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The Mechanism of the Aromatisation of Paraffinic Hydrocarbons on Oxide Catalysts

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Data obtained in studies on the mechanism of the aromatisation of paraffinic hydrocarbons are examined. Attention is concentrated on studies carried out by isotope methods. It is shown that aromatic hydrocarbons are formed from paraffins on oxide catalysts via a single pathway—the successive dehydrogenation of the aliphatic hydrocarbon with formation of a six-membered ring (cyclodiene) as a result of the thermal cyclisation of a triene.
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I. INTRODUCTION

The aromatisation reaction was discovered independently in 1936 by three groups of Soviet chemists on catalysts of different kinds[1-4]. This reaction, which makes it possible to obtain comparatively simple aromatic compounds from paraffinic hydrocarbons, has naturally attracted the attention of investigators in all countries with a developed petroleum processing industry. The interest in the reaction was due not only to the likelihood of the creation of a new industrial process for the synthesis of aromatic raw materials but also to the possibility of determining the nature of the cyclising effect of the catalyst and the cyclisation mechanism by studying the reaction, i.e. due to the possibility of elucidating a series of new fundamental catalytic laws.

Numerous studies devoted to the aromatisation reaction have been published in Soviet and foreign literature, but its mechanism was elucidated only in the last decade. It was found that no special cyclising functions are required from aromatising oxide catalysts. In the available reviews[5-9] attention has been concentrated on the technological aspects of the process (the composition and properties of the catalysts, the methods for their treatment and modification, etc.), but the reaction mechanism proper has been considered relatively little; furthermore, in most instances it is treated erroneously from the standpoint of modern ideas[10-11].

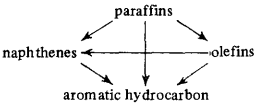
Although aliphatic hydrocarbons are aromatised on oxide catalysts in a fairly complex manner, the process can serve as a model reaction. Thus many characteristics of the aromatisation of paraffins established on oxide catalysts hold also for the platforming processes, the dehydrogenation of higher paraffins, etc.

The aim of the present review is to analyse the development and the present state of the ideas on the mechanism of the conversion of aliphatic hydrocarbons under aromatisation conditions on oxide catalysts mainly on the basis of the latest experimental data and information obtained with the aid of isotope research techniques.

II. THE MECHANISM OF THE AROMATISATION OF PARAFFINS ON OXIDE CATALYSTS

The first detailed discussion of the mechanism of the aromatisation reaction was held in 1939 at a session of the Faraday Society. A certain amount of experimental data had accumulated by that time, which permitted certain generalisations. It was established that aromatisation proceeds on chromium oxide and a number of other oxides in the temperature range 500–520 °C and on a platinum catalyst at a temperature 200° lower[12-17]. In the catalytic reaction mixtures obtained on oxides olefins were always present in addition to aromatic hydrocarbons[2-4,18], their content depending on the contact time[19]. The yield of aromatic products formed from olefins is higher than the yield obtained from the corresponding paraffins[20,21]. Paraffins and olefins without a straight six-carbon chain hardly form aromatic hydrocarbons.

Hoog et al.[21] proposed a scheme for the aromatisation reaction having included in the latter all the reaction pathways imaginable at the time. The scheme postulated the formation of olefins or cyclanes as intermediates:



(1)

According to the experimental data of Hoog et al.[21], the aromatisation of paraffins proceeds at least partially via a stage involving dehydrogenation to the corresponding olefins.

Consideration of thermodynamic data led to the conclusion[22] that the direct formation of benzene from hexane, by-passing any intermediates, i.e. the pathway leading to the conversion of paraffins into aromatic hydrocarbons in Scheme 1, is energetically the most favourable. From this standpoint (subsequently it was supported also by a series of other investigators), olefins are regarded as side products.

Pitkethly and Steiner[23] favoured two other mechanisms of the formation of aromatic hydrocarbons: via olefins as intermediates, by their cyclisation to a cycloparaffin and subsequent dehydrogenation of the latter to an aromatic hydrocarbon, or by the direct cyclisation of the paraffin to a naphthene via a stage involving a semihydrogenated state, which can also give rise to an olefin as a side product.

Both these mechanisms presuppose in one way or another the formation of a six-membered naphthene as an obligatory reaction stage. Probably at that time it was difficult to imagine the transformation of a paraffin into an aromatic hydrocarbon via a procedure other than the formation of a hexamethylene ring. Its further conversion into an aromatic hydrocarbon had been thoroughly investigated. It is noteworthy that the data of Pitkethly and Steiner with Hoog's correction[24] definitely indicated the intermediate formation of olefins, at least in the first reaction stage. Herington and Rideal[25] suggested that the first stage in the reaction is the obligatory cyclisation of the paraffin to a six-membered naphthene. They believe that the reaction is

possible only when at least one of the carbon atoms involved in cyclisation is located on the catalyst surface. Having calculated the probability of such cyclisation-promoting adsorption for different configurations of the hydrocarbon on the catalyst surface and having assumed that the degree of adsorption is proportional to the rate of reaction, the authors[25] found that these quantities agree with the experimental yields of aromatic hydrocarbons from the corresponding paraffins. They proposed the same mechanism also for the formation of aromatic hydrocarbons from olefins. However, this mechanism did not explain how *m*- and *p*-xylenes present in n-octane catalytic reaction mixtures are formed. In order to account for the origin of *m*- and *p*-xylenes (they cannot be obtained by the direct cyclisation of the paraffin to a six-membered naphthene), the authors[25] had to consider the formation of bicyclo-octanes of different structures, whose decomposition can give rise to the corresponding six-membered cyclanes.

At the same time studies in which olefins were detected among the reaction products continued to be published: the investigators discussed their role as intermediates[26-29]. As regards cyclohexane hydrocarbons, none of the investigators was able to detect them. This was explained by the fact that under aromatisation conditions the rate of dehydrogenation of cyclohexanes (according to the data of Kazanskii and Liberman[16]) greatly exceeds the rate of aromatisation of the corresponding paraffins. Komarevsky and Shand[30] attempted to detect *gem*-dimethylcyclohexane in the catalytic reaction mixtures obtained in the aromatisation of 2,2-dimethylhexane on an alumina–chromium oxide catalyst, assuming that it should not be dehydrogenated to an aromatic hydrocarbon. However, only *m*-xylene was found in the reaction products.

Nevertheless this result was insufficiently convincing to abandon the idea of the intermediate formation of cyclohexane in the aromatisation of paraffins[31-35], particularly since Kazanskii et al.[36] detected by Raman spectroscopy *gem*-dimethylcyclohexane in the catalytic reaction mixture obtained in the aromatisation of 3,3-dimethylhexane on platinised carbon, which indicated immediately the possibility of the direct cyclisation of the paraffin on a platinum catalyst. Comparison of the results of the studies of Komarevsky and Shand[30] with those of Kazanskii et al.[36] might have served as a basis for the hypothesis of significant differences between the mechanisms of the aromatisation of paraffins and oxide and metallic catalysts.

In subsequent years the attention of investigators was concentrated on oxide aromatisation catalysts, which appeared more promising at the time since new low-percentage alumina–platinum catalysts had not yet been introduced into practice. In Steiner's review[7], which deals exclusively with studies carried out on oxides, predominantly chromium oxide, catalysts, it is concluded that olefins must be formed as intermediates in the first stage of the aromatisation reaction on oxide catalysts.

However the kinetic evidence presented by Steiner[19,23,26,28,37] apparently proved to be insufficiently convincing to many other investigators and the latter continued to assume that olefins are formed as side products[31,35,38-41].

Inspection of the studies in the first stage of the research into the aromatisation reaction shows that mainly three possible reaction pathways were considered:

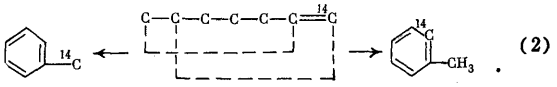
(1) the cyclisation of the paraffin to a six-membered naphthene in the first reaction stage followed by its dehydrogenation to an aromatic hydrocarbon;

(2) the formation of an olefin, which is subsequently converted into an aromatic hydrocarbon, also via a naphthene;

(3) direct transformation of the paraffin into an aromatic hydrocarbon on the catalyst surface.

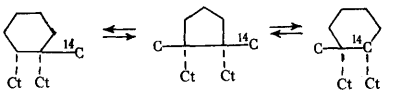
One should bear in mind that during the period when the above studies were carried out the methods for the analysis and separation of hydrocarbon mixtures were extremely complex and relatively uninformative. Studies involving a large number of analyses in the course of the experiment were therefore difficult. As soon as it became possible to use radioisotopes for the investigation of the mechanisms of chemical reactions, the latter were employed also in the investigation of the aromatisation of paraffins. These studies, involving the application of the method of tracer atoms[42], were begun as early as the 1950's and have continued up to the present time.

A study[43] of the transformation of [1-^{14}C]hept-1-ene over a chromium oxide catalyst revealed the presence of 50% of the radioactive label in the methyl group of the resulting toluene, which corresponds to the formation of aromatic hydrocarbons by the simple cyclisation of the aliphatic hydrocarbon via the mechanism



(2)

However only 26–29% of the label was found in the methyl group of toluene obtained[44] in the aromatisation of [1-^{14}C]heptane (depending on the degree of reaction). In order to account for these results, it was necessary to resort to more complex reaction mechanisms: with formation of a bicycloheptane (according to Herington and Rideal[25]) or with formation on the surface of the catalyst (Ct) of a cyclopentane-like adsorbed complex, which then isomerises to a six-membered cyclic compound and is subsequently dehydrogenated:



(3)

The formation of intermediate cyclopentanes was not confirmed experimentally[44].

In a study of the transformation of 2,2-dimethyl-4-[^{14}C]methylpentane, Cannings et al.[45] obtained *p*-xylene (yield 14%) and toluene (yield 3%) as the aromatisation products; the methyl groups of the xylene contained 50% of the label, while that of toluene contained 23–25% of the label. According to the authors, the reaction proceeds via a stage involving skeletal isomerisation with subsequent ring closure by the aliphatic molecule to give a six-membered cyclic compound.

The mechanism of the aromatisation reaction has been investigated in detail by the tracer atom method in studies by Pines and coworkers[46-60]. Three catalysts were used in studies during the period from 1959 to 1965:[46] chromium oxide (without a carrier), chromium oxide deposited on alumina with distinct acidic properties (type A), and chromium oxide deposited on alumina without pronounced acidic properties (type B). In the aromatisation of [1-^{14}C]-n-heptane it was observed[46-50] that the content of the label in the methyl group of toluene depends on the nature of the catalyst and varies during the experiment. In experiments with pure chromium oxide 44–47% of the radioactivity was detected in the methyl group of the toluene. In experiments with chromium oxide deposited on alumina the content of the label in the methyl group was 39 and 17% (for aluminas of types A and B respectively), increasing appreciably after several hours of the operation

of the catalyst. An analogous study has been carried out on the aromatisation of [1-^{14}C]-n-octane.

Since the results could not be explained on the basis of the known mechanisms, Pines suggested the intermediate formation of five-, seven-, and eight-membered rings, in addition to the six-membered rings, which then undergo isomerisation of the "contraction–expansion" type to give the six-membered rings. Pines and coworkers investigated the transformations of cyclanes—methylcyclopentane, substituted cyclohexanes[48], methylcycloheptane[47], and cyclo-octane[49], as well as paraffins for which these cyclanes might be aromatisation intermediates—and noted a similarity in the products of the aromatisation of paraffins and the corresponding cyclanes. The same analogy was noted in the distribution of the label in the hydrocarbon molecules when the products of the reactions of linear and the corresponding cyclic hydrocarbons were compared[49,51,59]. The authors regard this analogy as proof that the C_5, C_7, and C_8 cyclanes are intermediates in the aromatisation of the corresponding alkanes. They suggest that the size of the intermediate ring depends on the acidity of the catalyst. On chromium oxide and an acid catalyst of type A, five- and six-membered rings are formed preferentially, while on the "non-acid" catalyst of type B seven- and eight-membered rings predominate.

According to Pines' hypothesis, the distribution of the radioactive label in the aromatisation products should not depend on the position of the label in the initial paraffin, for example, in n-octane. Indeed, the site at which the contraction of the eight-membered ring begins involves any bond of the ring with equal probability. However, a comparative study of the aromatisation of [1-^{14}C]octane and [4-^{14}C]octane on a type B catalyst[48,49,51–53] showed that the distribution of the label in ethylbenzene and xylenes depends significantly on its position in the initial octane. Thus the content of the label in the aromatic rings of ethylbenzene and *o*-xylene obtained from [4-^{14}C]octane is from 92 to 97%, while the contents of the label in the same products obtained from [1-^{14}C]octane are respectively 68–50% and 39–8%.

Having considered next the possible distribution of the label under the conditions of the formation of an intermediate five-, six-, seven-, or eight-membered ring or even a bicyclic compound (according to Herington and Rideal[25]), Pines and coworkers concluded that the formation of only one of these intermediates cannot fully account for the experimental data. However, the combination of two or even three mechanisms involving the formation of intermediate rings of different structures can explain all the experimental results[51]. The studies by Pines have shown that the formation of cyclanes, including the six-membered cyclane, as aromatisation intermediates was not questioned in any way; other aromatisation pathways with participation of other intermediates were not in essence considered. Nor was the role of unsaturated hydrocarbons, particularly olefins, in the formation of aromatic hydrocarbons considered, although Pines and coworkers used gas–liquid chromatography for analysis and not only olefins but also dienes were detected in the catalytic aromatisation reaction products[49,51].

Thus the use of radioisotopes at this stage of the investigation helped little in elucidating the pathways leading to the transformation of paraffins under aromatisation conditions. This can probably be explained by the fact that the tracer atom method, which deals only with the location of the label in the starting materials and final reaction products, does not permit a conclusion concerning the nature of the intermediates. Experiment only indicated the location or transfer of the label to a particular position in the final product without any indication of the pathways leading to this transition.

In a study of the aromatisation of [4-^{14}C]heptane on catalysts of types A and B (in Pines' terminology), Feighan and Davis[61] observed that the bulk of the radioactive label is present in the $C_{(3)}$ position in toluene, but the $C_{(2)}$ and $C_{(1)}$ atoms as well as the carbon atom of the methyl group also proved to be radioactive. Comparison of the data obtained in a comparative study of the aromatisation of heptanes labelled in the 1- and 4-positions yielded a picture analogous to that obtained earlier by Pines for [1-^{14}C]- and [4-^{14}C]-octanes[62]. Feighan and Davis[61] suggested that, together with the direct cyclisation of heptane, there is also partial skeletal isomerisation of heptenes. The subsequent cyclisation of the iso-olefin can explain the transfer of the label from [4-^{14}C]heptane to the methyl group of toluene.

To demonstrate the direct cyclisation of the paraffin, Davis and coworkers[63,64] compared the products obtained on chromium oxide and alumina–platinum catalysts. Assuming that the possibility of the direct cyclisation on platinum has been demonstrated[36], the author claims that the difference which he nevertheless observed can be accounted for by the greater isomerising capacity of the chromium oxide catalyst compared with the platinum catalyst. For example, on the platinum catalyst Davis obtained toluene as the main product from *gem*-dimethylcyclohexane and 2,2-dimethylhexane. On the chromium oxide catalyst, toluene was also obtained from *gem*-dimethylcyclohexane, but 2,2-dimethylhexane gave rise to *m*- and *p*-xylenes and not the demethylated product. If the cyclohexane hydrocarbon had undergone isomerisation, the naphthene and paraffin aromatisation products would have been identical. Consequently Davis's results confirm the possibility of the skeletal isomerisation of the aliphatic molecule, but they do not demonstrate the existence of an intermediate naphthene. Thus in these studies too the role of unsaturated hydrocarbons was in essence not considered.

In a study of the formation of olefins from paraffins on the chromium oxide catalyst Timofeeva and coworkers[65–75] demonstrated with extensive experimental data that aromatic hydrocarbons are also always formed under these conditions. A small amount of olefins is then obtained from alkanes with a straight-chain structure, the amount of aromatic hydrocarbon being large, while isoalkanes (which are incapable of forming a six-membered ring without isomerisation) produced mainly olefins. Dienes were detected in the catalysts in both cases[70–72].

Studies[76–79] of the aromatisation of a series of paraffins and olefins ranging from C_6 to C_9 [77] on the alumina–chromium oxide–sodium oxide catalyst and of cyclanes ranging from C_5 to C_7 [78] and isoparaffins[79] also demonstrated, with a large number of examples, that the yield of aromatic hydrocarbons produced from olefins (particularly from alk-2-enes and alk-3-enes) is always greater than the yield obtained from paraffins. Furthermore, in the aromatisation of paraffins a sharp increment of the yield of aromatic hydrocarbons with increase of reaction temperature always follows the maximum content of olefins in the catalytic reaction mixture. On this basis, it has been concluded[76–79] that olefins play the role of intermediates in the aromatisation of paraffins. The above workers believe that the next stage of the reaction is cyclisation, preferentially the cyclisation of a C_6 olefin, since, according to their data, methylcyclopentane and methylcyclopentene give rise to very low yields of benzene under these conditions. However, Perrée and Blouri[77] did not detect either C_5 or C_6 hydrocarbons (other than

aromatic hydrocarbons) in the catalytic aromatisation reaction mixtures, but did find traces of dienes.

On the hypothesis that the rate of aromatisation must follow a first-order equation and that olefins must be formed as intermediates, Penchenkov and Zhorov[80-82] derived a kinetic equation for the two-stage reaction paraffins → olefins → aromatic hydrocarbons. Comparison of the experimental and calculated yields of heptane, octane, and nonane aromatisation products revealed a very great similarity[80,81]. It was observed that under these conditions the isomerisation of olefins with differing double bond positions proceeds faster than dehydrogenation[82]. Thus virtually an equilibrium mixture of isomeric olefins undergoes aromatisation and the olefin aromatisation reaction has been shown to be 7–8 times faster than the dehydrogenation of a paraffin.

Having used in the study of aromatisation mixtures of non-radioactiveheptane and heptanes with one of the carbon atoms replaced by the ^{14}C radioactive label, Lipovich and coworkers[83-86] showed definitely that heptenes are intermediates in the formation of toluene.

Thus the above group of studies again indicated the intermediate formation of olefins in the aromatisation of paraffins. However, subsequent olefin transformation pathways were virtually uninvestigated.

A new stage in the study of the mechanism of the aromatisation reaction became possible as a result of the application of a pulsed technique in combination with gas-chromatographic analytical methods. Rozengart et al.[87] investigated the composition of the heptene aromatisation products as a function of contact time on an alumina–chromium oxide–potassium oxide catalyst and observed that heptadienes were present in the catalytic reaction mixtures. It was found that, with increase of contact time, their contact passes through a maximum. For short contact times, the concentration of heptadienes is greater than that of toluene and the maximum heptadiene content occurs at the same time as the point of inflection in the S-shaped toluene curve. These data are fully consistent with the characteristics of consecutive reactions.

Since heptadienes can be regarded as intermediates, the authors[88-90] subsequently investigated kinetically the transformation of hepta-1,3-diene and observed that heptatrienes are present in the catalytic reaction mixtures. It was found that their content also passes through a maximum with increasing contact time, although the content of trienes is lower than that of toluene even for the shortest contact times. These results as well as data obtained in the study of the reactions of heptatriene and methylcyclohexadiene suggested[88] that the aromatisation of the paraffin proceeds via the successive dehydrogenation of the aliphatic molecule to trienes. Trienes readily undergo thermal cyclisation[91-93] with formation of cyclodienes, which are then dehydrogenated to the aromatic hydrocarbon: paraffin → olefin → diene → triene → alkylcyclohexadiene → aromatic hydrocarbon. In contrast to the previous schemes, this scheme does not postulate the intermediate formation of cyclohexane hydrocarbons.

It was necessary to test the reliability of this scheme by independent methods and to determine whether or not it constitutes the only pathway, the main pathway, or only one of many pathways to the transformation of alkanes into aromatic hydrocarbons.

The kinetic isotope method proposed by Neiman[94-97] and widely used in studies of the mechanisms of heterogeneous-catalytic reactions[42,98-113] was employed in subsequent investigations. In contrast to the tracer atom method, the kinetic isotope method is not concerned with the position of the label within the molecule, the molecule as a whole being treated as radioactive and the distribution of the label between the reaction products being estimated.

In order to determine whether or not cyclohexane hydrocarbons are intermediates in the aromatisation of a paraffin, for example, hexane, a study has been made[114] of the aromatisation on an alumina–chromium oxide–potassium oxide catalyst of mixtures of hexane and cyclohexane in which cyclohexane contained the radioactive label. If cyclohexanes were an intermediate in the reaction involving the conversion of hexane into benzene, one would expect a decrease of the molar radioactivity of cyclohexane in the catalytic reaction mixture relative to the initial value as a consequence of the formation of non-radioactive cyclohexane from n-hexane. This decrease should have been greater the lower the content of [^{14}C]cyclohexane in the initial mixture and the greater the degree of conversion of n-hexane. However, even in the case where the benzene content in the catalytic reaction mixture was many times greater than the cyclohexane content in the mixture, no decrease in the activity of cyclohexane was observed. Thus cyclohexane is not an intermediate in the aromatisation of n-hexane under the given conditions.

In order to elucidate the role of olefins, a study was made of the transformation of mixtures of n-hexane and hex-1-ene in which one of the components contained the radioactive label. In the aromatisation of non-radioactive hexane with added labelled hex-1-ene (with a molar radioactivity β) the benzene formed in the reaction was also radioactive (with a molar radioactivity γ). If hexene plays the role of an intermediate in this reaction, β should decrease in the course of the process (as a result of the formation of non-radioactive hexene from n-hexane), remaining, in conformity with the postulates of the kinetic isotope method[42], below the radioactivity of benzene:

$$\beta < \gamma. \qquad (4)$$

On the other hand, when the aromatisation of radioactive hexane mixed with unlabelled hexene is investigated, then the radioactivities of benzene and hexene should increase in the course of the reaction, but the increase should be such that the following condition is maintained:

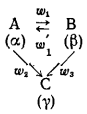
$$\beta > \gamma. \qquad (5)$$

The maintenance of this condition would suggest that hexene is indeed a precursor of benzene in the aromatisation of hexane. If other intermediates are formed during the reaction from the olefin, their molar radioactivities should have values intermedate between β and γ according to the postulates of the kinetic isotope method.

A study of the aromatisation of a mixture of hexane and [1-^{14}C]hexene showed[115] that the change in the radioactivities of hexenes and benzene during the reaction does indeed obey the rule indicated by inequality (4) (see Table). Thus, in contrast to cyclohexane, hexene is undoubtedly an intermediate in the aromatisation reaction. The tabulated data show that the radioactivity of hexadienes is intermediate between those of hexene and benzene. Consequently hexadienes are also obligatory intermediates in the aromatisation reaction.

Although it has been shown[114] that hexane does not undergo catalytic cyclisation in the first reaction stage, one cannot claim that cyclisation does not occur in the stages involving the formation of olefins or dienes. Furthermore, the results of the two studies quoted above do not rule out the possibility of the reaction on the surface of the catalyst without the liberation of intermediates into the reaction space—in the way imagined, for example, by Taylor and Turkevich[22].

An answer may be obtained to these questions by employing in the investigation the method involving the calculation and comparison of the reaction rates proposed by Balandin and coworkers[101–103]. Each multistage reaction can be represented by the triangular scheme



(6)

where A, B, and C are the initial reactant, the intermediate, and the final product respectively and α, β, and γ are their molar radioactivities. The reaction rates w_1, w_1', w_2, and w_3 via different pathways are calculated by the equations of the kinetic isotope method from the changes in the concentrations and molar radioactivities of the reaction components. The rate of accumulation of the final product $d[C]/dt$ is calculated wholly from the change in its concentration. It follows from Scheme (6) that, when $w_2 = 0$, the reaction is consecutive and involves the intermediate B; if $w_3 = 0$, then B is a side product; when $w_2 \neq 0$ and $w_3 \neq 0$, the reaction proceeds via the two pathways simultaneously.

Results of experiments on the aromatisation of the hexane–[^{14}C]hex-1-ene mixture (530 °C).[115]

Mixture components	Initial mixture	Content in catalytic reaction mixture, mole %					Molar radioactivity, %***					
		catalyst sample, mg					initial mixture	catalyst sample, mg				
		2.5	5.0	20.0	50.0	100.0		2.5	5.0	20.0	50.0	100.0
Cracking products*	—	0.6	2.0	1.9	5.2	6.1	—	—	—	—	—	—
n-Hexane*	59.0	59.0	58.0	56.0	47.8	45.7	—	—	—	—	—	—
Hexenes	41.0	34.0	30.3	13.7	4.6	3.1	100	102	101	90	71	10
Hexadienes**	—	3.2	5.1	11.1	5.2	2.2	—	100	97	92	73	18
Isohexadienes*	—	0.2	0.2	0.6	1.0	0.8	—	—	—	—	—	—
Benzene	—	2.2	4.2	16.7	36.2	42.1	—	99	97	95	80	77

*The radioactivity was not estimated quantitatively.

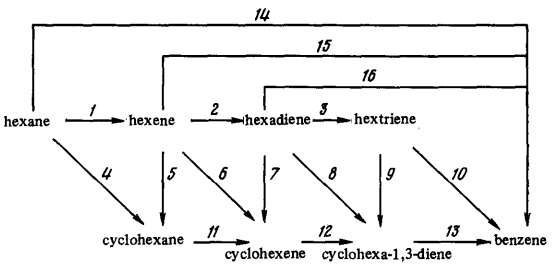
**The sum of all the isomers detected in the catalytic reaction mixture.

***The molar radioactivity of the products was calculated as a percentage relative to the molar radioactivity of the hexenes in the initial mixture.

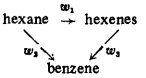
Evidently the reaction is in reality more complex than suggested by Scheme 6, because each stage also involves the adsorption and desorption of the reaction components on the surface of the catalyst. However, it is known[98–100] that the consecutive nature of the reaction, established with the aid of the kinetic isotope method, also implies that the desorption and adsorption of the reaction components are faster than the reaction itself.

We shall now consider the conversion of hexane into benzene from the standpoint of Scheme (6). Comparison of the literature data and the present author's results[114,115] makes it possible to set up a model of the hexane transformation reaction, which includes the three main aromatisation pathways (see Scheme A). Transformation via stages *1–3*, *9*, and *13* is consistent with the scheme proposed by Rozengart et al.[88] The cyclisation of hexane or of the successive intermediates corresponds to reactions *4–10*. Any other pathways leading to the transformation of hexane into benzene are included in pathways *14–16*.

Scheme A



The kinetic isotope method makes it possible to consider and investigate the pathways involved in the transformation of the reaction components at each stage. The first stage can then be represented as follows:



(7)

If $w_2 \neq 0$, the implication is that benzene can be formed from hexane not only via hexenes but also via some other pathway. Cyclohexane is ruled out as an intermediate[114], but there may be other intermediates which have not been detected in catalytic reaction mixtures for one reason or another. Furthermore, aromatisation can occur on the surface of the catalyst without the desorption of the intermediates into the reaction space. On the other hand, if hexane is converted into benzene via a single pathway, then evidently $w_2 = 0$ and w_3 and the rate of accumulation of benzene in the system $d[C]/dt$ should be equal.

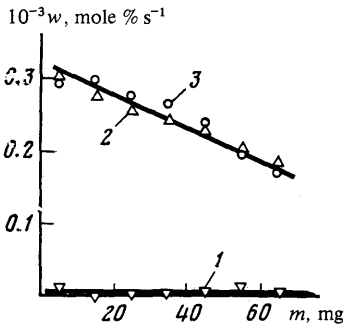
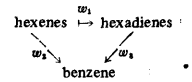


Figure 1. Variation of the rates of transformation of the components of the hexane–[^{14}C]hex-1-ene–benzene mixture with increasing contact time (catalyst sample):[117] *1)* w_2; *2)* dc/dt; *3)* w_3 [for the significance of the symbols, see Scheme (7)].

All these hypotheses have been tested[116,117] by investigating the aromatisation of the hexane–[^{14}C]hex-1-ene–benzene ternary system. The results of the calculation of the rates of reaction by the equations of the kinetic isotope method, in conformity with Scheme (6), from the experimental data of the above studies are presented in Fig.1. It was found that the rates of accumulation of benzene $\{d[C]/dt\}$ and of conversion of hexene into benzene (w_3) are the same within the limits of the accuracy of the calculation, while the rate w_2 of the transformation of hexane into

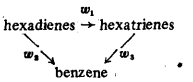
benzene by-passing hexene is virtually zero. Consequently there is no pathway other than that via hexene in the transformation of hexane into benzene and the possibility of reaction via pathway *14* is ruled out.

The same method was then used to investigate the transformations of hexenes and hexadienes:



(8)

It was found that only the dehydrogenation of hexenes to hexadienes takes place in the second stage of the reaction[118,119]. The results of the calculation of the rates in this system are illustrated in Fig.2. Furthermore, special experiments with [^{14}C]cyclohexane showed that there is no cyclisation of hexenes to cyclohexane or cyclohexene[119]. The transformations of hexadienes into hexatrienes† also proceed via a single pathway [see Scheme (9) and Fig.3]:[119]



(9)

There is no cyclisation at this stage, although the possibility of the direct transformation of hexadienes into cyclohexa-1,3-diene has been discussed in the literature as one of the probable cyclisation pathways[120].

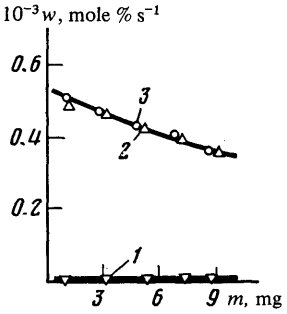


Figure 2. Variation of the rates of transformation of the components of the [^{14}C]hex-1-ene–hexadienes mixture with increasing contact time[119]: *1)* w_2; *2)* dc/dt; *3)* w_3 [see Scheme (8)].

Consequently pathways *5–8* and *15–16* (Scheme A), postulating the catalytic cyclisation or direct transformation of hexanes and hexadienes into benzene, do not occur.

An aliphatic molecule is dehydrogenated in the aromatisation reaction to the triene stage. Scheme A postulates two possible reaction pathways for the triene: thermal cyclisation to cyclohexa-1,3-diene with its subsequent dehydrogenation to benzene (pathways *9* and *13*) or direct transformation of the triene into benzene by-passing the cyclohexadiene formation stage *10*.

As was to be expected, hexatriene mixed with [^{14}C]hexadienes reacts wholly at 520 °C after very short contact times (Fig.4) [118] and is almost completely converted into cyclohexa-1,3-diene, the concentration curve of which has a distinct maximum. With increase of contact time, the concentrations of cyclodiene and benzene vary in opposition. The molar radioactivity of benzene is lower than that of cyclohexadienes and both increase with increasing contact time.

If the molar radioactivities of the hexadienes, cyclodienes, and benzene, are denoted by α, β, and γ respectively, then, taking into account the transformation of hexadienes into hexatrienes demonstrated above[119], one can set up the following sequence:

$$\alpha > \beta > \gamma.$$

This type of sequence for a mixture in which the first component is radioactive indicates, according to the kinetic isotope method, that the transformations of hydrocarbons investigated constitute a single chain: hexadiene → hexatriene → cyclohexa-1,3-diene → benzene. Returning now to Scheme A, one may conclude that the transformation proceeds via pathways *9* and *13*, while pathway *10* does not operate.

Thus, in considering the set of consecutive stages of the transformation of hexane into benzene, it is seen that, under the conditions of aromatisation on the alumina–chromium oxide–potassium oxide catalyst, neither hexane, nor hexene, nor hexadiene undergo catalytic cyclisation. Only the triene is converted into a cyclic product, but a catalyst is not required for this stage. All the remaining reactions constitute stages involving the dehydrogenation of the aliphatic molecule and then of cyclohexadiene. Presumably there are no pathways leading to the formation of the aromatic hydrocarbon on the chromium oxide catalyst other than those indicated below in Scheme (10).

hexane → hexenes → hexadienes → hexatriene → cyclohexa-1,3-diene → benzene. (10)

This scheme explains not only the obligatory presence of olefins and dienes in the catalytic reaction mixtures obtained on oxides but also the high yields of aromatic hydrocarbons from olefins. According to this scheme, hydrocarbons without a straight six-carbon chain can be aromatised only after passing through a skeletal isomerisation stage; consequently in this case one cannot expect high yields of aromatic compounds. It also becomes understandable why no investigators were able to detect cyclohexane hydrocarbons in the catalytic aromatisation reaction mixtures—they are not formed in this reaction.

The same scheme makes it possible to explain also the experimental data obtained in the study of the aromatisation of n-octane on the alumina–chromium oxide catalyst[121–128]. The question of the origin of *m*- and *p*-xylenes produced from n-octane is known to be the most complex in this instance. To account for their origin, the idea of the formation and isomerisation of cyclanes in the aromatisation process was in fact resorted to. However, the formation of isomeric xylenes can be readily understood if the aromatisation of n-octane is considered from the standpoint of the successive dehydrogenation scheme.

It has been shown that the isomerisation of aromatic C_8 hydrocarbons does not occur[46,47,53,121,122], so that the formation of structures leading to these xylenes takes place at intermediate stages of the reaction. If the formation of cyclanes constitutes this intermediate stage, then the ratio of *o*-xylene and ethylbenzene, on the one hand, and *m*- and *p*-xylenes, on the other, in the cyclane aromatisation products should be the same as in the aromatisation of n-octane. Furthermore, the content of *m*- and *p*-xylenes obtained in the aromatisation of 1,2-dimethylcyclohexane and ethylcyclohexane proved to be 3–100 smaller than in the aromatisation of n-octane[128]. Thus the isomerisation of

†Owing to the high reactivity of hexatriene, these experiments were performed at a temperature 100° lower than in the previous study.

the aliphatic intermediate actually accounts for the formation of *m*- and *p*-xylenes. The occurrence of this skeletal isomerisation of the aliphatic molecule under the conditions of the aromatisation on the chromium oxide catalyst is indeed confirmed by the presence of iso-octanes in the catalytic aromatisation reaction mixtures obtained from n-octane[121,122] and isohexadienes and in the catalytic reaction mixtures obtained from n-hexane[129], and it has been shown in the latter case that the skeletal isomerisation can be undergone not only by the unsaturated hydrocarbon but also by the alkane molecule. The increase of the yields of ethylbenzene and styrene with increasing temperature or degree of dilution of the reaction mixture by the inert carrier gas[125] can also be accounted for within the framework of this mechanism[88].

Subsequent studies showed that the kinetic picture observed in the aromatisation of n-hexane in the presence of molybdenum[139,140], vanadium[141], titanium[141], and tungsten[142] oxides deposited on alumina is fully consistent with the consecutive reaction and that the mechanism of aromatisation on these catalysts is the same as on the chromium oxide catalysts. Evidently the above scheme, involving the successive dehydrogenation of the aliphatic hydrocarbon, is applicable to the description of the aromatisation not only on chromium oxide but also on other oxide catalysts.

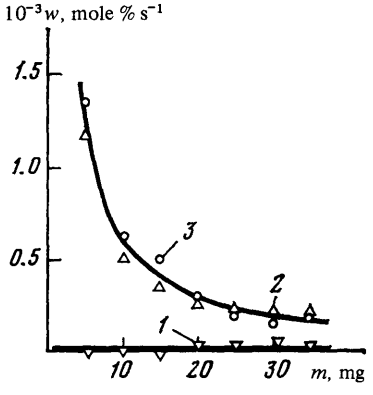


Figure 3. Variation of the rates of transformation of the components of the [^{14}C]hexadienes–hexatrienes mixtures with increasing contact time[119]: *1*) w_2; *2*) dc/dt; *3*) w_3 [see Scheme (9)].

It is noteworthy that in recent years studies have been published in which other aromatisation mechanisms have been put forward which in our view are not adequately supported. Thus, in studies[130,131] of the kinetics of aromatisation, the partial pressure of hexane in the system was varied by adding diluent gases (He, N_2, CH_4 and H_2) to a constant stream of hydrocarbon vapour. It was observed that the decrease of the partial pressure of hexane in a stream of helium, nitrogen, and methane hardly affects the yield of benzene, but reduces the yield of hexenes by a factor of 2. On the other hand, in a stream of hydrogen the yield of benzene decreases sharply, while the yield of hexenes increases somewhat. On the other hand, when the starting material is hexene, then the yield of benzene in a stream of helium, nitrogen, and methane increases with decrease of the partial pressure of hexene.

Being unable to account for these findings on the basis of Scheme (10), Shapchenko and Rudenko[130,131] therefore believe that the aromatisation of hexane on the alumina–chromium oxide–potassium oxide catalyst proceeds via a stage with formation of hexene, which is subsequently converted into a polymolecular complex on the catalyst surface[132,133]. The decomposition of this complex leads to benzene, cracking products, and coke formation. From our point of view, the anomalous results obtained in the above studies[132,133] can be simply explained. The independence of the yields of benzene of the partial pressure of hexane in a stream of helium, nitrogen, and methane observed in these investigations is only apparent, since in the experimental method employed the decrease of the partial pressure of hexane is accompanied by a decrease of contact time. Dilution of the system with a carrier gas (other conditions being equal) enriches the catalyst in benzene[134], while a decrease of contact time reduces its yield. The joint influence of these two factors can create the illusion that the yield of benzene is independent of the partial pressure of hexane.

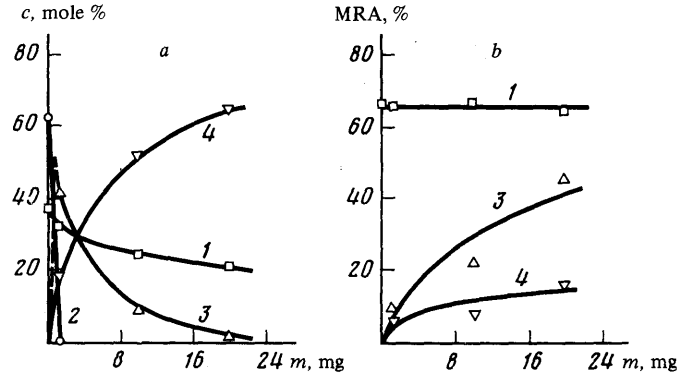


Figure 4. Variation of the concentration *c* (*a*) and the molar radioactivities (MRA) (% relative to the initial radioactivity) (*b*) of the products of the transformation of the [^{14}C]hexadienes–hexatrienes mixture at 530 °C as a function of contact time: *1*) hexadienes; *2*) hexatrienes; *3*) cyclohexa-1,3-diene; *4*) benzene[118].

As regards the influence of the hydrocarbon, which is manifested by an increase of the yield of olefins and a decrease of the yield of aromatic hydrocarbons, the above problem has already been considered and solved[127] in terms of mechanism (10).

Krzywicki and coworkers[135–137] detected cyclohexane and methylcyclohexane in the aromatisation of hexane and heptane on the comparatively little investigated alumina–chromium oxide–iron oxide catalyst[136,137]. The authors believe that these cyclic hydrocarbons are intermediates on the grounds that the curves representing their content in the catalytic reaction mixtures pass through a maximum as a function of time. However, it is difficult to regard this conclusion as sufficiently well founded because the kinetic picture presented by the authors is inconsistent with the kinetics of a consecutive reaction—the maxima are insufficiently distinct and the curve representing the content of the final product is not S-shaped.

Krzywicki et al.[135] did not detect dienes in the catalytic reaction mixtures obtained from paraffins and olefins, which is surprising because the formation of dienes had been detected earlier[138] on the same catalyst (up to 2%) but neither cyclanes nor cyclenes had been found. We therefore studied in greater detail[148] the transformations of hexane, hex-1-ene, and hexa-1,5-diene (on the catalyst prepared as described by Krzywicki and Malinowski[136]) mainly for short contact times. The kinetic picture obtained shows that hexenes and hexadienes are undoubtedly intermediates in the aromatisation of n-hexane on this catalyst.

In recent years studies on the aromatisation of paraffins on oxide catalysts have continued[143-147], but no new experimental facts have been observed which would necessitate a revision of the mechanism of this reaction presented above [Scheme (10)].

* * *

Thus analysis of the experimental data and in particular data obtained by the kinetic isotope method showed that the transformation of paraffins into aromatic hydrocarbons on the oxide catalysts investigated proceeds almost wholly via a single pathway—the successive dehydrogenation of the aliphatic molecule with formation of a six-membered ring by the thermal cyclisation of a triene. Only one function is required from the aromatisation catalyst, namely the ability to effect dehydrogenation.

Evidently this mechanism can be extended also to all other oxide catalysts used for the aromatisation of paraffins. However, the mechanism of the formation of the aromatic hydrocarbon on catalysts containing metals, including platinum group metals, is significantly more complex and therefore requires separate consideration.

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