yield with respect to initiator is equal to 6–8 for ethylene, ~ 4 for propene, ~ 3 for but-1-ene, and ~ 2 for hex-1-ene [104]. Thus 12 C atoms react for every CO molecule, irrespective of the molecules in which they are present. All these reacting atoms are apparently adsorbed on the catalyst surface; this may lead to some deformation of the carbon chains and bring about an increase in the ease of rupture of the C–C bonds in the reaction with the formation of heterogeneous radicals. Adsorption by all C atoms of the alkene takes place at low concentrations of CO under the conditions of the radical–chain reaction of growth and degradation of the carbon chains. At higher CO concentrations, the C atoms of the alkene which do not adjoin the multiple bond are displaced from the surface by the carbon monoxide being adsorbed. The alkene is then adsorbed only by the C atoms of the double bond without deformation of the other bonds, and chain growth takes place by a hydrocondensation scheme without rupture of the C–C bond (see p. 346). Thus depending on the concentration of CO and H_2 in the original gas and the adsorption properties of the alkene, one form of adsorption is replaced by the other, as a result of which the hydropolymerisation is replaced by hydrocondensation [107].

V. INITIATED HETEROGENEOUS-CATALYTIC REACTIONS

The heterogeneous-catalytic reaction examined above, namely the hydropolymerisation of alkenes in the presence of hydrogen, is initiated at 190–200° by small quantities of CO. A new heterogeneous-catalytic reaction, taking place only in the presence of initiator, was discovered recently. This is the hydropolymerisation of alkenes, initiated at 100–120° by small quantities of oxygen in the presence of hydrogen on Co catalysts [108–113]. Under the optimal conditions, this reaction takes place to the extent of 35–45%, and the hydrogenation of the alkene to the alkane with the same number of carbon atoms takes place to the extent of 17–30%, calculated on the original alkene (C_2–C_4). The optimal concentration of oxygen in the original alkene–hydrogen mixture amounts to ~ 2%. Hydropolymerisation under the influence of oxygen always takes place at the same time as hydrogenation of the alkene. A catalyst which is inactive with respect to hydrogenation is also inactive with respect to hydropolymerisation. As with the hydropolymerisation of alkenes initiated by carbon monoxide, the initiation of the hydropolymerisation by oxygen is followed by the formation of new intermediate active forms on the catalyst surface, indicating degradation processes. In addition to true polymeric forms, the reaction products contain hydrocarbons in whose molecules the numbers of carbon atoms are not multiples of the number in the original alkene. The results obtained have made it possible to develop the concept of "initiated heterogeneous-catalytic reactions" [114], an example of which is provided by the hydropolymerisation of alkenes under the influence of CO or O_2. A characteristic feature of initiated heterogeneous-catalytic reactions is that they take place entirely on the surface of the solid catalyst and that they require not only a specific catalyst but also the presence, in the reaction zone, of a compound which differs from the direct starting materials and which does not react in stoichiometric proportions. This compound starts the reaction and acts as initiator. The initiator may or may not take part in the development of the process and the formation of the final products, depending on the reaction conditions.

Conditions were found under which CO undergoes almost no reduction by hydrogen and is not included in the final products of the hydropolymerisation of ethylene at 190°. The quantities of CO taken for the reaction and obtained after the reaction were identical. The yields and compositions of the reaction products, however, differed little from those observed in the reaction involving the reduction of CO. The reaction does not take place in the absence of CO.

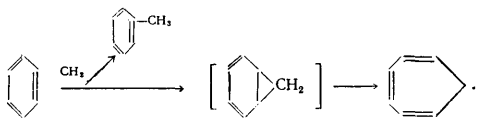
The $C_2H_4 : H_2$ ratio in the original gaseous mixture has a characteristic influence on the reduction of CO in the hydropolymerisation of ethylene. When this ratio is less than 1.0–1.2, CO reacts to the extent of 60%, but when the ratio is greater than 1.7, the CO is not used up. In the hydropolymerisation of propene, butene, and isobutene, the CO is reduced and used up in the reaction. In the joint hydropolymerisation of ethylene and its homologues, the quantity of CO used up is greater, the smaller the volume ratio of ethylene to hydrogen in the original gas [115].

It is possible to picture several ways in which hydropolymerisation is initiated by carbon monoxide. One possibility is that the carbon monoxide is reduced to some extent to surface intermediate products of the methylene and oxymethylene radical type, which take part in the initiation, and also possibly in growth of the carbon chains, so that they appear in the final products. During the reaction, the CO is regenerated, and the molecules of the regenerated CO may contain carbon atoms which come not from the original CO but from the alkene. Another way in which the reaction may be initiated by carbon monoxide does not involve the participation of CO at the start of formation and growth of the hydrocarbon chains and hence does not involve introduction of its carbon atoms into the final products. This takes place when the adsorption is hindered by a high concentration of ethylene. It may be assumed that in order to take part in the reaction in the form of CH_2, CHOH, and similar radicals or in the form of CO, the carbon monoxide should be adsorbed by both the C and O atoms. When adsorption is hindered, this is unlikely, and the CO is adsorbed through only the C atom. In this adsorbed form reduction is probably impossible, but the formation of $CO.nH_2$ complexes on the catalyst surface is still possible, and in these complexes the active hydrogen is capable of reacting with an alkene molecule, converting it into a heterogeneous radical which initiates the hydropolymerisation.

The hydropolymerisation of ethylene without consumption of CO and hence without the liberation of water indicates that the formation of hydrocarbon chains is in principle possible not by a dehydration-condensation scheme [29] but by a polymerisation scheme with a correction for degradation processes [86,87]; this is extremely important for an understanding of the mechanism of the reaction.

VI. HYDROCONDENSATION OF CARBON MONOXIDE WITH CYCLIC HYDROCARBONS

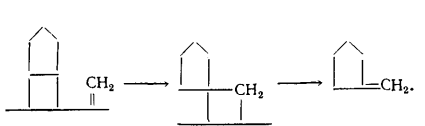
The catalytic hydrocondensation of carbon monoxide with alkenes [40] is one of the first stages of the Fischer–Tropsch reaction and the hydropolymerisation of alkenes under the influence of CO. It is also of independent importance, however. It demonstrates the ability of CO, mixed with H_2, to act as an alkylating agent, particularly a methylating agent, leading to the formation of the homologues of alkenes. Hydrocondensation takes place selectively with cyclic hydrocarbons, although the yields are low, since these hydrocarbons do not undergo further hydropolymerisation. This reaction was first used to prove the formation of surface methylene radicals from CO and H_2 on a skeletal Co–Ni catalyst during the conversion of benzene into toluene [116]. The formation of toluene from benzene, CO, and H_2 was also observed [117] over an Fe–Cu catalyst. When the same reaction was carried out at 190° and 1–20 atm (Co–ThO_2–kieselguhr catalyst) the reaction products were found to contain small quantities of cycloheptatriene in addition to toluene [118]. Its formation was attributed to the reaction of methylene radicals with benzene with the intermediate production of the norcaradiene structure:



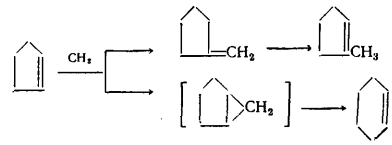
The formation of cycloheptatriene and toluene from benzene, CO, and H_2 takes place by parallel reactions [119].

A mixture of cyclohexene, CO, and H_2 gave up to 10% of the monomethyl and dimethyl derivatives [120,121]. Cyclopentadiene, CO, and H_2 gave 4–5% of the monomethyl, dimethyl, and trimethyl derivatives [122].

The hydrocondensation of CO with cyclopentene gave a mixture of hydrocarbons with C number greater than that of the original cycloalkene, in yields of 33% relative to the CO reacting or 5% with respect to the cyclopentene passed. After complete hydrogenation, the product was found to contain 45% methylcyclopentane, 20% ethylcyclopentane, 8% propylcyclopentane, and 27% cyclohexane hydrocarbons (10% cyclohexane, 10% methylcyclohexane, and 7% ethylcyclohexane) [74,123]. The process involving increase in the size of the ring is associated directly with the hydrocondensation [75]. It was shown [126] that the formation of a six-membered ring from a five-membered ring is not associated with isomerisation of the five-membered ring or with the formation of methylenecyclopentane according to Herington's scheme [34]:



It was suggested [124] that by analogy with the formation of cycloheptatriene from benzene via the norcaradiene structure, hydrocarbons with a six-membered ring are produced from cyclopentene with the intermediate formation of the bicyclo[1,0,3]hexane structure:



The ease of alkylation decreases in the order: cyclopentene > cyclohexene > benzene. Alkylation is favoured by a decrease in the concentration of CO in the original gas from 20% to 5%. [125]

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From the present review it may be concluded that in the preparation of hydrocarbons from CO and H_2, the latter form a primary complex (the C_1 complex) on the catalyst surface, and that the growth of the carbon chain begins from this complex. Chain growth involves the successive attachment of structural units containing one carbon atom to the primary complex. Experiments with the addition of a small quantity of compounds labelled with ^{14}C to the CO–H_2 mixture show that these compounds can be divided into two groups. The reaction with compounds of the first group gives liquid products whose molar radioactivity increases regularly with increase in the C number of the fraction. These compounds include formaldehyde, methanol, methyl formate, and keten labelled in the CO group. The reaction with gas containing compounds of the second group gives liquid products whose molar radioactivity remains constant with change in the C number. These compounds include ethanol, propanol, acetaldehyde, propanal, ethylene, propene, and keten labelled in the CH_2 group. These apparently take part in the formation of a primary complex which is analogous to or identical with the C_1 complex, either as the complete molecule or as a part of the molecule containing the labelled ^{14}C atom. For example, keten enters the primary complex in the form of the CH_2 group, and ethylene enters completely (or, less probably, as a CH_2 radical formed by the dissociation of $CH_2{=}CH_2$); alcohols enter the complex completely on Fe catalysts but in the form of the dehydration product (the alkene) on Co catalysts. Substances of the first group undergo preliminary decomposition with the formation of CO, which reacts further, taking part in chain growth. When added in larger quantities, ethylene may be included in the chain during its growth. This shows that a structural unit with two or more C atoms may also take part in chain growth. In the same way, the primary complex may contain not merely one, but also two or more C atoms. The initiation of the chains by methylene radicals formed by dissociation of keten shows convincingly that the presence of an oxygen-containing radical is not essential for chain initiation. This process also takes place with the participation of a hydrocarbon radical. The primary complex apparently may or may not contain oxygen, depending on the conditions; there is then an increase in the probability of the condensation or polymerisation scheme for C–C bond formation.

The fact that chain growth under certain conditions takes place exclusively according to the polymerisation scheme and not by condensation with the liberation of water is shown by new data, according to which the hydropolymerisation of ethylene under the influence of CO takes place under certain conditions with almost no consumption of the latter, and hence without the liberation of water.

It has been shown that degradation processes play an important part in the formation of carbon chains. The hydrocondensation of unsaturated hydrocarbons with CO may take place not only with the formation of a straight chain, but also via three-membered complexes analogous to the products of the reaction of multiple bonds with carbenes.

The concept of initiated heterogeneous-catalytic reactions has developed; according to this concept, an important part is played not only by the solid catalyst but also by an initiator which is not involved in the stoichiometry of the reaction.

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PHASE EQUILIBRIA BETWEEN IMMISCIBLE GASEOUS PHASES

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INTRODUCTION

Until very recently there were reckoned to be five types of equilibria: crystal–crystal, crystal–liquid, crystal–gas, liquid–liquid, and liquid–gas. The theory of these phase equilibria was developed by Konovalov[1], Stoletov[2], Gibbs[3], van der Waals[4], Kuenen[5], and others. There was also convincing experimental confirmation of the theoretical predictions.

It now seems astonishing to us why the possibility of the existence of yet another type of equilibrium — gas–gas equilibrium (the existence of which could have been postulated even by simple analogy) — was generally not discussed right up to the end of the XIXth century. Even at the time of Dalton, scientists were surprised[6] that gases did not behave as liquids and did not take up positions in relation to one another according to their specific gravities. The explanation for such behaviour of gases was found in the fact that at low pressures they are mechanically (energetically, in modern terminology) independent.

The concept of the energetic independence of gases, true only at moderate pressures, greatly suppressed interest in a search for equilibrium between gaseous phases. Even after van der Waals[7] and Kammerlingh-Onnes and Keesom[8] had made, in the 1890's, a theoretically based prediction of the possibility of the existence of such an equilibrium, about 50 years elapsed before the first experimental work appeared, carried out by Krichevskii[9]. The results completely confirmed the predictions of the Dutch scientists.

Such a prolonged break is explained not solely to the viability of the concept of the energetic independence of gases. van der Waals and his students correctly predicted that the phenomenon of restricted mutual solubility of gases is possible because there is a great similarity between liquids and strongly compressed gases. Hence it seemed natural to search for this phenomenon at high pressures. The absence of the technical means necessary for this was a second reason, which for long delayed the experimental confirmation of this interesting phenomenon. However, as we shall see subsequently, it can also be observed at comparatively low pressures.

But somehow or other, if the honour of the theoretical prediction of and basis for the new type of equilibrium belongs to the Dutch scientists, that of resurrecting their forgotten ideas, experimentally verifying these ideas, and developing further the theory of phase equilibria with allowance for this new equilibrium belongs wholly to Soviet scientists[10].

RESTRICTED MUTUAL SOLUBILITY OF GASES

The works of van der Waals and his coworkers contained not only an indication of the possibility of equilibrium between two gaseous phases at temperatures above the critical temperatures of the two components of a binary mixture but also predictions about the form of the critical curve.

According to these predictions two types of such equilibria are possible. *The first type* (to which belong systems containing helium) is characterised by the critical curve (in coordinates of pressure and temperature) in leaving the critical point of the less volatile component (Fig. 1) being directed towards the side of high temperatures. The curve is convex towards the temperature axis and at the point *M* turns towards lower temperatures. The reversal occurs at appreciable pressures and after it the curve is directed towards the side of the critical point of the more volatile component. Fig. 2 shows the phase diagram for this type of equilibrium.

Second type. On leaving the critical point of the less volatile component, the critical curve (Fig. 3) is at first directed towards the side of lower temperatures. The curve is convex towards the temperature axis and passes through a minimum — point *D*. Its name, according to van der Waals terminology, is the double homogeneous point. Then the curve turns towards the side of high temperatures and subsequently its form does not differ from that described for the first type†.

Fig. 4 shows a phase diagram for this type of equilibrium as we visualise it now. In the temperature region from the critical temperature of the less volatile component to the temperature of the double homogeneous point both liquid–gas and gas–gas equilibria exist. In the temperature region from the critical point of the less volatile component up to the temperature maximum *M* there is only gas–gas equilibrium.

METHOD OF INVESTIGATION

Phase equilibria between two gaseous phases have been investigated by analytical and synthetic methods. These methods (details of the apparatus and experimental technique) have been described in sufficient detail already[12]. Here it is possible only to mention that by analytical is meant those methods in which the compositions of the coexisting phases are determined by the analysis of specimens taken from each phase. In working by synthetic methods a mixture of the two components of known quantitative composition is made up and then the moment for the disappearance or appearance of one of the phases is observed, by measuring the temperature, pressure, or volume (or all three parameters) of the system.

Many of the studies carried out in our country employed analytical methods in equipment with a mercury piezometer (Fig. 5) (a Callietet tube[13]). The piezometer is a metal

† We will not deal with the form of the critical curve in the region close to the critical point of the more volatile component (see, for example, Vogel[11]).