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Study of the Mechanisms of Heterogeneous-catalytic Reactions by the Method of Labelled Molecules (labelled with ^{14}C)

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The present review differentiates between the method of labelled atoms (the LA method) and the method of labelled molecules (the LM method). Unlike the LA method, in which an experimental study is made of the distribution of the isotopic tracer over various positions in the molecules of the starting materials and reaction products, the LM method involves the study of the distribution of the isotopic tracer between the molecules of different substances. The basic equations of the LM method for integral and differential reactors are given, and literature on the application of the LM method with the ^{14}C isotope to study the mechanisms of heterogeneous-catalytic reactions is reviewed. The bibliography contains 163 references.

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1. INTRODUCTION

At the present time there are two main ways in which isotopes are used to study the mechanisms of catalytic reactions. In the first, it is possible to follow experimentally the distribution of the isotopic tracer in various positions in the molecules of the starting materials and reaction products, and this in turn makes it possible to obtain information on the relative reactivity of the atoms in the positions selected, on the course of the reaction, etc. This method could be called the labelled atom method in the narrow sense (the LA method).

In the second, we follow the distribution of the isotope not inside the molecules, but between the molecules of different substances or, as for example in the isotopic differential method for studying the surface of catalysts, between different parts of molecules of the same substance. This makes it possible to determine the role of the labelled substance in a multi-stage catalytic process, and to study the properties of the catalyst and the nature of the products of its interaction with the reacting molecules. This method might be called the labelled molecule method (the LM method).

The LM method can be used to study a wider range of specific problems in heterogeneous catalysis than is possible by the LA method. It need only be pointed out that this method has been used to study inhomogeneity (see for example Refs. 1–3), acid–base properties[4], surface area[5,6], the poisoning of catalysts[7], the interaction of adsorbed substances on a surface[8–10], the kinetics of heterogeneous-catalytic reactions[11–15], etc. Many theoretical aspects of the use of isotopes in catalysis were examined in detail in a monograph by Roginskii[16] and to a lesser extent in other monographs (see for example Refs. 17–19). A brief review by Trimm[20] was devoted to the use of carbon isotopes to study heterogeneous catalysis.

At the present time, however, there is no sufficiently complete review of work carried out by the LM method in various fields of heterogeneous catalysis, and in the study of the mechanisms of the reactions in particular. The aim of the present work is to fill this gap.

2. POSSIBILITIES OF THE LM METHOD IN THE STUDY OF THE MECHANISMS OF CATALYTIC REACTIONS

A particular example of the method of "labelled molecules" is provided by the analytical method of isotopic dilution[21,22], which makes it possible to determine extremely small quantities of substance when radioactive tracers are used; it is better to have the tracer in the substance being determined then to have it in the diluent. An example of the use of this method for the analysis of the products of a heterogeneous-catalytic reaction was described by Blau and Willard[23], who studied the reaction of benzene-^{14}C and ethyl chloride vapours over solid aluminium chloride (sublimed on the walls of the flask) at room temperature. The reaction products, obtained in small quantities, were diluted with a measured amount of unlabelled benzene, ethylbenzene, and diethylbenzene, after which the mixture was fractionated and the yields of the corresponding products were determined from the specific radioactivity of the components. In this work it was possible to show that the rate of formation of ethylbenzene depends on the pressures of both starting materials.

The method of isotopic dilution as such apparently will not be very important for the study of organic reactions, since the development of chromatography has given research workers more convenient and sufficiently sensitive methods of analysis. The determination of specific radioactivity is widely used, however, in other isotopic methods for studying reaction mechanisms, in particular in the kinetic isotopic method, which makes it possible to determine quantitatively the rates of formation and consumption in given directions for a given substance in a reacting system, and this helps to establish a scheme of genetic relationships for the products.

As early as 1937, Wilson and Dickinson[24] showed that for the reversible redox reaction

$$H_3A^{V}O_3 + I_3^{-} + H_2O \rightleftarrows H_3AsO_4 + 3I^{-} + 2H^{+} \quad (1)$$

it is possible, by using radioactive tervalent arsenic, to study the rates of the forward and back reactions at equilibrium by making use of the equation

$$\frac{d\alpha}{dt} = \frac{R}{[As^{V}]}(\beta - \alpha) \quad (2)$$

where α is the specific radioactivity of H_3AsO_4; β the specific radioactivity of H_3AsO_3; R the reaction rate; and $[As^{V}]$ the concentration of H_3AsO_4 (assumed constant). To calculate R, Wilson and Dickinson[24] used the integral form of this equation.

The kinetic features of biochemical processes have been studied with labelled substances by Zilversmit[25], Barnum and Huseby[26], and others. A review of work by non-Soviet authors in this field is given in Aronoff's monograph[27].

Neiman[28-30] gave the derivation of the equation

$$\frac{d\alpha}{dt} = \frac{w(\beta - \alpha)}{[X]} \quad (3)$$

where w is the rate of formation of the product from a single radioactive precursor; [X] the concentration of the product X; β the specific radioactivity of the precursor; and α the specific radioactivity of the product, and used it to find the rates of the formation and decomposition of the intermediate products; he called this method the kinetic isotopic method (KIM) for studying reaction mechanisms.

Eqn. (3) can be written for the general case of the formation of a substance X from any number of radioactive precursors[31]:

$$\frac{d\alpha_X}{dt} = \frac{1}{n[X]}\sum_{i=0}^{i} w_i(\alpha_i - \alpha_X) \quad (4)$$

where w_i is the rate of the process i leading to the formation of the substance X; α_i the specific radioactivity of the corresponding precursor; α_X the specific radioactivity of the substance X; [X] the concentration of the substance X, %; and n the total number of moles of the substance in the system. The overall equation of the material balance for X can evidently be written in the form

$$\frac{dn[X]}{dt} = \sum_{i=0}^{i} w_i - \sum_{j=0}^{j} w_j \quad (5)$$

where w_j is the rate of consumption of the substance X.

In integral form and applied to the conditions of heterogeneous catalysis, Eqns. (4) and (5) are written in the form

$$\frac{\alpha_X - \alpha_{X_0}}{st} = \frac{1}{n_0[X]_0}\sum_{i=0}^{i} w_i(\alpha_i - \alpha_X) \quad \text{or}$$
$$\frac{\alpha_X - \alpha_{X_0}}{s} = \frac{1}{u[X]_0}\sum_{i=0}^{i} w_i(\alpha_i - \alpha_X) \quad (6)$$

and

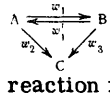
$$\frac{n_0\{[X] - [X]_0\}}{st} = \sum_{i=0}^{i} w_i - \sum_{j=0}^{j} w_j \quad \text{or} \quad \frac{u\{[X] - [X]_0\}}{s} = \sum_{i=0}^{i} w_i - \sum_{j=0}^{j} w_j \quad (7)$$

where α_{X_0} is the specific radioactivity of the substance X in the original mixture; n_0 the number of moles of the starting material; $[X]_0$ the percentage concentration of the substance X in the original mixture; [X] the same in the reaction products; s the catalyst surface area; and u the rate of supply of the starting material ($u = n_0/t$).

Eqns. (4) and (5) [or (6) and (7) respectively] are the most general equations of the kinetic isotopic method, and they make it possible to find the rates of formation and consumption of a substance in complicated reactions.

In the study of genetic relationships and in the verification of stepwise schemes, the first problem which arises concerns the extent to which a product B, formed from the starting material A, takes part in the formation of the final product C.

To solve these problems, Balandin and coworkers[32,33], beginning in 1958, used the triangular scheme



(8)

The equations for the reaction rates in this system can readily be obtained from a system of equations of types (4) and (5) or (6) and (7) respectively.

Differential reactor

$$w_1 = \frac{u[B_0](\alpha_{B_0} - \alpha_B)}{s(\alpha_B - \alpha_A)} \quad (9)$$

$$w_1' = \frac{u[A_0](\alpha_{A_0} - \alpha_A)}{s(\alpha_A - \alpha_B)} \quad (10)$$

$$w_2 = \frac{u\{[C] - [C_0]\}}{s} - w_3 \quad (11)$$

$$w_3 = \frac{u\{[C](\alpha_C - \alpha_A) + [C_0](\alpha_A - \alpha_{C_0})\}}{s(\alpha_B - \alpha_A)} \quad (12)$$

Integral reactor

$$w_1 = \frac{d\beta}{d\tau}\frac{[B]n}{(\alpha_A - \alpha_B)} \quad (13)$$

$$w_1' = \frac{d\alpha}{d\tau}\frac{[A]n}{(\alpha_B - \alpha_A)} \quad (14)$$

$$w_2 = \frac{dn[C]}{d\tau} - w_3 \quad (15)$$

$$w_3 = \frac{\frac{d\alpha_C}{d\tau}n[C] + \frac{dn[C]}{d\tau}(\alpha_C - \alpha_A)}{\alpha_B - \alpha_A} \quad (16)$$

The significance of the symbols in Eqns. (9)–(16) is clear from the foregoing.

It is obvious that when $w_3 = 0$, B and C are formed by parallel independent paths. When $w_2 = 0$, the formation of the product C is a purely consecutive process. In this case the rate w_3 can be found from Eqn. (3)

$$w_3 = \frac{d\gamma}{d\tau}\cdot\frac{[C_3]}{\beta - \gamma} \quad (17)$$

or

$$w_3(\beta - \gamma) = [C_3]\cdot\frac{d\gamma}{d\tau} \quad (18)$$

Eqn. (18) has important consequences:

$$\text{for } \frac{d\gamma}{d\tau} > 0, \quad \beta > \gamma \quad (19)$$

and

$$\text{for } \frac{d\gamma}{d\tau} < 0, \quad \beta < \gamma \quad (20)$$

The inequalities (19) and (20) are necessary but not sufficient conditions for formation of the product C from a single precursor B. Although these conditions follow from the equations of the kinetic isotopic method, they are of independent importance, and, as shown below, they are used more widely than the other equations of the method.

Hightower and Emmett[34], in a study of the cracking of cetane, expressed the fraction of the consecutive path for the formation of the product i through the product a in the form of the ratio

$$\alpha_a^i(\text{obs})/\alpha_a^i(\text{max})n \qquad (21)$$

where α_a^i (obs) is the experimental value of the ratio of the specific radioactivities of the product i and the product a in the catalysate, α_a^i (max) the calculated maximal value of this ratio, and n the number of moles of substance a required for the formation of one mole of substance i. Assuming that the consecutive reactions in this instance are of first order, the authors cited find that the value of α_a^i (max) lies in the range 1–3.

A number of authors (see for example Refs. 35 and 36), in experiments with mixtures containing a labelled substance, calculate the so-called intensities of the reaction, by which is meant the yields of the products separately from each component of the original mixture. The ratio of the intensities indicates the relative reactivity of the substances when present together in the reaction zone, and can be used to obtain information on the reaction mechanism; the ratio of the intensities, however, unlike the ratio of the rates of the processes, does not contain information on the reaction paths, and in most instances it does not make it possible to obtain unambiguous information on the adequacy of the proposed and real sequence of processes.

In concluding this section we may point out that the LM method is fundamentally related to the analytical method of radiochromatography, which makes it possible to carry out the simultaneous chemical and radiometric analysis of complex mixtures of substances.

The high efficiency of this method makes it possible in turn to use micro-catalytic apparatus to carry out experiments, and this is extremely convenient from the safety viewpoint and in connection with the use of expensive radioactive materials. The foundations of the application of radiochromatography combined with micro-catalytic apparatus were laid by Emmett and coworkers[37], and in the Soviet Union the use of radiochromatography in catalysis was pioneered by Roginskii and Yanovskii and coworkers[38–40].

3. DETERMINATION OF THE STOICHIOMETRIC NUMBER

The stoichiometric number of a reaction characterises the reaction mechanism[41]. The stoichiometric number γ can be determined experimentally if the rates of the forward and back reactions are measured under the same conditions

$$\gamma = \frac{-\Delta G/RT}{\ln \frac{v_+}{v_-}} \qquad (22)$$

where ΔG is the Gibbs free energy under the conditions of the reaction; R the gas constant; T the absolute temperature; v_+ the rate of the forward reaction; and v_- the rate of the back reaction.

When isotopes are used to determine the forward and back reaction rates, a reasonable integral value of the stoichiometric number can be expected only if the isotope takes part in the limiting stage of the reaction. Thus to determine precisely the limiting stage it is best to determine the stoichiometric number by means of various isotopes. Using ^{14}C, Kaneko and Oki[42] determined the forward and back reaction rates for the conversion of water gas:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (23)$$

in the presence of iron(III) oxide, and this enabled them to determine γ, which was found to be equal to 1. After examining three possible mechanisms:

$$\left.\begin{array}{l} H_2O \rightarrow 2H\,(a) + O\,(a) \\ CO + O\,(a) \rightarrow CO_2 \\ 2H\,(a) \rightarrow H_2 \end{array}\right\} \qquad (24)$$

$$\left.\begin{array}{l} H_2O \rightarrow H_2O\,(a) \\ CO \rightarrow CO\,(a) \\ H_2O\,(a) + CO\,(a) \rightarrow H_2 + CO_2 \end{array}\right\} \qquad (25)$$

$$\left.\begin{array}{l} H_2O \rightarrow H_2O\,(a) \\ H_2O\,(a) + CO \rightarrow H_2 + CO_2 \end{array}\right\} \qquad (26)$$

where (a) denotes the adsorbed state, and pointing out that according to published data[43] the value of γ determined by means of deuterium is also equal to 1, the authors cited rejected mechanism (24), since it does not contain a stage in which carbon and hydrogen atoms take place simultaneously, and concluded that the mechanism operating is either (25) or (26).

In analogous studies, Atkins and Happel[44] used ^{14}C to determine the stoichiometric number for the dehydrogenation of butane

$$C_4H_{10} \rightleftarrows C_4H_8 + H_2\ . \qquad (27)$$

In this instance also, γ was found to be equal to 1. From this it follows that the adsorption or desorption of hydrogen cannot be the limiting stage of the reaction; a limiting stage, if one exists, can only be a stage in which transformation of the carbon framework of the molecule takes place. Atkins and Happel[44] assume that the reaction has not one but several limiting stages, the stoichiometric number of each being equal to unity.

4. PROBLEM OF THE ISOTOPIC EXCHANGE OF CARBON

For the interpretation of the results obtained by the labelled molecule method, it is important that intermolecular isotopic exchange of carbon in the organic compounds is unlikely under the usual conditions in which catalytic reactions are carried out. In a number of studies the possibility of exchange has been verified experimentally.

For example, Emmett and coworkers[45] showed that methane, n-butane, and acetylene under the conditions of the Fischer–Tropsch synthesis remain almost non-radioactive after contact with labelled carbon deposited on the catalysts: appreciable transfer of radioactivity (2%) was observed only for but-1-ene. Under the severe conditions of cracking over an aluminosilicate catalyst (500°) the transfer of radioactivity between ethane and propane, and between methane and ethylene, amounted to fractions of 1%[46]; there was almost no transfer of radioactivity between methane and carbon. In the interpretation of the results obtained, it must of course be borne in mind that the transfer of radioactivity from one product to another (in the works cited) does not in itself prove that exchange

takes place, if the back reaction has not been studied experimentally. It is quite probable that labelled compounds took part in the synthesis of those substances in which the radioactivity was determined.

In this connection, mention must be made of the so-called isotopic-radical exchange of carbon. Vasserberg and coworkers [47-49] found that when substances containing radiocarbon, for example $^{14}CH_3OH$ (called the "tracer donor") are passed over alumina together with an unlabelled oxygen-containing compound, for example ethanol (called the "tracer acceptor"), the products of the transformation of the latter (in this instance ethylene) were found to contain a small amount of radioactivity. This led to the development of the idea that exchange of carbon takes place between methanol and ethanol and also between other compounds as a result of the reaction of intermediate radical-like formations on the surface of the alumina.

These observations attracted some attention [50], but it was later shown [51,52] that under the conditions of dehydration on alumina, methanol gave small quantities of ethylene and propene, and ethanol gave propene. The addition of non-radioactive ethanol to radioactive methanol does not increase the formation of radioactive ethylene. It is evident that in the interpretation of the results of this work [47-49] we may be dealing not with the exchange of carbon but with side reactions involving the transformation of the tracer donor. The use of the acceptor merely facilitated the detection of small quantities of these side products.

It may thus be concluded that at present there is no evidence of the possibility of heterogeneous-catalytic exchange of carbon in organic compounds.

5. CATALYTIC CRACKING OF HYDROCARBONS

First in Roginskii's laboratory, and subsequently in work by Emmett and coworkers, it was shown that in the cracking of hydrocarbons, alkenes with lower molecular weight are the primary reaction products; the addition of ethylene-^{14}C to n-hexane [53], propene-^{14}C to 2,2,4-trimethylpentane [53], and propene-^{14}C, pent-1-ene-^{14}C, and hept-1-ene-^{14}C to n-hexadecane [34,54,55] over aluminosilicate catalysts under the conditions of cracking led to the formation of products whose specific radioactivity was close to or greater than that of the added labelled substance in the catalysate.

The addition of labelled alkanes to the starting materials in the cracking usually did not lead to the formation of hydrocarbons with appreciable radioactivity [34,53-55]. An exception is provided by work [56] in which labelled ethane mixed with n-octane at 500° over an aluminosilicate was dehydrogenated with the formation of ethylene.

These results show good agreement with the idea that cracking takes place by an ionic mechanism. In agreement with the fact that primary carbonium ions require more energy for their formation than secondary carbonium ions, ethylene takes a smaller part in the formation of the final products compared with other alkenes used as labelled additives to alkanes [34,53,55]. It should be noted, however, that the labelled compounds added to alkanes during cracking influence the reactivities of the original hydrocarbons.

It has been found [53] that labelled ethylene added to 2,2,4-trimethylpentane and propene under the conditions of cracking over an aluminosilicate takes part in the formation of products with the C_3 and C_4 compositions; in the experiments in which labelled ethane was added to 2,2,4-trimethylpentane, an even greater interaction was observed. In the opinion of the authors cited, these changes are due to degradative alkylation, taking place with the formation of intermediate bimolecular complexes, for example:

$$^{14}C_2H_6 + C_3H_8 \rightarrow (^{14}C_2H_6 \cdot C_3H_6) \begin{matrix} \nearrow {}^{14}C_4H_8 + CH_4 \\ \searrow C_4H_8 + {}^{14}CH_4 \end{matrix} . \qquad (28)$$

It is possible that in these processes a definite part is played by the recently discovered reaction of alkene disproportionation. It has been suggested [57,58] that this reaction involves the intermediate formation of a bimolecular complex with a four-membered ring structure:

$$\begin{matrix} R_1{-}CH{=}CH_2 \\ +CH_2{=}CH{-}R_2 \end{matrix} \rightarrow \begin{matrix} R{-}CH \cdots \vdots \cdot CH_2 \\ H_2C \cdots \vdots \cdot CH{-}R_2 \end{matrix} \rightarrow \begin{matrix} R_1{-}CH & CH_2 \\ \| & + \| \\ CH_2 & CH + R_2 \end{matrix} . \qquad (29)$$

Andrianova and Roginskii [56,59] showed that the addition of small quantities of alkenes (up to 2.5%) increases the extent of the cracking of n-octane, whereas an increase in the quantity of additive decreases the rate of cracking. The addition of alcohols has a similar influence, and this, in the opinion of the authors cited, is due to the formation of alkenes from the alcohols under the conditions of the reaction. They suggested that the cracking reactions take place by a chain mechanism, and that small quantities of alkenes initiate the process, whereas large quantities suppress it.

It might be expected that aromatic hydrocarbons would also take part in alkylation in the same way as alkenes, but the experiments of Hightower and Emmett [34,55] with the addition of labelled benzene and toluene to n-hexadecane under the conditions of cracking over an aluminosilicate catalyst showed that when these hydrocarbons are used, only a small proportion of alkylaromatic compounds are obtained. These are obtained chiefly from the products of the cracking of n-hexadecane as a result of the polymerisation and copolymerisation of alkenes with three or more carbon atoms in the molecule.

The use of labelled mixtures of alkanes and alkenes established that under the conditions of cracking, the carbonaceous deposits on the catalyst are also obtained chiefly from the alkenes [53,54,56,59,70]; with increase in the molecular weight of the alkane, the extent to which it takes part in the formation of carbon increases [59,61].

To study the problem of whether carbon is obtained by the gradual loss of hydrogen atoms or by the removal of terminal carbon atoms from the hydrocarbon molecules, McMahon [62] determined the specific radioactivity of the carbon after passing n-heptane-4-^{14}C, n-octane-1-^{14}C, and oct-1-ene-1-^{14}C over a catalyst. In all instances the specific radioactivities of the starting material and the carbon were equal, providing evidence in support of the first hypothesis. In Wynnemer's experiments [63], however, the specific radioactivities of carbon deposits obtained at 454° and 510° from the same substance (n-decane-2-^{14}C) were different, indicating that the mechanism of carbon formation may depend on the temperature.

6. OXIDATION OF HYDROCARBONS

The mechanism of the extensive oxidation of alkenes has been studied by Neiman's method, chiefly by Margolis and coworkers in Roginskii's laboratory; this work has been reviewed in sufficient detail [64,65] and we shall give only a brief description here. A series of experiments were undertaken to observe the reaction sequence: alkene → product of incomplete oxidation → carbon dioxide,

which might indicate the primary product of the oxidation of the alkene. Oxides of hydrocarbons, aldehydes, and other compounds were considered as possible primary products. It was shown that over a silver catalyst, ethylene is oxidised to carbon dioxide by a parallel-consecutive mechanism—through the intermediate formation of ethylene oxide and also directly[66-68]. Formaldehyde and acetaldehyde decreased the rate of oxidation, so that they could not be intermediate products[67,68]. Ethylene oxide and acetaldehyde added to ethylene over vanadium oxide took an active part in the formation of carbon monoxide and dioxide, but since almost no ethylene oxide and acetaldehyde are detected in the oxidation of ethylene, the authors cited[69,70] concluded that ethylene is for the most part oxidised directly to carbon dioxide.

In studies of the oxidation of propene on copper catalysts, it was established that carbon dioxide is formed by a parallel-consecutive mechanism with the participation of acrolein formed as an intermediate[71,72].

It has also been shown[69,70] that aldehydes take an active part in the formation of the carbonaceous film on the catalyst, and that this has some influence on the selectivity of the oxidation processes.

Radiocarbon ^{14}C has also been used to study the mechanism of the extensive oxidation of toluene over a copper catalyst[73]. In experiments in which labelled benzyl alcohol and benzaldehyde were added to toluene, the authors cited concluded that toluene is oxidised to carbon dioxide partly through the intermediate formation of benzyl alcohol. Unfortunately, the results of this work are not reported in sufficient detail.

7. SYNTHESIS OF HYDROCARBONS AND ALCOHOLS FROM CARBON DIOXIDE AND HYDROGEN

Radiocarbon ^{14}C has been used in a large number of studies to investigate the problems of the mechanism of the synthesis of hydrocarbons and alcohols from CO and hydrogen. Most of this work was recently reviewed by Eidus[74], and we shall here list only the main features and the results obtained in this work.

Emmett and coworkers[45] used catalysts carbonised in the presence of radioactive carbon monoxide, and found that the radioactivity is transferred to the products of the synthesis to only a slight extent; this proved that surface metal carbides are not intermediate products of the synthesis. Subsequently, similar results were obtained in other studies over cobalt[75] and iron[76,77] catalysts. It is now generally accepted that some surface complexes involving CO and H_2 must be formed during the reaction to act as intermediate link. Ganguli[78], in a study of the simultaneous adsorption of CO and H_2 on a cobalt catalyst, showed that whereas exchange of the adsorption complex with gaseous CO takes place to a slight extent, the reaction products contain appreciable radioactivity; this proves that the CO–H_2 complex take part in the synthesis. In a large number of studies, various labelled substances have been added to the gas taken for the synthesis, in order to detect intermediate compounds. Examination of the published material shows that all the radioactive additives used can be divided into three groups according to the nature of their participation in the synthesis. The first group contains substances capable of generating radioactive carbon monoxide—methanol[79-81], formaldehyde[80], methyl formate[82], and keten[83] labelled in the carbonyl group. A characteristic feature of this group of substances is that in their presence, the molar radioactivity of the products increases with increase in molecular weight, and this can be regarded as confirming their role as the source of radioactive carbon monoxide, which is the chief "building material" in the synthesis.

The second group contains labelled substances whose addition leads to the formation of hydrocarbons with constant molar radioactivity—ethylene[77,84-86], ethanol[82,87-91], n-propanol[79-81], acetaldehyde[82], propionaldehyde[85], and keten labelled in the methylene group[92]. These substances are apparently capable of generating methylene radicals, which can initiate the synthesis[93].

In a study of the addition of ethanol to the gas taken for the synthesis[87,90,91], it was shown by the LA method that C_3 hydrocarbons are obtained by the attachment of a new carbon atom to the carbonyl carbon atom of the alcohol. Added aldehydes under the conditions of the synthesis are apparently readily hydrogenated with the formation of alcohols[82], and this explains the similarity in the behaviour of aldehydes and alcohols. It should be noted, however, that over a fused iron catalyst, added acetaldehyde was converted into higher alcohols more rapidly than added ethanol, by a factor of several orders of magnitude[94].

The third group contains substances which take little part in the synthesis (propene[75], butenes[95], isopropyl alcohol, and n-butanol[79-81]), and also methane[96,97] and carbon dioxide[80] which take almost no part in the synthesis.

Among the substances added to the gas taken for the synthesis, a unique position is occupied by ethylene. Fletcher and Gibson[98] showed that a mixture of hydrogen and ethylene in the presence of a small quantity (5%) of ^{14}CO gave hydrocarbons whose specific radioactivity was several times smaller than that of the original carbon monoxide; the low radioactivity of methane and the absence of any periodicity in the radioactive higher hydrocarbons with even and odd numbers of carbon atoms suggested that during the synthesis, ethylene is first dissociated to methylene radicals. When large quantities were added, it was found that ethylene takes part not only in the initiation of the synthesis but also in the growth of the hydrocarbon chains[75]. In recent years, the hydropolymerisation of ethylene in the presence of small quantities of CO over a cobalt catalyst has acquired independent interest. It has been shown[99] that the quantity of CO in the mixture remains almost unchanged during the experiment, whereas the process does not take place without CO. It might be suggested, however, that the maintenance of the CO concentration is due to the attainment of equilibrium in reactions involving its consumption and formation. This possibility was examined[100] by means of labelled CO and it was found that under certain conditions its specific radioactivity remains unchanged, so that CO is not formed during the synthesis, whereas ethylene is used up intensively in the reaction; it was thus proved that CO under these conditions acts as reaction initiator.

Radiochromatographic analysis has indicated that the highest radioactivity is shown by α-alkenes and the corresponding alkanes; β-alkenes, among which the cis-isomers predominated, showed a lower radioactivity, so that they were obtained by a different mechanism, and were not produced from the α-alkenes by isomerisation. An interesting feature is that in this work, although ^{14}CO was only the reaction initiator, an increase in the molar radioactivity of the hydrocarbons with increase in molecular weight was observed. A possible explanation is that with increase in the length of the chain there is an increase in the probability of a type of hydrocarbon desorption in which the primary complex on the surface decomposes and

the radioactive carbon is introduced into the molecule; it is suggested that most of the hydrocarbon molecules are desorbed in a different way, without decomposition of the primary complex.

It is also interesting to note that under the conditions of the synthesis of alcohols with the addition of labelled ethylene to the gas taken for the synthesis, propanol with a high specific radioactivity was obtained [86,101], and this has made it possible to come closer to the development of conditions for the preparation of propanol from ethylene, carbon monoxide, and hydrogen [86].

8. SYNTHESIS OF BIVINYL FROM ALCOHOL

^{14}C has been used to study the mechanism of the formation of bivinyl from alcohol on Lebedev's catalyst. It has been shown that ethylene and ether are not intermediate products [102,103], and that methanol takes part only in the formation of side products of the synthesis of bivinyl [104,105]. On the other hand, the addition of labelled crotonaldehyde to the original alcohol led to the formation of highly radioactive bivinyl [102,103]. Although crotonaldehyde was not detected in the condensates under the conditions of the experiments, so that the specific radioactivities of these products could not be compared, the results can be taken as confirming Gorin's familiar scheme [106], in which crotonaldehyde takes part as an intermediate product.

When labelled acetaldehyde was added to the alcohol, it was established that these substances in the mixture are readily interconverted [102,103]:

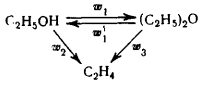
$$^{*}C_2H_5OH + CH_3CHO \rightleftarrows C_2H_5OH + {}^{*}CH_3CHO. \qquad (30)$$

Because of this, the part played by acetaldehyde in the synthesis of bivinyl could not be determined by this method. A radiochromatographic study [38] established that the formation of butenes takes place not as a result of the hydrogenation of bivinyl but by the dehydration of butanol produced in the reaction. The use of ^{14}C also showed that under the conditions of the synthesis of bivinyl by Lebedev's method the formation of carbonaceous deposits on the catalyst takes place chiefly from the original alcohol, and not from the bivinyl [107]. It may also be noted that in the dehydration of alcohol over titanium dioxide the carbonaceous film is again formed chiefly from the alcohol, and not from the alkene [108]; in the decomposition of alcohol over a dehydrogenating catalyst (copper on silica gel), the carbonaceous film was obtained chiefly from the acetaldehyde [109].

9. DEHYDRATION OF ALCOHOLS AND ACCOMPANYING REACTIONS

^{14}C has been used to make detailed studies of various problems of the mechanism of the dehydration of alcohols. Thus a discussion has been going on for a long time in the literature on the mechanism of formation of ethylene in the dehydration of ethanol over alumina.

Some authors consider that the formation of the alkene takes place by consecutive reactions, and that ether is first formed as an intermediate product. Others consider that ethylene and ether are formed by two independent parallel reactions. In 1958, a parallel-consecutive scheme was proposed for the dehydration of ethanol:



(31)

and the rates of the separate processes were determined experimentally [32,110]. For this purpose the dehydration of ethanol was studied with the addition of ^{14}C-labelled diethyl ether, at 275, 300, 350, and 400° in a flow reactor over industrial alumina.

It was found that at 275°, ethylene is formed directly from the alcohol and with the intermediate formation of ether at approximately equal rates; with increase in temperature the direct formation of ethylene from alcohol predominates. Thus on alumina, direct decomposition of alcohol to ethylene and water is possible; the bimolecular dehydration with the formation of ether and water takes place independently, but the ether formed is unstable under the conditions of the reaction and is itself able to undergo dehydration with the formation of ethylene and water. The mechanism of the dehydration of alcohol on an aluminosilicate catalyst is analogous [111].

In connection with the suggestion that the formation of ether and ethylene takes place through a common surface intermediate compound, which is present in equilibrium with the alcohol and ether [112,113], the method of isotopic dilution was used to study the chemosorption of mixtures of alcohol and ether on alumina at 120°; transfer of the radioactive tracer between the alcohol and the ether was not observed, so that, at low temperatures at least, there is a difference between the surface compounds formed from alcohol and ether [10].

Unlike alumina, a number of other oxides bring about not only dehydration but also dehydrogenation of alcohols with the formation of aldehydes or ketones. Saturated hydrocarbons are often detected in the catalysate gas together with unsaturated hydrocarbons and hydrogen. It is often assumed that the saturated hydrocarbons are formed by hydrogenation of an alkene. A number of authors, however, have pointed out the possibility of hydrogenolysis of alcohols at the C–C bond under the conditions of the reaction, since the catalysates were found to contain alkanes with one carbon atom less than the original alcohol [114,115]; in this connection it was suggested that alkanes may also be formed by the hydrogenolysis of alcohol at the C–O bond [116].

Experiments in which ethanol containing labelled ethylene was passed over titanium dioxide [108] and in which isopropyl alcohol with added propene was passed over vanadium(III) oxide [116] showed that the radioactive tracer was not converted into ethane and propane respectively, and was not detected in the liquid catalysates. These experiments confirmed that under the conditions of dehydration the alkanes are probably produced by the hydrogenolysis of alcohols, and not by hydrogenation of alkenes liberated into the gaseous phase.

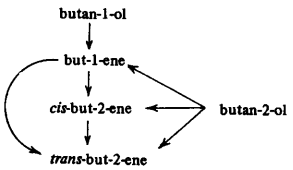
The isotopic-kinetic method has also been used to study the genetic relationships between the products in the more complex system formed in the dehydration of butanols.

The aim of the study was to follow the change in the ratio of the rates of the dehydration of alcohols and the isomerisation of the resulting butenes, and also to determine the reasons for the frequently observed preferential formation of but-1-ene and *cis*-but-2-ene from secondary butyl alcohol, which cannot be explained on the basis of a mechanism of dehydration involving a classical carbonium ion and for which the concept of a π-complex has been introduced [117] or for which it has been suggested that but-1-ene is an intermediate product of the formation of but-2-ene from butan-2-ol [118].

The studies were carried out over two specimens of alumina: grade A-1 [119] and industrial fluorinated grade [120]. These catalysts differ in their isomerising properties.

^{14}C-labelled butan-1-ol was added to the butan-2-ol to act as a source of labelled but-1-ene (it should be noted that in this instance the labelled hypothetical intermediate compound was not introduced in prepared form into the reaction zone but was synthesised during the reaction on the surface of the catalyst).

The reaction products were studied by the radiochromatographic method. Interconversion of the primary and secondary alcohols was not observed. The genetic relationships between the products according to scheme (32) was studied:



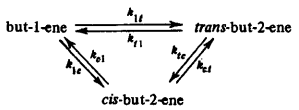
(32)

Determination of the rates in this scheme showed that most of the but-2-enes are obtained directly by the decomposition of butan-2-ol, and not by the isomerisation of but-1-ene, although the rate of isomerisation of but-1-ene into but-2-enes is also appreciable. The ratio of the rates of dehydration of butan-1-ol and the isomerisation of but-1-ene did not change on going from A-1 alumina to fluorinated alumina, indicating that the rates of dehydration and isomerisation change in the same sense on going from one alumina specimen to the other.

Butan-2-ol gave a relatively larger quantity of but-1-ene on the fluorinated alumina. The acidity of the surface apparently influences the selectivity of the dehydration of the secondary alcohols. The specific radioactivity of *trans*-but-2-ene was always greater than that of *cis*-but-2-ene, so that the *cis*- and *trans*-but-2-enes are formed by independent paths and through different intermediate surface compounds, whose interconversion is possibly difficult.

10. ISOMERISATION OF BUTENES

Hightower and coworkers [121,122], using original mixtures of two butenes, one of which was labelled with ^{14}C, showed that on catalysts based on alumina, all possible transformations of the three butenes take place according to the scheme



(33)

Thus when a mixture of *cis*-but-2-ene and but-1-ene-1-^{14}C was used, the specific radioactivity of the *trans*-but-2-ene was not greater than or equal to that of the but-1-ene in the catalysate, indicating direct formation of *trans*-but-2-ene from *cis*-but-2-ene.

It was shown that the isomerisation is a first-order reaction. By selecting rate constants to satisfy the experimental dependence of the specific radioactivities on the degree of transformation, the authors cited obtained, for example for an aluminosilicate catalyst at 23°: $k_{c1}/k_{1c} = 0.15$, $k_{t1}/k_{1t} = 0.04$, and $k_{tc}/k_{ct} = 0.26$.

Examination of the selectivity of the processes of butene isomerisation led the authors cited to the conclusion that the reaction takes place by different mechanisms on different catalysts based on alumina. Thus in the case of the aluminosilicate catalyst the selectivity of the isomerisation was independent of the butenes used as starting material, the origin of the catalyst and its degree of poisoning, and temperature, in agreement with the idea that a common intermediate compound is formed; this was assumed to be the classical s-butyl carbonium ion:

$$CH_3\overset{+}{C}HCH_2CH_3. \qquad (34)$$

With alumina, however, the selectivity depended to a marked extent on the butenes used as starting material, and this does not agree with the suggestion that the reaction takes place through a common intermediate compound. In this respect, fluorinated alumina is intermediate between the aluminosilicate and alumina. These results show good agreement with other observations and conclusions [119,120] regarding the isomerisation of butenes under the conditions of the dehydration of butanols on Al_2O_3.

11. DEHYDROGENATION OF HYDROCARBONS

The dehydrogenation of hydrocarbons, leading to the formation of alkenes or aromatic hydrocarbons, is an important industrial reaction. In the study of this process, Balandin and coworkers were the first to use the kinetic isotopic method under the conditions of heterogeneous catalysis. The studies were carried out in a flow assembly on a chromium catalyst (KI) with dilution by water vapour [123-127] and on an aluminium–chromium catalyst (K-544) at reduced pressure [127,128].

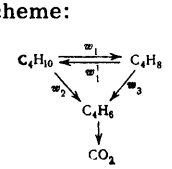
Mixtures of butane and butene in which one of the components contained ^{14}C were studied. The dependence of the experimentally determined specific radioactivities and the concentrations of butane, butene, butadiene, and carbon dioxide (or the carbonaceous deposits on the catalyst) on the duration of contact were examined. Experiments were also carried out on the dehydrogenation of mixtures of butane and butene with added labelled butadiene [125].

The chief source of loss in the dehydrogenation of butane and butene is by deposition of carbon, or, when the process is carried out with dilution by water vapour, by the formation of carbon dioxide.

The specific radioactivity of the carbon dioxide in all instances was found to be very close that of the butadiene obtained, and calculation of the rates of decomposition of butane, butene, and butadiene to carbon dioxide showed that these rates are in the ratio 1 : 4 : 60. Thus more than 90% of the carbon dioxide is obtained from the butadiene formed [125]. These results show qualitative agreement with the results of an earlier study [128], in which it was found that in the dehydrogenation of butane with the addition of labelled butene over a chromium catalyst the extent to which butane takes part in the formation of the carbonaceous deposits amounted to only 25%.

The results obtained show that the formation of carbon dioxide in the experiments with water vapour and the formation of carbonaceous deposits in the experiments in a vacuum are related processes, and led to the suggestion that water vapour in the dehydrogenation prevents the formation of carbonaceous deposits on the catalyst by oxidising the corresponding intermediate products [125].

With the assumption that the overall process can be represented by the scheme:



(35)

the value of the specific radioactivity of the butadiene was used to estimate the rate ratio $w_2 : w_3$; the values found were 1 : 1000 for the KI chromium catalyst and 1 : 25 for the aluminium–chromium catalyst. The calculations showed that for both catalysts the proportion of butadiene obtained by the consecutive path through butene is greater than 90%.

Comparison of the results shows that the ratio of the rates of the dehydrogenation of butane to butene and to butadiene is approximately the same for the two catalysts ($w_1 : w_2 \simeq 20 : 1$). The ratio of the rates w_2 and w_3 is different for these catalysts, however. Thus the formation of butadiene is a consecutive process with the intermediate formation of butene and its desorption from the catalyst surface. This result is important for the kinetics of dehydrogenation and shows that in accordance with the theory of reaction on quasi-donor surfaces, the constants of the kinetic equation in this instance have the significance of adsorption coefficients [127].

In the experiments with the chromium catalyst it was found that the rates of the transfer of the radioactive tracer from butane to butene and from butene to butane at 635° are similar [123,124,129].

Since the thermodynamic equilibrium

$$C_4H_{10} \rightleftarrows C_4H_8 + H_2 \qquad (36)$$

under the conditions of the experiments was displaced considerably to the right, it must be assumed that redistribution of the hydrogen takes place between butane and butene:

$$\begin{array}{l} CH_3{-}CH_2{-}CH_2{-}CH_3 \\ \quad + \\ {}^{14}CH_3{-}CH_2{-}CH{=}CH_2 \end{array} \rightarrow \begin{array}{l} CH_3{-}CH_2{-}CH{=}CH_2 \\ \quad + \\ {}^{14}CH_3{-}CH_2{-}CH_2{-}CH_3 \end{array} \qquad (37)$$

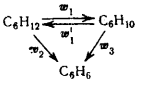
Since the products of this reaction do not differ from the starting materials (if we do not consider the isotopic composition), the equilibrium constant at any temperature should be close to unity, so that the rate constants in the forward and back directions should be approximately equal.

A number of interesting observations are reported in papers by Roginskii and Yanovskii and coworkers, who used radiochromatography to study the transformations of mixtures of butenes containing a radioactive tracer over dehydrogenating [130,131] and bismuth–molybdenum [132] catalysts. In particular, it was shown that the dehydrogenation is accompanied by cis–trans isomerisation of the butenes.

Radiochromatography and Neiman's method have been used in Balandin's laboratory to study the mechanism of the dehydrogenation of cyclohexane and methylcyclohexane over a number of catalysts.

In the multiplet theory, doublet and sextet models of the dehydrogenation of cyclohexane on oxide and metallic catalysts respectively have been developed [133]. In later papers, the sextet mechanism has been introduced for the interpretation of data obtained on oxide catalysts [134,135]; on the other hand, a number of authors [136–139] relate the hydrogenation–dehydrogenation of cyclohexane on metallic catalysts to the intermediate formation of cyclo-alkenes. Conclusions regarding the relationship between cyclo-alkenes and the process of benzene formation are based on indirect results.

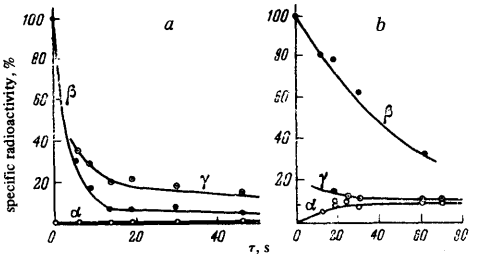
For the dehydrogenation of cyclohexane with the addition of labelled cyclohexene, studies have been made [140,141] of genetic relationships according to the scheme:



(38)

over metallic rhenium [140] and chromium oxide [140] and holmium oxide [141] catalysts; the rates of the analogous transformations of methylcyclohexane with the addition of labelled methylcyclohexene over a chromium catalyst have been determined [142].

The Figure illustrates two examples of the determination of the specific radioactivities of the products in catalysates for chromium and rhenium catalysts. It can be used to obtain information on the reaction mechanism in qualitative form by means of relationships (19) and (20).



Dependence of the specific radioactivities on the duration of contact: a: chromium catalyst; α-methylcyclohexane, β)-methylcyclohexene, γ-toluene; b: rhenium catalyst; α-cyclohexane, β-cyclohexene, γ-benzene.

For the chromium catalyst, the curve for the specific radioactivity of toluene lies above the curve for methylcyclohexene. This indicates a consecutive path with the intermediate formation of the cyclo-alkene. On the other hand, for the rhenium catalyst the specific radioactivity of cyclohexene is much greater than that of benzene ($\beta > \gamma$), indicating the direct formation of the aromatic hydrocarbon without the intermediate formation of the cyclo-alkene. Calculation of the rates of scheme (38) from Eqns. (13)–(16) confirms these conclusions, but shows that the direct formation of benzene or toluene also takes place on chromium oxide in addition to the consecutive reactions. The calculation of the rates also shows that the chief path by which cyclohexene is transformed is by dehydrogenation to benzene on the chromium catalyst and by hydrogenation to cyclohexane on the rhenium catalyst. On holmium oxide at 560° the ratio of the rates of scheme (38) is the same as that for chromium oxide.

In the doublet mechanism there should be a consecutive path for the dehydrogenation. Thus the experimental confirmation of the consecutive path for the formation of benzene (and also toluene) on chromium oxide and on holmium oxide, in contrast to the results for the rhenium catalyst, indicate than on these catalysts the dehydrogenation may take place by a doublet mechanism.

The results indicate a similarity in the mechanisms of dehydrogenation on oxide catalysts, which differ significantly from the mechanism of formation of benzene on metallic rhenium catalyst.

Tétényi and coworkers [143] suggest that over a metallic nickel catalyst the dehydrogenation of cyclohexane takes place by a consecutive path, since in experiments with

mixtures of labelled cyclohexane and non-labelled cyclohexene they detected transfer of the tracer to the cyclohexene. In this work, however, the specific radioactivities of the products were not determined, so that there is insufficient justification for this conclusion. It is possible that the cyclohexene was obtained under the conditions of the experiments by a parallel-consecutive scheme.

12. DEHYDROCYCLISATION OF PARAFFINIC HYDROCARBONS

A recently published review[144] on the dehydrocyclisation of paraffinic hydrocarbons examined the most important work in this field, including work carried out by the labelled atom method with ^{14}C. Work carried out by the labelled molecule method appeared only recently and was not included in the review[144].

The problems of the mechanism of dehydrocyclisation which can be solved by this method relate chiefly to the possibility of establishing stepwise mechanisms involving the participation of unsaturated compounds with an open chain or cyclic six-membered compounds as intermediate products.

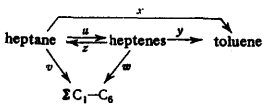
Table 1. Dehydrocyclisation of hydrocarbons on a potassium–aluminium–chromium catalyst[145].

Original mixture	Volume rate, h^{-1}	Specific radioactivity, counts min^{-1} (mg $BaCO_3$)$^{-1}$		
		heptane	heptene	toluene
n-Heptane + hept-1-ene-4-^{14}C	2.1	34	258	254
	7.4	32	280	226
n-Heptane-4-^{14}C + hept-1-ene	2.1	253	75	82
	7.5	288	58	66
n-Heptane + hept-2,3-enes-4-^{14}C	2.2	28	250	258
	7.2	34	291	274

Results obtained by Lipovich and coworkers[145] on the dehydrocyclisation of paraffinic hydrocarbons on an aluminium–chromium–potassium catalyst indicate that this reaction takes place with the intermediate formation of the alkene. Table 1 gives the characteristic values of the specific radioactivities of the chief products, obtained in experiments with mixtures of alkanes and alkenes.

Despite the slight scatter in the results, it can be seen from Table 1 that the specific radioactivities of toluene are extremely close to those of the alkenes, indicating a consecutive path for the reaction. The slight decrease in the value of the specific radioactivity of toluene compared with the values for alkenes at high volume rates is apparently due to the fact that under these conditions, adsorption equilibrium is not established between the alkene in the gaseous phase and on the catalyst surface.

From the results obtained, Lipovich and coworkers[36] calculated the "intensities" of the processes in the scheme:



(39)

The authors cited found the value of y by multiplying the mole fraction of the heptane taken by the fraction of the radioactivity converted into toluene; the value of x was found as the difference between the quantity of toluene formed and y, etc. As expected, the alkene is converted into toluene more rapidly than the alkane (that is $y \gg x$)†.

The authors cited also found that in mixtures with heptane, labelled hept-2,3-ene was converted into toluene much more slowly than hept-1-ene; this was attributed to the more intensive deposition of carbon on the catalyst by hept-2,3-ene, leading to a decrease in its activity. It may be suggested, however, that in this instance an important part is played by the specific orientation of the molecule on the catalyst surface as a result of the interaction of the π electrons of the double bond with the surface.

A study of the same reaction on metallic Ni, Pt, and mixed (Ni/Al_2O_3, Pt/Al_2O_3) catalysts was described by Tétényi and Paal[146,147]. Using a pulse procedure and radiochromatography, the authors cited reached analogous conclusions regarding the consecutive nature of the reaction, and showed that in the dehydrocyclisation of hexane, alkenes and dialkenes with the normal structure are intermediate products, whereas cyclanes and cyclenes are not formed. Characteristic values of the specific radioactivities of the products in arbitrary units from various series of experiments are given in Table 2.

Table 2. Dehydrocyclisation of hydrocarbons on metallic catalysts.

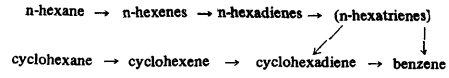
Catalyst	Original mixture	Specific radioactivities of products (arbitrary units)					Refs.
		n-hexene	n-hexane	cyclohexane	cyclohexene	benzene	
Pt	n-Hexane-1-^{14}C	0.5	33.5	—	—	34	146
Ni/Al_2O_3	n-Hex-1-ene, n-Hexane-1-^{14}C	36.5	4.8	—	—	4.6	146
Pt	n-Hex-1-ene, n-Hexane-1-^{14}C, cyclohexane	64	80	1.6	—	27	147
Pt	n-Hexane, cyclohexane-^{14}C	background level	—	38	—	15	147
Ni/Al_2O_3	n-Hexane-1-^{14}C, cyclohexane	52*	—	0.9	—	10	147
Pt	n-Hex-1-ene-1-^{14}C, cyclohexane	94	94	0.5	22**	63	147
Pt	n-Hex-1-ene-1-^{14}C, cyclohexene	74*	—	—	6	52	147
Pt	Hex-1-ene-1-^{14}C, cyclohexa-1,3-diene	355*			6.3***	2.6	147

*Hexane + hexenes.
**Cyclohexane + hexadienes.
***Cyclohexa-1,3-diene.

By comparing their own and published results on the mechanism of the dehydrocyclisation of alkanes, the authors cited concluded that the main features of the mechanism of this reaction are the same for metallic and for oxide catalysts, and that for hydrocarbons with an open chain and for

† In the interpretation of the results obtained it is important to remember the inadequacy of the concepts of intensity and reaction path. For example, the observed magnitude of the intensity x by itself does not make it possible to conclude that heptane under the conditions of the experiments is converted directly into toluene: the intensity x merely shows that part of the heptane is converted into toluene by some means or other (possibly through the alkene).

cyclic hydrocarbons the mechanism can be described by the scheme:



(40)

Experiments with mixtures of labelled hex-1-ene and hexatriene showed[148] that the latter is in fact an intermediate product in the formation of cyclohexadiene and benzene on a platinum catalyst. The relatively low value of the specific radioactivity of hexatriene compared with that of cyclohexadiene and benzene in the catalysates, however, may indicate that there is another reaction path by which the dialkene undergoes cyclisation.

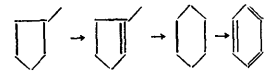
13. HYDRO-DEHYDROISOMERISATION OF CYCLANES

A number of papers describe the use of radiocarbon to study the mechanism of the interconversion of methylcyclopentane, cyclohexane, and benzene in an atmosphere of hydrogen over bifunctional (oxide–metallic) catalysts, and also over tungsten sulphide. Kalechits and coworkers[149,150] showed that when cyclohexane is heated with labelled benzene in an autoclave over tungsten sulphide, the product is methylcyclopentane, whose specific radioactivity is greater than that of the cyclohexane in the catalysate.

When a mixture of benzene and labelled cyclohexane was used, the specific radioactivity of the latter in the catalysate was greater than that of the methylcyclopentane; radioactivity was not detected in the benzene. When mixtures of cyclohexane and methylcyclopentane were passed over a platforming catalyst[151], the radioactivity of the cyclohexane in the catalysate was considerably greater than that of the benzene when the cyclohexane was labelled; when the methylcyclopentane was labelled, however, the specific radioactivities of the cyclohexane and benzene in the catalysate were approximately equal. According to conditions (19) and (20), these results show that on both catalysts studied, the interconversion of methylcyclopentane and benzene takes place partly without desorption of any intermediate substances, including cyclohexane; the other reaction path lies through cyclohexane. It has been shown[152] that the concentration of non-stoichiometric sulphur has no influence on the overall rate of hydrogenation of benzene, but influences the ratio of the rates of the two paths for the formation of methylcyclopentane. The authors cited believe that on the surface of the catalyst the cyclic hydrocarbons undergo a number of transformations, including the intermediate formation and isomerisation of cycloalkenes, which may not be related to the gaseous phase by an adsorption equilibrium. These ideas formed the basis of the familiar stepwise scheme for the reforming of cyclanes, proposed by Mills and coworkers[153].

The experimental justification for this scheme was provided by the characteristic properties of bifunctional catalysts combining the dehydrogenating properties of metals of the platinum group with the isomerising properties of an acidic oxide. The theoretical justification was the possibility of applying the ideas of the mechanism of homogeneous isomerisation in accordance with Whitmore's concept, with the formation of a carbonium ion as a result of the reaction of a proton of the catalyst with the π electrons of the double bond of the alkene. An analysis of published results shows that although this scheme has been in existence and has been used for 15 years, there are no results which confirm it directly or indicate the part played by cyclenes as intermediate products, in particular in the isomerisation and dehydrogenation of cyclohexane and the dehydroisomerisation of methylcylopentane.

To obtain these results, experiments were carried out[154–159] with cyclohexane and methylcyclopentene. Studies were made of the transformation of methylcyclopentane into benzene according to the scheme[157]:



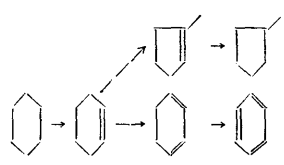
(41)

The experiments were carried out in a flow assembly at a pressure of 20 atm and 480°, at a molar ratio of hydrogen to carbon equal to 5 : 1, on a number of specimens of bifunctional catalysts (platinum on alumina and palladium on alumina). The reaction products were analysed by radiochromatography. Labelled methylcyclopentene was added to the original methylcyclopentane. In accordance with Eqns. (19) and (20), if the methylcyclopentene were a necessary intermediate product [according to scheme (41)], its specific radioactivity into the catalysate should be less than that of benzene or cyclohexane.

A detailed study of the reaction products indicated that dehydroisomerisation of the five-membered rings, splitting of the rings, and hydro-cracking with the formation of lower molecular-weight products take place. It was found that the specific radioactivity of benzene and cyclohexane were close to that of methylcyclopentane and much less than that of methylcyclopentene, and this contradicts the above scheme. A remarkable feature was that the specific radioactivities of the lighter hydrocarbons, particularly the pentanes, was very high and in a number of instances exceeded the specific radioactivity of the methylcyclopentene. This means that methylcyclopentene is an intermediate product in the hydro-cracking. The marked difference in the specific radioactivities of the products of the cracking and the products of the isomerisation of the cyclo-alkanes indicates that these processes take place through different intermediate surface compounds. The similarity in the specific radioactivities of the methylcyclopentane, cyclohexane, and benzene apparently indicates not only that methylcyclopentene is not a necessary intermediate product, but also that methylcyclopentane undergoes isomerisation more rapidly than methycyclopentene.

Similar results were obtained[160] when methylcyclopentane and labelled methylcyclopentene were passed over AP-56 catalyst under the conditions of platforming. The authors cited point out that if methylcyclopentane forms a complex "corresponding to the cyclo-alkene structure", it differs from the complex obtained directly from the unsaturated hydrocarbon.

The transformation of cyclohexane and cyclohexene according to scheme (42) was studied on catalysts consisting of palladium on alumina, rhenium on alumina, and molybdenum oxide on alumina[155].



(42)

A mixture of labelled cyclohexane and cyclohexene was used. In this instance, if the cyclohexene were an intermediate product, its specific radioactivity in the catalysate should have been greater than that of the benzene

and methylcyclopentane. Radiochromatographic analyses showed the opposite, however. Radioactivity was detected in methylcyclopentane and benzene, but not in cyclohexene. This indicates the possibility of isomerisation of cyclohexane independently of cyclohexene; the latter is not an intermediate product. Later, a similar result was obtained[160] when a mixture of cyclohexane and labelled cyclohexene was passed over an AP-56 platinum catalyst under the conditions of platforming.

It is now assumed by a number of authors[161-163] that in reforming reactions the intermediate alkenes are not only formed, but are necessarily desorbed. In early papers, however, it was suggested that the alkene may undergo further transformation without desorption. In some studies[154], cyclohexene remained in the catalysates, so that it was either desorbed or did not reach the catalyst surface during the reaction.

Special experiments with deuterium[155] showed that at atmospheric pressure the cyclohexene of the original mixture takes part in deuterium exchange almost quantitatively, so that it passed through a stage involving adsorption on the catalyst.‡ In experiments under pressure, the degree of exchange was also fairly high, and some of the molecules of the cyclohexene remaining had undergone multiple exchange. Almost no exchange took place in the absence of a catalyst.

These results showed that the transformations of the cyclo-alkanes and -alkenes under the conditions studied apparently take place by independent paths. In this connection, the problem of the mechanism of the action of bifunctional reforming catalysts is becoming more urgent.

The solution of this problem will make it possible to improve the technology of one of the most important petrochemical processes.

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The material examined shows that the LM method is most effectively used in the study of the mechanism of multi-stage catalytic reactions, when the usual chemical methods lead to ambiguous results and it is necessary to make a choice between several possible reaction paths. This situation usually arises at a definite stage in the experimental study of a given process. Thus the reactions studied are often familiar reactions for which definite views, widely encountered in scientific circles, already exist regarding the mechanism. The use of the LM method makes it possible in many instances to develop significantly more penetrating views regarding the mechanisms of these processes; in some instances the results are extremely unexpected and make necessary a new approach to the interpretation of familiar results and stimulate their further study at a new and higher level.

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