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The Mechanism of the C_5- and C_6-Dehydrocyclisation and Skeletal Isomerisation Reactions of Hydrocarbons in the Presence of Metal-Containing catalysts

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A systematic account is given of data on the most important reactions of hydrocarbons in the presence of metal-containing catalysts. The modern ideas concerning the mechanisms of the isomerisation and C_5- and C_6-dehydrocyclisation of alkanes are described. The role of hydrogen in these reactions in the presence of metal-containing and in the first place platinum catalysts is analysed. The influence of the structure of metallic catalysts on the mechanisms of the dehydrocyclisation of skeletal isomerisation reactions of alkanes is examined.
The bibliography includes 170 references.

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I. INTRODUCTION

The dehydrocyclisation and isomerisation of hydrocarbons are some of the most important processes in organic and petrochemical synthesis. More than half of the aromatic hydrocarbons are obtained nowadays from petroleum raw materials with the aid of dehydrocyclisation (DHC), dehydrogenation, and dehydroisomerisation reactions. It is therefore natural that these processes have been investigated most vigorously during the last decade.

The DHC reactions are divided into two types—C_5- and C_6-DHC. This classification is based on the different natures of the hydrocarbons formed, the considerable differences between the mechanisms of the reactions, and finally, in many instances, the differences between the catalysts employed. C_5-DHC results in the formation of cyclopentane hydrocarbons or a new five-membered ring in condensed systems; C_6-DHC leads to the formation of aromatic (mono- or poly-nuclear) hydrocarbons.

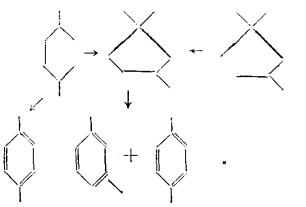
It is noteworthy that both types of DHC, in the presence of both metallic and oxide catalysts, were discovered in the Soviet Union[1-4]. The work of D.A.Kazanskii and his co-workers has made a particularly large contribution to the investigation of DHC reactions. These and certain subsequent researches into C_5- and C_6-DHC were described in monographs and reviews[5-11]. However, the problems of the interrelation between the C_5- and C_6-DHC reactions of alkanes, the specific details of the mechanisms of both types of cyclisation, the skeletal isomerisation reactions of alkanes and the hydrogenolysis of cyclopentanes, which are closely related to the above processes, and finally the involvement and role of hydrogen in these reactions merit special consideration.

II. CATALYTIC REACTIONS OF ALKANES AND CYCLOPENTANES IN THE PRESENCE OF PLATINUM CATALYSTS

C_6-Dehydrocyclisation of Alkanes

In the majority of studies in the presence of various metallic and in the first place platinum catalysts the C_5- and C_6-DHC reactions were investigated jointly because their conditions are very similar. In the first studies on reforming[9] the possibility of the intermediate formation of cyclopentane in the aromatisation of n-pentane was pointed out, because the catalytic reaction mixture contained a certain amount of alkylcyclopentanes.

Subsequently, this aromatisation pathway received a rigorous experimental confirmation, particularly as a result of the study of the reactions of 2,5-dimethylhexane, 2,2,4-trimethylpentane, and 1,1,3-trimethylcyclopentane in the presence of various platinum catalysts:



It was found that, in the presence of monofunctional platinum catalysts, 2,2,4-trimethylpentane as well as 1,1,3-trimethylcyclopentane give rise to approximately equal amounts of *m*- and *p*-xylenes[12-15], i.e. the aromatisation proceeds via

the intermediate formation of a C_5 ring. It has been suggested[15] that the rate-limiting stage in C_6-DHC involves the expansion of the five-membered ring. On the other hand, the main product of the aromatisation of 2,5-dimethylhexane is *p*-xylene, which shows that the C_5- and C_6-DHC reactions take place simultaneously and independently. Thus the pathway followed in the aromatisation proceeds depends significantly on the structure of the initial alkane.

The possibility of the direct 1,6-ring closure in the presence of Pt/C and various Pt/Al_2O_3 catalysts has been discussed[5,14,16-19]. This conclusion is based on the reactions of 2,2- and 3,3-dimethylhexanes[17,20], which partially cyclise to *gem*-dimethylcyclohexane and the latter is in its turn dehydrogenated under the experimental conditions with formation of aromatic hydrocarbons. An analogous alkane aromatisation pathway was discussed by Ivan'kovich et al.[21] The results of the study of the C_6-dehydrocyclisation of n-[1-^{14}C]- and n-[4-^{14}C]-heptanes have been analysed in detail[16].

On the other hand, Paal and Tetenyi[22-24] concluded that n-hexane undergoes successive dehydrogenation to a triene in the presence of nickel and platinum catalysts with subsequent cyclisation and aromatisation. This reaction mechanism and the absence of intermediate cyclohexane and cyclohexene in the reaction chain were confirmed by the same workers by introducing the ^{14}C label. Kazanskii and co-workers[25-28] reached an analogous conclusion concerning the n-alkane aromatisation pathways in the presence of Pt, Pt/Al_2O_3, and Pt/C catalysts.

Thus it can be assumed that the aromatisation of n-alkanes proceeds via intermediate dehydrogenation stages. At the same time, alkanes with a quaternary carbon atom cannot be dehydrogenated quite so readily under the reaction conditions and their aromatisation proceeds at least partially via the direct "cyclohexane" mechanism.

Analysis of data on aromatic C_7-hydrocarbons in the presence of Pt/Al_2O_3 [29,30] demonstrated yet another possibility for the formation of aromatic hydrocarbons from alkanes—namely as a result of the primary formation of a C_7 ring and its subsequent contraction. This is indicated by the formation of small amounts of cycloheptane from ethylcyclopentane and by the position of the ^{14}C label in the [1-^{14}C]heptane aromatisation products.

Under real conditions of catalysis, the aromatisation of alkanes in the presence of metal-containing catalysts apparently proceeds via all the mechanisms indicated above. One of these may predominate to a significant extent depending on the structure of the initial hydrocarbon, the reaction conditions (the temperature and the carrier gas), the chemical composition of the catalyst, etc. Thus it has been stated that, with decrease of the acidity of the platinum/alumina catalyst[32-35] and with increase of temperature[36], the contribution of the C_5-dehydrocyclisation to the aromatisation process diminishes. In the presence of the Pt/Al_2O_3 catalysts the dehydroisomerisation reaction plays an appreciably greater role in aromatisation than in the presence of the palladium catalyst[9].

The C_6-DHC of n-hexane in the presence of platinum deposited on "non-acid" Al_2O_3 has been investigated[14]. The authors suggested that the reaction proceeds via two pathways: (a) via consecutive mechanism involving the dehydrogenation and subsequent cyclisation of a triene and (b) via the direct aromatisation of n-hexane. The important role of hydrogen in the reaction and the undoubted dependence of the aromatisation mechanism on the hydrogen pressure in the reaction mixture were noted.

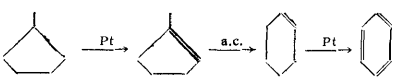
The results of studies of the aromatisation of n-heptane in the presence of Pt/Al_2O_3 catalysts by the thermal desorption and kinetic methods are of undoubted interest[37-39]. The temperature ranges of the desorption process and the number of active centres were determined. It was suggested that at least two types of platinum active centres are present on the surface of the Pt/Al_2O_3 catalyst. According to the authors[37-39], the C_6-DHC reaction takes place predominantly on one of them with formation of toluene, while the second type of centres are characterised by a greater activity in relation to the dissociation of the C–C bond and lead to the formation of benzene from toluene. The authors suggest that one of the two types of catalytically active centres is associated with the existence of crystalline platinum and the other with platinum complexes; the latter may also consist of cluster formations whose composition includes aluminium ions and OH groups as well. Overall, the results presented are in good agreement with the consecutive aromatisation mechanism. The authors[37-39] point out the possibility that the reaction rate is limited by the stage involving the desorption of the superdehydrogenated forms of aromatic compounds (with participation of hydrogen) on centres of one of the types. On centres of the other type the reaction rate is limited by the dehydrogenation stage[39].

As shown above, one of the pathways leading to the formation of aromatic hydrocarbons from alkanes is dehydroisomerisation of the intermediate alkylcyclopentanes.

Dehydroisomerisation of Cyclopentanes

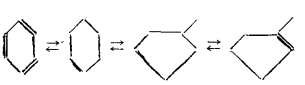
It has been shown by the kinetic isotope method[40] that, in the presence of Pt/C at 310 °C in a stream of helium, benzene is not formed from n-hexane via methylcyclopentane. The methylcyclopentane dehydroisomerisation reaction is suppressed under these conditions. Under other conditions (550 °C, p_{H_2} = 2.25 atm), it was established by the same method[25] that approximately 20% of benzene is formed from hexane via methylcyclopentane in the presence of the platinum/alumina catalyst, the rate of formation of benzene from methylcyclopentadiene being significantly higher than the rate of its formation from methylcyclopentane and methylcyclopentenes. On this basis, it is suggested that the C_6 ring is formed after the dehydrogenation of the cyclopentane hydrocarbon to methylcyclopentadiene.

In studies where the bifunctional character of dehydroisomerisation catalysts is emphasised, the occurrence of a process with participation of the acid centres (a.c.) of the carrier[34,35], for example via a carbonium ion mechanism[41-43], has been postulated:



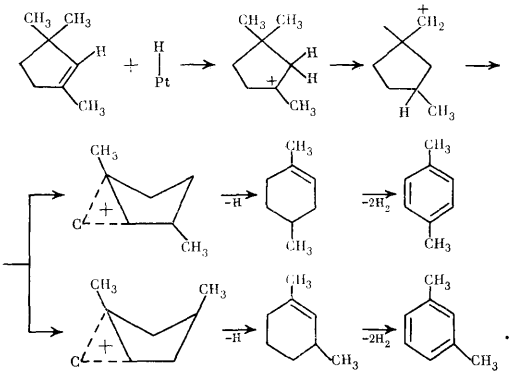
It has also been suggested that the dehydroisomerisation reaction proceeds at an active centre formed by a platinum atom or crystal and the adjoining acid centre[42].

The application of the kinetic isotope method made it possible to demonstrate that the dehydroisomerisation of methylcyclopentane in the presence of the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts under reforming conditions (480 °C, p_{H_2} = 20 atm) can take place also without the intermediate formation of a cyclene[44]:



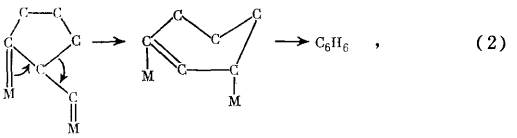
However, it is not clear which factor (hydrogen pressure, the acidity of the carrier, etc.) is involved in the discrepancy between the results of two studies by Isagulyants and co-workers[25,44].

The study of the dehydroisomerisation reaction in the presence of platinum/alumina catalysts with a suppressed acid function and also in the presence of a platinum film or platinum deposited on a relatively inert carrier (activated charcoal) demonstrated the possibility that the reaction takes place only at metallic centres. According to Lesger[15] the dehydroisomerisation mechanism consists in the formation of electron-deficient cyclopentyl rings on electron transfer from the semihydrogenated alkylcyclopentene to the platinum atom (functioning as a weak Lewis acid) accompanied by the 1,4-hydrogen shift or a series of 1,2-hydrogen shifts with subsequent ring expansion via a bicyclic intermediate:



(1)

It is emphasised[15] that the acid centres of the carrier of an industrial platinum/alumina catalyst may be more active in the isomerisation reaction than the platinum centres. According to the authors[8,15] the above mechanism (1) is preferable to the mechanism



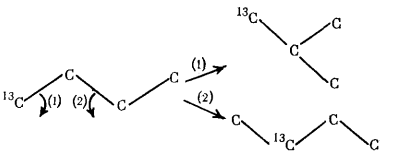
(2)

proposed by Muller and co-workers[13,45], according to which the preliminary abstraction of four hydrogen atoms is required. We may note that the proposed dehydroisomerisation mechanisms have overall features in common with the alkane isomerisation reaction.

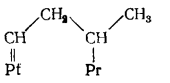
Isomerisation of Alkanes

The C_5-dehydrocyclisation and skeletal isomerisation reactions of alkanes as well as the hydrogenolysis and dehydroisomerisation of cyclopentanes in the presence of monofunctional catalysts are closely related and under certain conditions can occur simultaneously via parallel-consecutive mechanisms. Two main mechanisms of the isomerisation of alkanes in the presence of monofunctional platinum catalysts are distinguished at the present time[5,6]: the bond shift mechanism and the C_5-cyclic mechanism. However, despite the large number of studies carried out, there is as yet no unanimous view concerning the detailed reaction mechanism.

The bond shift mechanism was proposed to account for the characteristic features of the isomerisation of n-butane, isobutane, neopentane, and neohexane in the presence of sputtered platinum films[46,47].



Here (1) and (2) denote the possible directions of the bond shifts on formation of the corresponding product. Since isobutane and neopentane reacted at the same rates and with the same activation energies and the formation of a 1,2-diadsorbed or π-bonded intermediate cannot be postulated for neopentane, it has been suggested that the isomerisation proceeds via 1,3-adsorbed intermediate forms:



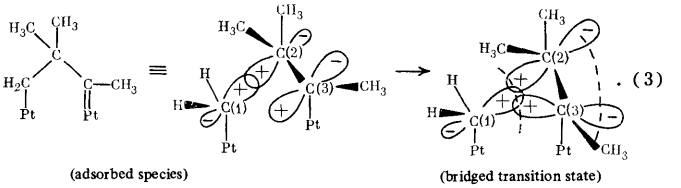
This structure of the adsorbed species is consistent also with data for the deuterolysis of 1,1-dimethylcyclopropane[13].

The study of the isomerisation reaction on oriented platinum films showed[47] that isobutane isomerises on the (111) face of a platinum single crystal more effectively than on the other faces, while for n-butane there are no great differences between the activities of different faces. This was explained by the possibility of the formation of a triadsorbed intermediate for isobutane on the platinum (111) face:



It is noteworthy that the isomerisation of neopentane is a structure-sensitive reaction[48]. Changes in the selectivity of the neopentane isomerisation as a function of the preliminary treatment of the catalyst and the degree of dispersion of the metal were explained on the basis of the characteristic features of the changes in the concentrations of triplets of platinum atoms and the corners and edges in polycrystalline platinum with increase in the size of crystallites. The possibility of three-point adsorption of neopentane on the platinum(111) face and the stepped platinum faces and the impossibility of such adsorption on the (110) and (100) faces were demonstrated with the aid of simple geometrical considerations.

The bond shift mechanism has been examined[49] from the standpoint of the molecular orbital method. The rearrangement of neohexane to 2-methylpentane can be represented as follows (henceforth referred to as Anderson's mechanism):

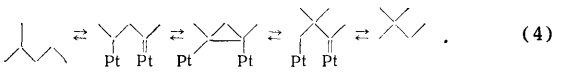


(adsorbed species) (bridged transition state)

(3)

It has been suggested that the electrons of the pπ orbital of the C(3) atom are partly displaced towards the metal, so that a structure intermediate between a carbonium ion and a radical is produced. Calculation of the energy of the bridge bond makes it possible to arrange alkanes in the sequence $n\text{-}C_4H_{10} < iso\text{-}C_4H_{10} < neo\text{-}C_5H_{12}$, which had been established previously[47] for the relative reactivities of these hydrocarbons in the presence of platinum. It has been noted[49] that,

whereas the sp^3 hybridisation of the C(2) atom does not prevent the isomerisation of neopentane, the sp^2 hybridisation of the C(3) atom [see mechanism (3)] to which the migrating group is transferred, rules out the possibility of the formation of neopentane from isopentane, which has been observed experimentally[47]. However, small but not negligible amounts of neohexane are formed from methylpentanes in the presence of platinum. It has been suggested[13] that in this case the isomerisation proceeds via the mechanism

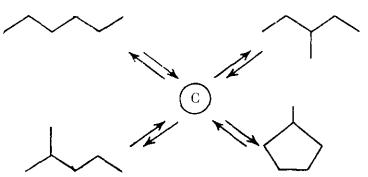


(4)

We may point out that the proportions of the products of the hydrogenolysis of methylcyclopropane observed experimentally[50] differ significantly from those of the butane isomerisation products[47]. The above mechanism can therefore be considered as one of the possible mechanisms of the isomerisation reaction only if it is assumed that the adsorbed cyclopropane is a transition state but not an intermediate in the reaction.

Thus the two bond shift isomerisation mechanisms examined differ mainly by the structure of the transition state. In both cases, firstly, the metal atom must be sufficiently electronegative and, secondly, the surface metal atoms must be capable of undergoing a rapid change in their valence in the rearrangement. The characteristic features of the catalytic action of iridium and platinum, which are the only Group VIII metals capable of catalysing the isomerisation of neopentane, have been treated from these standpoints[51]. For a long time it was impossible to observe the isomerisation of neopentane in the presence of palladium[47,51], although isobutane undergoes a rearrangement on palladium. It has only recently been reported[52] that neopentane can isomerise on an oriented palladium (111) film under the conditions of a high H_2/hydrocarbon ratio.

Isopentanes, n-hexane, and their homologues isomerise more readily than neopentane and neohexane in the presence of monofunctional platinum catalysts. Methylcyclopentane is then always formed, its concentration passing through a maximum with increase of the degree of conversion. It has been shown that methylcyclopentane and isomeric hexanes give identical initial proportions of the products (C_6 alkanes) on contact with the Pt/Al_2O_3 catalyst whose acidic function has been suppressed[45,53]. Analogous proportions of products are characteristic also of reactions in the presence of platinum deposited on activated charcoal and pumice and on platinum films, but they differ significantly from the proportions of the products obtained in the presence of explicitly bifunctional catalysts. On the basis of these findings, it has been suggested that there is a single transition complex in the isomerisation of hexanes and hydrogenolysis of methylcyclopentane in the presence of monofunctional platinum catalysts (the C_5-ring mechanism); the reactions of hydrocarbons are then represented schematically in the following manner[45]:



Here © represents a set of hydrocarbon interconversion products, some of which must have a cyclic structure, and the intermediates in the dehydrocyclisation reaction of alkanes are the same as in the hydrogenolysis of methylcyclopentane[54]. Thus the isomerisation and C_5 dehydrocyclisation reactions of alkanes, on the one hand, and the hydrogenolysis reactions of alkylcyclopentanes, on the other, are interrelated, which must be taken into account in explaining the structure of the interconversion products ©. We may note that the possibility of the isomerisation of alkanes as a result of the hydrogenolysis of an intermediate C_5-cyclic hydrocarbon was pointed out by Liberman et al.[55]

Hydrogenolysis of Cyclopentane

The hydrogenolysis of cyclopentane and its homologues has been most thoroughly investigated among this group of reactions. Detailed information about this process can be found in a number of communications[7,56-58]. Here we shall briefly discuss only the principal characteristic features and the proposed mechanisms of this reaction. The hydrogenolysis of cyclopentane hydrocarbons takes place successfully in the presence of platinum, rhodium, iridium, and osmium catalysts[59]. In the presence of platinum catalysts the hydrogenolysis slows down with increase of the number of substituents in the five-membered ring[58]. Data on the selectivity of the hydrogenolysis of substituted cyclopentanes via different pathways are of greatest importance. The selectivity depends on a number of factors: the size, number, and location of the substituents in the C_5 ring[58,60], the partial pressure and surface concentration of hydrogen†,[59,61] and the degree of dispersion of the metal[62-64].

Thus an increase of the partial pressure of hydrogen from 10 to 50 atm decreases the 2-methylpentane/n-hexane ratio in the hydrogenolysis of methylcyclopentane in the presence of different platinum catalysts[61]. It is of interest to note that at 50 atm in the presence of the 0.3% Pt/Al_2O_3 catalyst the tertiary-secondary C–C bonds are exclusively ruptured in the five-membered ring. It has been suggested[61-65] that the pathway followed in the hydrogenolysis of the C_5 ring is determined by the structure of the monoadsorbed complex, which depends on the relative contributions of two factors: the distribution of electron density in the alkylcyclopentane molecule and the electrophilicity (electron-donating properties) of the transition metal atoms in the catalyst, which is influenced by the hydrogen pressure. The influence of the hydrogen pressure on the pathway in the cyclisation of n-octane, namely an increase of the yield of 1,2-ethylmethylcyclopentane relative to propylcyclopentane with increase of hydrogen pressure, has been treated from the same standpoint[66]. However, the role of the carrier in the hydrogenolysis of alkylcyclopentanes remains obscure. The preferential dissociation of the tertiary-secondary C–C bonds in the C_5 ring can be logically explained on the assumption[67,68] that the hydrogenolysis of alkylcyclopentanes takes place preferentially at the acid centres of the 0.3% Pt/Al_2O_3 catalyst at a hydrogen pressure of 50 atm.

In his study of the influence of the platinum concentration in platinum/alumina catalysts on the hydrogenolysis of methylcyclobutane and methylcyclopentane, Gault[63] concluded that there are at least two hydrogenolysis mechanisms: the selective mechanism in which only the bonds between the secondary carbon atoms in the ring are ruptured and the non-selective mechanism leading to the equally probable dissociation of all the ring C–C bonds. The first mechanism is characteristic of the reaction on platinum films at low temperatures and in the presence of the 10% Pt/Al_2O_3 catalyst. The second

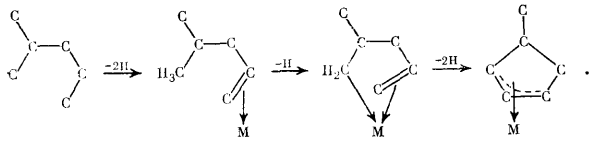
†See also C.Corolleur, F.G.Gault, and L.Beránek, React. Kinet.Catal.Letters, 1976, 5, 459.

mechanism operates on platinum films at high temperatures and in the presence of the 0.2% Pt/Al_2O_3 catalyst; in this case the proportions of the products are independent of the degree of conversion[62]. It has been suggested that the hydrogenolysis via the non-selective mechanism proceeds via the intermediate formation of α, β, γ-triadsorbed (π-bonded) species, while the reaction via the selective mechanism proceeds via α, α, β, β-tetra-adsorbed species. In the former case the plane of the ring is parallel and in the latter case perpendicular to the surface of the metal. The principal features of the selectivity of the hydrogenolysis of various cyclic hydrocarbons can be logically explained from the above standpoints. For example, an increase of the partial pressure of hydrogen should suppress the formation of the tetra-adsorbed species, i.e. should diminish the contribution of the selective mechanism to the hydrogenolysis of cyclopentanes, which is in fact observed experimentally.

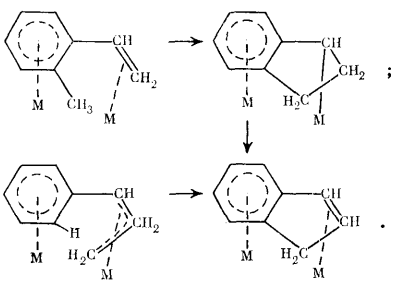
We may note that by no means all experimental data can be described in terms of the selective and non-selective mechanisms (or their linear combination). Maire et al.[62] were therefore forced to introduce the concept of the partially selective mechanism of hydrogenolysis, but it proved difficult to put forward any postulates concerning the character of the intermediate species. The results of a study[69] in which it was shown that the partially selective mechanism can be observed in those cases where the acid centres of the catalyst exhibit an appreciable activity in the hydrogenolysis of cyclopentanes are of interest in this connection. We may note that the interpretation of the results for the hydrogenolysis of alkylcyclopentanes must be treated with caution, since the monofunctional character of the catalysts employed has been no means always reliably demonstrated.

The C_5-Dehydrocyclisation of Alkanes

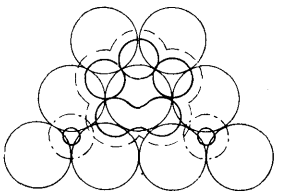
Data on the hydrogenolysis of alkylcyclopentanes in the presence of platinum catalysts suggested the following mechanism of the C_5-dehydrocyclisation of alkanes[45]:



An analogous mechanism has been proposed previously[70] for the C_5-dehydrocyclisation of alkylbenzenes in the presence of the Pt/Al_2O_3 and Pt/SiO_2 catalysts:



Other views concerning the structure of the transition state in the C_5-dehydrocyclisation of alkanes and the hydrogenolysis of cyclopentanes in the presence of Pt/C have been developed[54,59,71]. The hydrogenolysis of cyclopentane to pentane in the presence of this catalyst is known to proceed without the formation of side products at 200–290 °C. Neither n-pentane[71,72] nor cyclohexane[73] undergoes hydrogenolysis at these temperatures. These facts cannot be interpreted from the standpoint of the strain in the cyclopentane molecule[74] or the differences between the energies of the C–H and C–C bonds in these hydrocarbons[75]; however, they can be rationally accounted for within the framework of this sextet-doublet mechanism of the hydrogenolysis of cyclopentane hydrocarbons in the presence of the Pt/C catalyst, according to which[54,71] the carbon atoms of the five-membered rings are located in the interstices of the platinum (111) lattice on adsorption of the hydrocarbon. The geometrical requirements are such that one of the bonds in the ring is then extended, dissociating in the presence of adsorbed hydrogen. According to Liberman[54], the structure of the transition state can be represented schematically as follows:



where the large circles represent platinum atoms, the medium circles represent carbon atoms, and the small circles represent hydrogen atoms; the dashed lines denote the van der Waals volumes of the carbon and hydrogen atoms.

In conformity with the principle of microscopic reversibility, the C_5-dehydrocyclisation reaction of alkanes should proceed via the same transition state. According to this mechanism, an increase of the surface concentration of hydrogen should entail a decrease of the probability of the disposition of the substituents in the interstices of the platinum lattice following the adsorption of the cyclopentane hydrocarbon (which facilites the attack by hydrogen on the C–C bond adjoining the substituent), i.e. entails a decrease of the selectivity of the hydrogenolysis[59,76,77]. The increase of the fraction of 1,2-dimethylcyclopentane compared with ethylcyclopentane in the products of the C_5-dehydrocyclisation of n-heptane on passing from a flow to a pulsed system can be explained analogously[78]; here it is suggested that the lowest surface concentration of hydrogen is attained under the conditions of the flow system.

In the presence of rhodium, iridium, and osmium catalysts the hydrogenolysis takes place equally successfully for both cyclopentanes and for cyclohexanes and alkanes, which, together with certain other facts, led Bragin et al.[59] to the conclusion that the reaction proceeds via a doublet mechanism.

We may note that, although the models of the sextet-doublet and doublet mechanisms differ significantly in detail from the concepts of the selective and non-selective mechanisms of the hydrogenolysis of cyclopentanes, they also have certain features in common. In particular, in the hydrogenolysis via the non-selective mechanism[62] and the sextet-doublet mechanism, it is assumed that the ring of the molecule is arranged parallel to the surface of the metal. On the other hand, the question of the nature of the adsorption of the reacting molecule remains open within the framework of the sextet-doublet mechanism[54,71], although the authors have in fact indicated the possibility of physical adsorption.

Among other Group VIII metals, palladium[79,80], iridium[81,82], rhodium[83,84] and its alloys[85,86] exhibit a catalytic activity in the C_5-dehydrocyclisation of alkanes and their isomerisation via the C_5-ring mechanism.

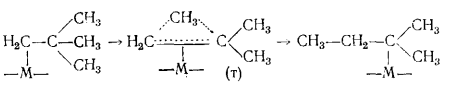
The characteristics and mechanisms of the isomerisation and cyclisation of aromatic alkyl-substituted hydrocarbons in the presence of platinum catalysts have been described in detail in recently published reviews[8,87].

III. THE MECHANISMS OF THE ISOMERISATION AND C_5-DEHYDROCYCLISATION REACTIONS OF ALKANES AND THE HYDROGENOLYSIS OF CYCLOPENTANES

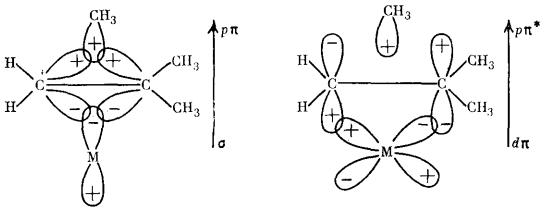
One of the fruitful methods for the investigation of reaction mechanisms involves the study of the reactions of model hydrocarbons (the term "model hydrocarbons" is treated here in a broad sense). With their aid, the investigator can make a choice between several alternative reaction mechanisms or can estimate the contributions of different mechanisms to the overall process. Hydrocarbons with a characteristic feature in the structure of the carbon skeleton, for example, the position of the substituents and the presence of a quaternary carbon atom or an isotope label, can be used as models. In most cases the difficulty of the synthesis of such hydrocarbons is compensated by the ease of the interpretation of the experimental data and the possibility of observing detailed features in the course of the reactions.

Thus the application of neopentane as a model hydrocarbon made it possible to introduce the concept of 1,3-diadsorption in isomerisation via the bond shift mechanism (the Anderson mechanism). Rooney and co-workers[88-90] demonstrated the ease of isomerisation on platinum (at 160–300 °C) and palladium (at 200–300 °C) of a series of polycyclic hydrocarbons for which the formation of 1,3-diadsorbed intermediate species is impossible or difficult. For example, the adsorption of the adamantane dimer during isomerisation then proceeds with elimination of only one hydrogen atom. This is also indicated by data for the D_2 exchange with this hydrocarbon.

In order to account for the characteristics of the isomerisation of polycyclic hydrocarbons, the following mechanism (henceforth referred to as the Rooney mechanism), considered for simplicity in relation to neopentane, has been suggested[90,91]:



In the transition state (T), the occupied $p\pi$ orbital of the hydrocarbon species overlaps with the σ orbital of the metal. Simultaneously the $d\pi$ orbital of the metal overlaps with the unoccupied antibonding $p\pi$ orbital of the hydrocarbon fragment:



The electron-deficient character of the $p\pi$ orbital explains some similarity of this mechanism with the carbonium ion mechanism of isomerisation. The character of the bonding in the transition state (T) resembles that in metal–olefin complexes. In conformity with this finding, platinum, which forms stronger metal–olefin bonds, is a better catalyst of isomerisation via the bond shift mechanism than palladium. Similarly, the greater selectivity of the (111) face of platinum compared with the other faces in isomerisation[53] cannot be explained by the more effective adsorption of the hydrocarbon on this face; the true explanation is that the (111) face has no affinity for the formation of a strong bond between the hydrocarbon and the surface, which is necessary for hydrogenolysis[6]. We may note that the transition state (T) cannot be common to the isomerisation and hydrogenolysis reactions of alkanes[91], in contrast to the Anderson mechanism according to which identical intermediate species are formed in these two reactions. We may draw attention to the similarity of the Rooney mechanism to the mechanism of the dehydroisomerisation of alkylcyclopentanes on platinum discussed above [see mechanism (1)].

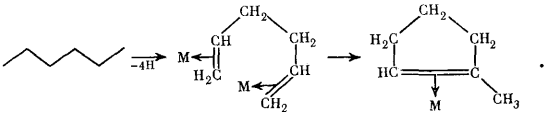
The isomerisation of neopentane on a platinum film in the presence of D_2 involves the formation of an appreciable amount of monodeuterated isopentane[92], which confirms, according to the authors, the formation of intermediate adsorbed alkyl species in the isomerisation reaction.

It was stated earlier that intermediate species of the type



may play an important role in the C_5-dehydrocyclisation and skeletal isomerisation of alkanes. This possibility is also confirmed by the results of the study of the C_5-dehydrocyclisation from the standpoint of the characteristics of electrocyclic reactions[93].

Comparative study of the reactions of a series of hexenes, hexadienes, hexa-1,3,5-triene, and n-hexane in a stream of hydrogen and helium on the Pt/Al_2O_3 catalyst[26] and in a mixture of these gases (20% H_2) on platinum black[24] showed that the yields of five-membered cyclic hydrocarbons are a maximum in the case of the initial hexa-1,5-diene. The amount of methylcyclopent-1-ene formed under these conditions increases with decrease of the dehydrogenating activity of the catalyst. The following cyclisation mechanism has been proposed on the basis of the facts presented above[94]:



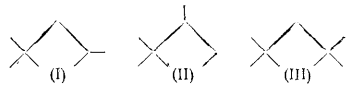
However, one should bear in mind that, together with processes involving the formation of a five-membered ring, other reactions proceed vigorously: skeletal isomerisation, double bond shift, aromatisation, dehydrogenation processes, and hydrocracking. Thus small changes in the yields of five-membered carbocyclic products may be associated, depending on the nature of the initial hydrocarbon, with a change in the contribution of different reactions to the overall process, particularly when the closure of the five-membered ring is the rate-limiting stage.

In order to investigate the role of olefins in the C_5-dehydrocyclisation reactions of alkanes, experiments were performed in which the alkane, alkene, and then again the alkane were passed over the Pt/C catalyst[27,95]. In the absence of a stream of H_2, different effects of the replacement of the initial hydrocarbon on the C_5- and C_6-dehydrocyclisations were demonstrated: in the latter case the introduction of an olefin into the reaction zone instead of the alkane increased the yield of the aromatic hydrocarbon, while the yield of alkylcyclopentanes fell. These facts indicate definite differences between C_5- and C_6-dehydrocyclisations; under the conditions investigated, the former proceeds in the presence of the Pt/C catalyst mainly via the direct pathway, bypassing the olefin-formation stage.

Under more severe conditions and in the presence of bifunctional catalysts[26,96-98], the reaction can also proceed differently, for example via two independent pathways: via the intermediate formation of olefins and via the direct closure of the five-membered ring. Quantitative data for these two pathways have been obtained by the kinetic isotope method[97,99];

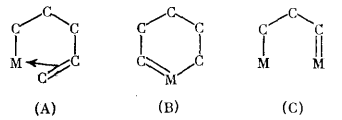
it was observed that the relative contributions of the two pathways vary with the experimental temperature and the nature of the catalyst. It is noteworthy that the rigorous application of the kinetic isotope method to the determination of the intermediates in the reaction is possible only in the presence of the adsorption–desorption equilibrium between the surface species and the corresponding compounds in the gas phase; however, this is not always achieved[25].

Another approach to the study of the possibility of the intermediate formation of π-adsorbed α-olefins in the C_5-DHC of alkanes has been used[100]: the reactions of 2,2,4-tri-methylpentane (I), 2,2,3-trimethylpentanes (II), and 2,2,4,4-tetramethylpentanes (III) on platinum and palladium films were investigated:

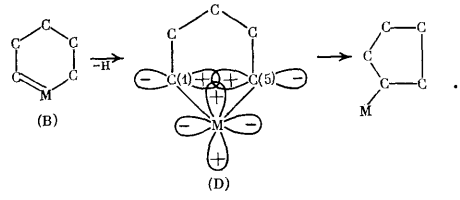


On platinum, the C_5-dehydrocyclisation of these hydrocarbons is the main process, the ratios of the rates of cyclisation of compounds (I), (II), and (III), being 1.2:1.2:1.0. In the presence of palladium, compound (II) cyclises at a rate higher by an order of magnitude than compound (I) and higher by two orders of magnitude than compound (III), the C_5-dehydrocyclisation of these hydrocarbons not being the main process. In an earlier study[111] similar results were obtained in the presence of the 20% Pt/C catalyst: under the same conditions, the yields of the cyclic products were 14% from compound (I) and 21% from compound (III). However, no conclusions about the reaction mechanism were reached[101].

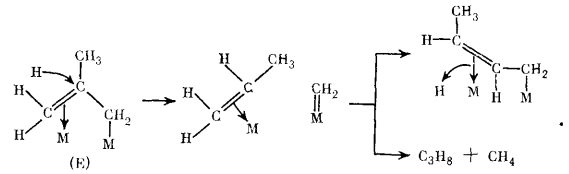
The results of Muller and Gault[100] suggested that the cyclisation on platinum takes place via the intermediate formation of the species (B) but not (A), while on palladium the species (A) cyclise:



Cyclisation via the (B) stage can proceed as a result of simple *cis*-ligand inclusion; this results in the formation of adsorbed cyclopentane. An alternative pathway (possibly more favourable) involves the formation of the (D) state in which the 2*p* orbitals of the C(1) and C(5) atoms and the *d* orbital of the metal atom form an occupied bonding molecular orbital, two unoccupied non-bonding orbitals, and an antibonding orbital:

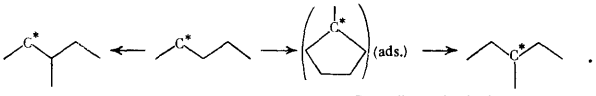


This mechanism of cyclisation on platinum [via the formation of the (B) or (D) state] is analogous to the mechanism of the skeletal isomerisation via bond shift with the intermediate formation of (C). Intermediates of type (C) do not account for the characteristics of the isomerisation on palladium. In the latter case the following mechanism of isomerisation and hydrogenolysis with participation of adsorbed hydrogen has been suggested[100]:



The necessity for the formation of an intermediate of type (E) explains the difficulty of isomerisation on palladium with participation of a quaternary atom. Thus the expansion of the ring of 1,1,3-trimethylcyclopentane on palladium proceeds via a tertiary carbon atom, while on platinum the expansion involves a quaternary carbon atom[13]. Neopentane readily isomerises on platinum, while on palladium the reaction does not occur under the usual conditions[47].

The use of mass spectrometry to determine the position of ^{13}C in labelled hydrocarbons[15] made it possible to use the latter to investigate the mechanisms of catalytic reactions. Thus in the case of the ^{13}C-labelled 2-methylpentane it is possible to distinguish the bond shift and C_5-cyclic isomerisation mechanisms:



The reactions of isomeric hexanes labelled with ^{13}C have been studied in the presence of the 0.2% Pt/Al_2O_3 [102] and 10% Pt/Al_2O_3 [103] catalysts and also on a platinum film [104] in a stream of hydrogen. The distribution of the label in the products shows that the isomerisation in the presence of the Pt/Al_2O_3 catalyst containing 0.2% Pt proceeds mainly via the C_5-cyclic mechanism; in the presence of Pt/Al_2O_3 with a 10% content of platinum and on a platinum film, the bond shift mechanism makes a significant contribution to the isomerisation process. It was found that in the adsorbed phase several consecutive rearrangements can occur in the molecule, their number being greater in the presence of the 10% Pt/Al_2O_3 catalyst and a platinum film than in the presence of the 0.2% Pt/Al_2O_3 catalyst. Not only the content (and the degree of dispersion) of the platinum in the catalyst, but apparently also the partial pressure of hydrogen influence the number of rearrangements in the adsorbed phase under these conditions, but the authors did not investigate the influence of this factor. Unfortunately, no data are quoted[102,103] concerning the hydrogen/hydrocarbon ratio; the conclusion that the ratio was small in the above studies[103,104] can be reached only on the basis of later investigations, for example, that of Garin and Gault[105].

The examples examined above demonstrate the great effectiveness of the study of the reactions of model hydrocarbons whose geometry permits a choice between the possible reaction mechanisms. However, the extension of certain conclusions to a wider range of starting materials always requires some caution, because one cannot rule out the possibility that the molecular geometry (for example, stereochemical limitations) actually prevents the occurrence of the reaction via an alternative pathway. When geometrical limitations are removed, such a pathway may become entirely possible. The application of labelled compounds, which permit the determination of the relative contributions of different reaction pathways without influencing the course of the reaction, is promising from this standpoint. In a number of instances the study of the position of the ^{13}C label in the reaction product makes it possible to determine the rate-limiting stage of the reaction.

IV. THE INFLUENCE OF HYDROGEN ON THE DEHYDROCYCLISATION AND ISOMERISATION REACTIONS OF ALKANES. KINETIC STUDIES

The role of hydrogen in the hydrogenolysis of alkylcyclopentanes and the dehydrocyclisation and skeletal isomerisation of alkanes was elucidated both in independent studies and within the framework of kinetic investigations. Whereas hydrogen is a direct participant in the first of the above reactions, in C_5-dehydrocyclisation and skeletal isomerisation it is involved as an astoichiometric component[106]. The study of the role of hydrogen in these reactions made it possible to discover certain additional details of their mechanisms.

A characteristic feature of the influence of hydrogen on the catalytic reactions of hydrocarbons in the presence of platinum catalysts is the presence of a maximum on the plot of the reaction rate (the yield of reaction products) against the partial pressure of hydrogen when p_{H_2} is varied within fairly broad limits. Such relations have been observed for the dehydrocyclisation and skeletal isomerisation of C_6-hydrocarbons on platinum black[107-112], in the presence of the Pt/C catalyst[113] and bifunctional Pt/Al_2O_3 and $Pt-Re/Al_2O_3-F$ catalysts[114] for the dehydroisomerisation of methylcyclopentane[41], the skeletal isomerisation of n-heptane[115] and certain C_4-C_6 alkanes[116-118], and for the dehydrocyclisation of n-heptane[119] in the presence of bifunctional platinum/alumina catalysts.

The position of the maximum depends in the general case on the experimental conditions: on the catalysts employed, on the type of reaction considered, on the structure of the initial hydrocarbon, on the experimental temperature, etc. As an example, we shall consider the results of our investigations[113,114,120] in which the influence of the concentration of hydrogen on the C_5-DHC and the skeletal isomerisation of alkanes and alkenes was studied on deposited platinum catalysts of different types—platinised charcoal and bifunctional platinum/alumina and platinum–rhenium/alumina catalysts. The positions of the maximum are different on plots of the yield of C_5-DHC products and the products of the skeletal isomerisation of alkanes against the partial pressure of hydrogen. In the case of C_5-DHC the coordinates of the maximum depend little on the reaction temperature and the structure of the initial alkane. The optimum H_2 concentration for the skeletal isomerisation of alkanes depends on their structure: for a more branched hydrocarbon, the maximum lies at higher H_2 concentrations. A decrease of temperature shifts the position of the maximum towards lower H_2 concentrations, which indicates the important role of the surface hydrogen in the skeletal isomerisation reaction (the concentration of such hydrogen increases with decrease of temperature). We may note the similarity of the relations obtained in the reactions of 3-methylpentane and 3-methylpent-2-ene in the presence of the Pt/C catalyst. This shows that the formation of methylcyclopentane from an alkane and alkene in the presence of H_2 apparently proceeds via similar intermediate stages.

We may note that the five-membered carbocyclic products derived from both alkanes and olefins and dienes are formed only in the presence of hydrogen[94,107,108]. In the presence of platinum black the skeletal isomerisation of alkanes in H_2 proceeds via both the C_5-cyclic mechanism and the bond shift mechanism. In the absence of hydrogen the isomerisation can take place only via the bond shift mechanism[109]; the C_6-DHC reaction of n-hexane on platinum black[107] and in the presence of the Pt/Al_2O_3 catalyst[79] takes place at an appreciable rate also in a stream of helium, in contrast to C_5-DHC. However, it has been stated[119] that under reforming conditions the rate of aromatisation of n-heptane on the Pt/Al_2O_3 catalyst is virtually zero in the absence of hydrogen.

Comparative study of the influence of the partial pressure of hydrogen on the C_5-cyclisation and skeletal isomerisation of 3-methylpentane and 3-methylpentenes on platinum black enabled Paal et al.[121] to postulate the operation of two different mechanisms of the formation of the C_5 ring. According to the authors[121], at a low hydrogen concentration the cyclisation proceeds via the intermediate formation of highly dehydrogenated species (for example, of the alkenyl type). At higher pressures, the cyclisation takes place via a "two-centre" mechanism involving the intermediate formation of semihydrogenated products, which are apparently "weakly" adsorbed on platinum centres, while the new C–C bond is formed as a result of the interaction of the terminal atoms of the carbon chain with other platinum centres. The operation of the "two-centre" mechanism of the C_5-dehydrocyclisation may be indicated by the following facts: the similarity of the nature of the reaction of 3-methylpentane and 3-methylpentenes under these conditions (there are no differences between the reactivities of *cis*- and *trans*-3-methylpent-2-enes), the proportionality of the rate of cyclisation and the hydrogenating activity of the catalyst[121], and data for the deactivation of platinum black under the influence of the hydrocarbon[122].

An attempt has been made[111] to describe the kinetics of the isomerisation of 3-methylpentane on platinum black in a static system. The kinetic equation obtained for the "two-centre" mechanism of isomerisation describes satisfactorily the character of the influence of hydrogen on the rate of reaction in qualitative terms, but the authors[111] did not provide a complete multistage scheme for the reaction and did not carry out a mathematical treatment of the experimental results.

The data examined show that hydrogen exerts a promoting or inhibiting influence on the reactions of hydrocarbons depending on the experimental conditions and the catalyst. This is associated with various functions performed by hydrogen on the surfaces of metallic catalysts. We may note the most important of these, which are discussed in the communications quoted above.

Vigorous dehydrogenation processes, leading to the formation of strongly adsorbed hydrocarbon fragments on the surface, take place at low H_2 pressures in the presence of platinum catalysts. By suppressing the above process, hydrogen increases the working area of the catalyst, which accelerates the reactions. On the other hand, hydrogen promotes the desorption displacement of the products of the reactions of hydrocarbons.

At fairly high partial pressures of hydrogen, the chemisorption of the hydrocarbon is suppressed as a consequence of the competitive character of the adsorption of hydrogen and the hydrocarbon. Hydrogen also prevents the dissociation of the initial hydrocarbon on the surface, which inhibits the reactions. Overall, when p_{H_2} is varied widely, the causes considered here lead to the appearance of maxima on the curve relating the yields of the reaction products to p_{H_2}.

One cannot rule out the possibility that, for different degrees of coverage of the catalyst surface with hydrogen, the rate-limiting state and the reaction mechanism can be different. Thus, according to our data[113], the skeletal isomerisation in the presence of the Pt/C catalyst proceeds via the C_5-cyclic mechanism over the entire range of hydrogen concentrations investigated. In the presence of bifunctional catalysts[114], the relative contributions of different mechanisms depend on the partial pressure of hydrogen and the acidity of the catalyst. At high partial pressures of

hydrogen the C_5-cyclic mechanism of isomerisation predominates and at comparatively low partial pressures another pathway, apparently involving the acid centres of the catalyst, makes a significant contribution.

The possibility of the involvement of hydrogen as an astoichiometric component in the reactions of hydrocarbons is of fundamental importance. Its role may not reduce solely to influencing the adsorption-desorption stages. It has been suggested[96,98] that hydrogen not only promotes the removal of the strongly adsorbed carbon-containing species but is also directly involved in the C_5-dehydrocyclisation reaction of alkanes itself. In our studies these views were further developed[113,114,120,123].

New data concerning the role of hydrogen in the C_5-DHC reaction of alkanes in the presence of the Pt/C catalyst have been obtained[120,123] in a study of the kinetics of the C_5-DHC of iso-octane. It was shown that, in the range of partial pressures of the reactants investigated, the C_5-DHC reaction is accelerated by hydrogen and inhibited by 1,1,3-trimethylcyclopentane. We put forward the following kinetic equation:

$$r = (kp_A - k'p_B p_H) \Big/ \left[\frac{p_A}{p_H^{0.5}} + A_1 \frac{p_B}{p_H^{0.5}} + A_2 p_H^{0.5} + A_3 p_A \left(\frac{A_4}{p_H} \right)^{0.5(n+1)} \right] ,$$

where r is the rate of reaction, p_A, p_B, and p_H are the current partial pressures of iso-octane, 1,1,3-trimethylcyclopentane, and hydrogen respectively, and k, k', A_1, A_2, A_3, and n are constants whose physical significance is discussed by Krasavin et al.[123] Analysis of this equation using the numerical values of the constants indicated by Krasavin et al.[123] makes it possible to predict the appearance of a maximum on the curve relating the reaction rate to the partial pressure of hydrogen when p_{H_2} is varied widely. The position of the maximum depends on the stability of the surface carbon-containing compounds: with its increase, the maximum shifts towards higher values of p_{H_2}.

An important factor, observed by the present authors[120], is the occurrence of a kinetic isotope effect in the C_5-DHC reaction of iso-octane in the presence of a Pt/C catalyst when hydrogen is replaced by deuterium. The kinetic isotope effect $r_H/r_D = 2$ indicates the involvement of hydrogen in the slow stages of the C_5-DHC reaction. Under the same conditions, the rate of exchange of deuterium for hydrogen in iso-octane greatly exceeded the rate of the C_5-DHC reaction. This shows that the adsorption stage must apparently be regarded as rapid. The set of data obtained enabled us to describe the C_5-DHC reaction in terms of the following multistage scheme[123]:

(1) $H_2 + 2Z \rightarrow 2HZ$,

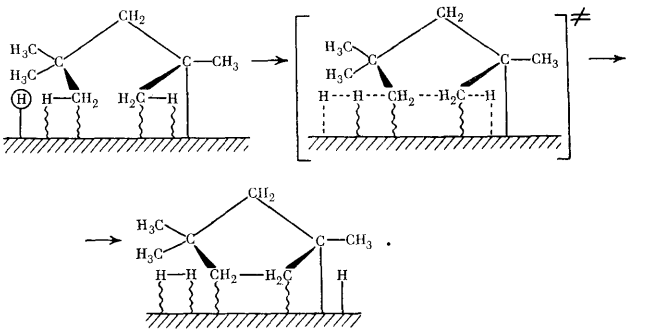
(2) $C_8H_{18} + HZ \rightarrow C_8H_{17}Z + HZ \rightarrow C_8H_{17}Z + H_2$,

(3) $C_8H_{17}Z + nHZ \rightarrow C_8H_{17-n}Z + nH_2 + nZ$,

(4) $C_8H_{17}Z + HZ \rightarrow (\text{cyclo-}C_8H_{15})Z + HZ + H_2$,

(5) $(\text{cyclo-}C_8H_{15})Z + H_2 \rightarrow \text{cyclo-}C_8H_{16} + HZ$.

Here Z denotes a site on the surface of platinum. Dissociative adsorption of the initial hydrocarbon when the latter interacts with surface hydrogen with simultaneous evolution of molecular hydrogen is postulated in stage (2). The $C_8H_{17}Z$ fragment formed can undergo further dissociation (stage 3). This pathway apparently does not lead to the formation of the C_5-DHC products under the conditions investigated, but stage (3) explains the multiple exchange of deuterium for hydrogen in the higher alkanes and certain characteristic features of the behaviour of the Pt/C catalyst at $p_{H_2} < 0.4$ atm. Stage (4) describes the cyclisation of the $C_8H_{17}Z$ fragment. The formation of the C_5 ring on the surface can be represented as follows:



Here the continuous lines denote the chemisorption linkages with the surface, the wavy lines indicate the topography of the disposition of the atoms at the surface, and the dashed lines represent the redistribution of bonds in the associative transition state.

Thus the hydrogen chemisorbed on the catalyst reacts with the $C_8H_{17}Z$ surface fragment to form a transition state in which the loosening of the H–C bond is accompanied by the simultaneous formation of a C–C bond in the hydrocarbon under the influence of the activated hydrogen species (the latter is enclosed in a circle). The surface cyclic compound formed reacts with molecular hydrogen in stage (5) of the mechanism under consideration to form the final reaction product and adsorbed hydrogen. According to the views developed here, adsorption and cyclisation takes place at different fairly close centres on the catalyst surface.

In the experimental temperature range (280–325 °C) stage (1) is rapid. Stages (2) and (3) can also be regarded as rapid, since the rate of isotope exchange between deuterium and the hydrocarbon is much higher than the rate of the C_5-DHC reaction. Stage (5) should likewise be regarded as rapid, since otherwise it would be impossible to explain the observed inhibition of the reaction by its product. It remains to assume that the slow stage in the above mechanism is stage (4), which agrees with the acceleration of the reaction when the hydrogen concentration is increased and with the presence of the kinetic isotope effect on replacement of H_2 by D_2.

Thus the results of the study of the influence of hydrogen on the C_5-DHC reaction of alkanes can be interpreted on the basis of the multistage scheme considered and the equation presented above. Other possible C_5-DHC mechanisms proposed in the literature are in poorer agreement with experimental data. However, we may note that, when the C_5-DHC reaction is carried out under other conditions (for example, in the presence of highly dispersed catalysts at higher temperatures or in the presence of a deficiency of hydrogen), the mechanism as a whole can change. On the basis of the above scheme, it is easy to set up a multistage scheme for the skeletal isomerisation of alkanes via the C_5-cyclic mechanism and to derive a kinetic equation which, as for the C_5-DHC reaction of alkanes, makes it possible to interpret the appearance of maxima on the curves relating the yields of skeletal isomers to the partial pressure of hydrogen.

It was shown previously[124,125] that the activation energy for the C_5-DHC of alkanes on platinised charcoal is almost independent of the structure of the hydrocarbon and amounts to 83.7 kJ mol^{-1} (the data were obtained under the conditions

of a zero-order reaction). For alkylbenzenes, this quantity increases by 31.4 kJ mol^{-1}.

Negative formal reaction orders with respect to hydrogen as well as apparent activation energies have been found for the isomerisation of n-butane and isobutane on platinum black[126] (the activation energies are respectively 100 and 121 kJ mol^{-1}).

Few kinetic studies have been made on the isomerisation of alkanes; most of them[116-118,127-131] were carried out in the presence of industrial platinum/alumina bifunctional reforming catalysts. In the analysis of the kinetics, the slow stage is usually assumed to be that involving the isomerisation on the acid centres of the catalyst; the kinetic equations are characterised by negative or zero reaction orders with respect to hydrogen. Account has also been taken[128] of the influence of the poisoning of the catalyst by coke on the rate of isomerisation.

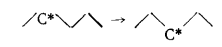
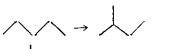
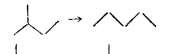
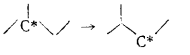
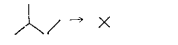
In a study of the isomerisation of pentane in the presence of a platinum/alumina catalyst by the flow-circulation method, the reverse kinetic isotope effect was observed[130,131] on replacement of hydrogen by deuterium. The rate of reaction was characterised by a positive order with respect to hydrogen, equal to 0.5, and the rate of exchange of deuterium in pentane under these conditions was higher than the rate of isomerisation. The above facts suggested that hydrogen is involved in the slow stage of the reaction—the isomerisation of the adsorbed fragment on the acid centres of the catalyst.

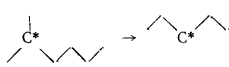
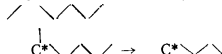
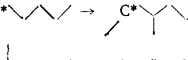
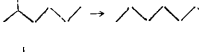
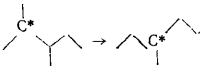
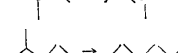
Interesting studies on the isomerisation reaction, particularly the C_5-DHC of alkanes in the presence of platinum/alumina catalysts under the conditions of monofunctional catalysis, have been carried out in recent years by Gault and co-workers[132]. We may note the fruitfulness of the approach by the authors, which combines kinetic studies with the employment of the method of labelled (^{13}C) molecules for reactions of the groups of C_5–C_7 alkanes in the presence of platinum catalysts with different degrees of dispersion. Since the change in the position of the ^{13}C label in the isomerisation products could always be predicted as a result of only one rearrangement (via the C_5-cyclic mechanism or the bond shift mechanism) of the adsorbed fragment on the surface, it was suggested that the rate-limiting stage is skeletal rearrangement on the catalyst surface, while the adsorption–desorption stages are fast. The Table presents the apparent activation energies and the formal reaction orders with respect to hydrogen according to the results of Garin and Gault[105]. For C_6 alkanes, it has only been stated that the orders of the isomerisation reaction with respect to hydrogen are negative[132].

According to the analysis by Sinfelt[133], a negative reaction order *b* with respect to hydrogen implies that the initial hydrocarbon is adsorbed dissociatively with abstraction of at least 2*b* hydrogen atoms. In order to account for the high negative orders of the pentane isomerisation reaction with respect to hydrogen (see Table), it is necessary to postulate extensive dehydrogenation of the initial hydrocarbon molecule, which appears unlikely under the conditions of an excess of hydrogen. On this basis, preference was given[105,134] to the so-called reaction mechanism in which the Frennet adsorption model[135,136] is used. The competative adsorption of hydrogen and the alkane on the same active centres of the catalyst is considered within the framework of this model, hydrogen occupying one such surface centre and the hydrocarbon a group (ensemble) of several centres.

It has been shown[105] that, in the dissociation of an alkane via the "bimolecular reaction" mechanism, the order of the reaction *b* with respect to hydrogen corresponds to the abstraction of only *b* hydrogen atoms; in addition, comparatively simple explanations have been found for the positive reaction order with respect to hydrogen in the isomerisation of C_7 alkanes and also for the characteristic features of the variation of the selectivity of the isomerisation reaction with the H_2 concentration in the system. Overall, the employment of the Frennet model for the interpretation of kinetic data appears to us extremely fruitful, but a quantitative test of the kinetic equations obtained on the basis of the "bimolecular reaction" is difficult because it requires the knowledge of the alkane adsorption isotherm in the presence of hydrogen, which is itself a fairly difficult experimental problem.

The activation energies (kJ mol^{-1}) and the kinetic orders with respect to hydrogen (*b*) of the isomerisation reactions of various C_5 and C_7 alkanes in the presence of a platinum/alumina catalyst (according to the data of Garin and Gault[105]).

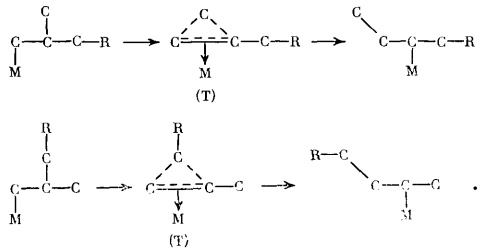
No.	Reaction	E_a	*b*
1		297.3±6.3	−3.4
2		231.5±6.3	−1.8
3		244.3±6.3	−2.3
4		189.7	−1.9
5		188.4	−1.65

No.	Reaction	*b*
6		0.9±0.2
7		1.8±0.2
8		0.2±0.2
9		0.8±0.1
10		1.4±0.1
11		0.7±0.1

Note. The molecular skeleton and the position of the ^{13}C label are indicated. Reactions (1), (6), (9) and (10) have the C_5-cyclic mechanism, while others proceed via the bond shift mechanism.

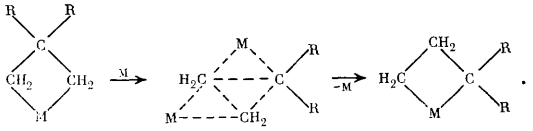
On the basis of kinetic data (see Table), it has been suggested[132] that isomerisation reactions involving the bond shift mechanism be divided into two groups: the "chain elongation" reaction (for example, the isomerisation of isopentane to pentane and conversely) and the "methyl shift" reaction. They have different activation energies and formal orders with respect to hydrogen and also exhibit variations,

characteristic of each group, of the relative rates of isomerisation via different pathways with the structure of the initial hydrocarbon for reactions of the homologues of C_5–C_7 alkanes (the so-called structural effect).[134,137,138]. It has been suggested that the mechanisms of these two isomerisation reactions are different. The characteristic features of the "chain elongation" reaction are best described by the Rooney mechanism:

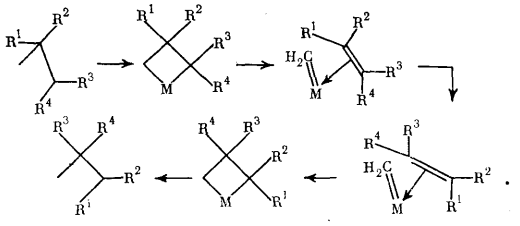


Thus, from an analysis of the stabilisation of the transition state (T), it proved possible[137] to explain the character of the variation of the relative contributions of the above reaction pathways in the isomerisation of alkanes with different alkyl substituents.

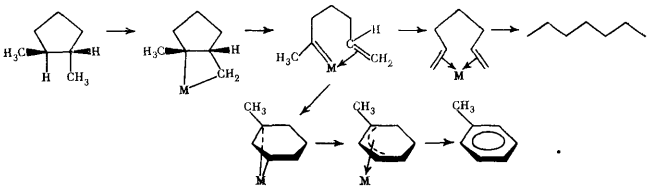
In order to account for the characteristic features of the "methyl (alkyl) shift" reaction, two new mechanisms were proposed, since the bond shift isomerisation mechanisms considered previously did not explain the entre set of data obtained[138,139]. In an earlier study[105] it was postulated that the isomerisation proceeds via the formation of intermediate methylcyclobutane species and a quasicyclopropane intermediate, arranged in a virtually flat position on the catalyst surface:



An alternative concept is in better agreement with the chemistry of coordination compounds and consists in the reversible dismutation of methylcyclobutane to a metallocarbene and a π-adsorbed olefin[138,139]:

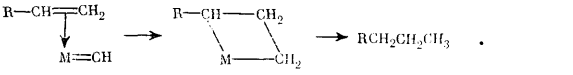


A characteristic feature of this mechanism is that its occurrence requires the free rotation of the olefin about the bond with the metal. The introduction of bulky alkyl substituents hinders the rotation; this made it possible to explain the differences between the rates of isomerisation of different labelled [^{13}C] heptanes. It has been suggested that the cyclopentane ring can also undergo hydrogenolysis via an analogous mechanism[139]—one of the variants of the partly selective mechanism of hydrogenolysis:



This mechanism explained certain features of the hydrogenolysis of 1,2-dimethylcyclopentane and also the C_5- and C_6-DHC of labelled [^{13}C] heptanes[138,139].

Although the methylcyclobutane mechanism provides a satisfactory explanation of the fundamental features of the hydrogenolysis of alkanes, it was recently criticised from an unexpected direction. Clarke, Rooney, and co-workers[86,140] observed the conversion of alkanes into higher homologues on films of different metals (W, Pd, Pt, Rh, Ru, Nb, Mo) and obtained evidence for the following mechanism:



(it is the reverse of the mechanism of the hydrogenolysis of alkanes examined above). It was found that platinum is relatively inactive in the homologue generating reaction although it is one of the active metals in the isomerisation of hydrocarbons via the bond shift mechanism. On the other hand, tungsten is relatively inactive in isomerisation and is the most active among the metals investigated in the formation of higher homologues of alkanes. This shows that the mechanism of isomerisation via the reversible dismutation of a metallocarbene and an olefin is not important in the presence of platinum catalysts. It is believed[86,140] that the principal mechanism of the bond shift isomerisation in the presence of platinum is that of Rooney, i.e. the reaction proceeds via the formation of adsorbed species analogous to non-classical carbonium ions. A mechanism involving α,ε-diadsorbed species has also been proposed for C_5-DHC.

The mechanisms of the isomerisation of alkanes in the presence of other Group VIII metals have been investigated significantly less thoroughly than the mechanisms of reactions in the presence of platinum catalysts. In many instances the study of the characteristic features of the isomerisation suggested new isomerisation mechanisms. Thus a concerted mechanism via the formation of a quasi-cyclobutane intermediate (the 1–3-ethyl shift mechanism) has been postulated for the isomerisation of methylpentanes in the presence of the Ir/Al_2O_3 catalyst[141].

V. THE INFLUENCE OF THE STRUCTURE OF METALLIC CATALYSTS ON THE MECHANISMS OF THE DEHYDROCYCLISATION AND SKELETAL ISOMERISATION REACTIONS OF ALKANES

The structure of metallic catalysts (the concentration and degree of dispersion of the metal, the orientation of the crystal faces, and the nature of the carrier) influence significantly the character of the processes occurring. Thus in a series of studies[142–146] of the kinetics of various reactions in the presence of metal single crystals with simultaneous determination of the structure and composition of the surface by low energy electron diffraction and Auger spectroscopy, it was shown that the rates and selectivities of many reactions depend on the structure of the platinum single crystal face. For example, the stepped faces are the most active in the dehydrocyclisation of n-heptane to toluene. The important

role of the formation of a new phase (a carbon-containing layer) on the catalyst surface in the reaction was noted. The ordered carbon-containing layer formed on the stepped faces has little influence on the dehydrocyclisation of n-heptane. On smooth faces a disordered layer is formed, which is one of the causes of the rapid loss of activity by the catalyst[146].

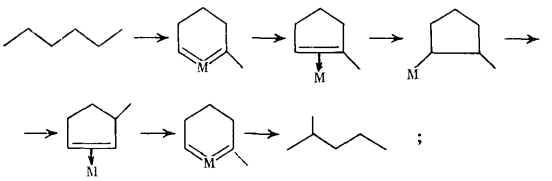
The question of the dependence of the selectivity of the hydrogenolysis of methylcyclopentane and the isomerisation of hexanes on the degree of dispersion of the catalyst was discussed vigorously in earlier studies. Whereas the influence of the degree of dispersion of the deposited metal on the selectivity of these reactions has been demonstrated in a number of studies[45,62,147,148], the data of Dautzenberg and Platteeuw[14,149] indicate the independence of the selectivity of the reactions on the size of the platinum crystals (when the latter is varied in the range 15–80 Å). Without dwelling in detail on this controversy, we should like to draw attention to the conclusion[150] that the ratios of the numbers of different centres are determined by the size of the crystallites in the early stages of the reduction of the catalyst. This conclusion is confirmed by the fact that sintering of identically reduced catalysts does not alter the selectivity of the hydrogenolysis of methylcyclopentane with increase in the size of the platinum crystallites[103]. From this conclusion, certain differences between the results obtained by the two groups of investigators mentioned above can be explained by the significant difference between the reduction temperatures of the catalysts which they employed. On the whole, one may regard it as established that the non-selective C_5-cyclic mechanism of isomerisation and hydrogenolysis predominates in the presence of highly-dispersed platinum catalysts reduced under mild conditions. In the presence of a catalyst with a low degree of dispersion, the hydrogenolysis of the C_5 ring becomes selective and the isomerisation of alkanes takes place to a significant extent via the bond shift mechanism[102,103,151,152].

More detailed studies in the presence of a series of platinum/alumina catalysts with different degrees of dispersion showed[153–155] that the overall rates of isomerisation of hexanes and of the hydrogenolysis of methylcyclopentane are independent of the degree of dispersion, i.e. these reactions are structure-insensitive as regards rate, but are structure-sensitive as regards selectivity. The following features were discovered. In the reaction 2-methylpentane → 3-methylpentane the relative contributions of the C_5-cyclic and bond shift mechanisms remain constant over a fairly wide range of crystallite dimensions. However, the character of the hydrogenolysis of the C_5 ring varies continuously from selective to non-selective with decrease in the size of the crystallites.

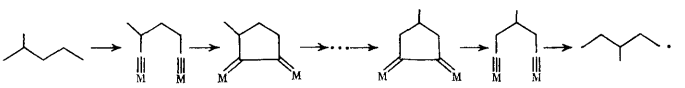
As the size of the crystallites falls below 20 Å, sharp changes take place in the character of the reaction. In the presence of such catalysts, the selectivity of the isomerisation of neopentane with respect to its hydrogenolysis diminishes significantly[156]. The mechanism of the hydrogenolysis of the five-membered ring becomes fully non-selective[153–155]. On very small particles (less than 10 Å), the isomerisation of hexanes via the bond shift mechanism hardly occurs. Somewhat different data were obtained in a study[157] where the sensitivity of the isomerisation reaction of n-hexane to structure is attributed solely to particles with dimensions less than 20 Å, while on larger platinum crystallites the reaction is structure-insensitive.

The characteristic features of the influence of the size of crystallites on the mechanism of the hydrogenolysis of alkylcyclopentanes justified the following schemes for isomerisation via the C_5-cyclic mechanism with participation on metallocarbenes and metallodicarbynes as intermediates[132,155]:

(1) the non-selective mechanism



(2) the selective mechanism



The additional hypothesis that both mechanisms involve a common intermediate, namely an α-adsorbed olefin which is then converted into a metallocarbene or a metallodicarbyne, has been put forward[138]. Although this hypothesis explained the proportions of the products of the C_5-DHC of 3-methylhexane, it made it difficult to interpret data[100] showing the equality of the rates of cyclisation of 2,2,4-tri-, 2,2,2-tri-, and 2,2,4,4-tetra-methylpentanes in the presence of platinum.

We may note that neither the metallocarbene nor the metallodicarbyne mechanism of the hydrogenolysis of alkylcyclopentanes explains the hydrogenolysis of the quaternary-secondary C–C bonds in the cyclopentane ring. However, it has been shown recently[158] that the quaternary-secondary C–C bond in *gem*-dimethylcyclopentane can be cleaved in the presence of the Pt/C catalyst.

The operation of the selective mechanism of the hydrogenolysis of cyclopentanes (and hence of the isomerisation of alkanes) in accordance with the schemes examined above, requires a larger ensemble of platinum atoms than for the non-selective mechanism and the relative contributions of these two mechanisms must therefore be influenced by the geometrical factor. If it is supposed that only the edge atoms of the platinum crystallites promote the formation of reactive species, then the critical size of the crystallite required for the transition from one mechanism to another must be approximately 25 Å. This is the minimum dimension for a crystallite which has two neighbouring edge (but not corner) platinum atoms[132].

The decrease of the selectivity of the isomerisation of neopentane in the presence of highly dispersed catalysts is attributed analogously[156] to the transition from the many-centre bond shift mechanism (via the formation of 1,1,3-adsorbed species) to the one-centre isomerisation mechanism (the Rooney mechanism), which, however, is characterised by a lower rate.

It has been suggested that the relative contributions of the C_5-cyclic and bond shift isomerisation mechanisms depend primarily on electronic factors[155], which may be significant for crystallites whose size is less than 10–15 Å[159] (the second critical size of crystallites). Thus the two critical dimensions of crystallites in the reactions involving the isomerisation of alkanes and the hydrogenolysis of cyclopentanes are a consequence of the operation of geometrical and electronic factors[132].

Certain additional evidence for the influence of the electronic and geometrical factors on the isomerisation mechanism can be obtained from a comparison[132] of the catalytic effects of different metals with the same degrees of dispersion (particle size 80 Å). Thus the isomerisation in the presence of the Ir/Al_2O_3 catalyst takes place only via the selective C_5-cyclic mechanism[82], in the presence of the Pd/Al_2O_3 catalyst the reaction involves the non-selective C_5-cyclic mechanism with a small contribution by the bond shift mechanism[160], while in the presence of the Pt/Al_2O_3

catalyst the reaction proceeds mainly via the bond shift mechanism with participation of both C_5-cyclic isomerisation mechanisms. However, one should note that the comparison of the catalytic activities of the above catalysts cannot be regarded as sufficiently rigorous: the published data for the reaction mechanisms refer to different temperatures (the reaction temperature can influence the process selectivity).

Certain features of the structure sensitivity of the alkane isomerisation reaction suggested[154] the possibility of the migration of the reactive adsorbed species from the adsorption–desorption centres to the reaction centres and conversely. Thus the overall isomerisation mechanism includes the stages involving the adsorption of an alkane molecule from the gas phase on a crystal face of platinum with formation of a weakly adsorbed species, surface migration from the adsorption centre to the reaction centre located on the surface of the metallic particle, the formation of highly dehydrogenated species on the reacton centre, their skeletal rearrangement and subsequent rehydrogenation, and surface diffusion and desorption of the reaction products. Analysis of the relative rates of different stages in the above mechanisms as well as the number of active centres led to a classification of the reactions in terms of their structure sensitivity. However, within the framework of the above study[154], one cannot assume that the surface diffusion of carbon-containing species has been proved. On the other hand, in the presence of an excess of hydrogen the formation of highly dehydrogenated species of the type of metallocarbenes and metallodicarbynes appears unlikely. This confirms indirectly the results of a study[140] in which it was shown that platinum is relatively inactive in the formation of carbene species.

One must not fail to mention, at least briefly, yet another promising method for the elucidation of the mechanisms of catalytic reactions in the presence of platinum catalysts—by the study of the reactions of hydrocarbons in the presence of alloys of platinum with Group IB metals, for example, gold or copper (the latter are virtually inactive in the reactions considered). A change in the platinum concentration in the alloy can alter the size of the platinum ensembles and also their electronic properties. It is difficult to separate the geometrical and electronic factors (it is probably actually impossible to do this); however, in many studies only the influence of the geometrical factor has been considered as the alloy composition was varied.

The study of the reactions of hydrocarbons in the presence of deposited Pt–Au and Pt–Cu alloys[161–165] permitted the following conclusions. At a high platinum concentration in the alloy the reactions proceed mainly via many-centre mechanisms: the selective C_5-cyclic mechanism of isomerisation and C_5 ring closure and opening and the bond shift mechanism involving the intermediate formation of, for example, 1,1,3-adsorbed species. A decrease of the concentration of platinum in the alloy suppresses the many-centre isomerisation mechanisms as a consequence of which the reaction proceeds via the non-selective C_5-cyclic mechanism with a small contribution to the isomerisation by the one-centre bond shift mechanism (the Rooney mechanism). The nature of the reactions of hydrocarbons in the presence of alloys with a low platinum content is analogous to the characteristic features of the reactions in the presence of highly dispersed platinum catalysts. On highly dilute alloys (with a platinum concentration of several per cent), the isomerisation of alkanes proceeds only via the one-centre bond shift mechanism. Certain characteristics of the reactions in the presence of platinum alloys have been explained[165] by the influence of the nature of the carrier and heat treatment temperature on the degree of carbidisation of the alloy surface or on the topography of the surface. It has been suggested in all cases that the isomerisation via the many-centre mechanisms is faster than via the one-centre mechanisms.

In many instances there are discrepancies between the experimental data obtained by different groups of investigators[164,165]. The characteristic features of the catalytic activity of alloys probably require further study. The importance of the investigation of reactions on alloys is also confirmed by the fact that the possibility of the C_5-DHC of alkanes in the presence of rhodium catalysts was demonstrated for the first time precisely in the presence of rhodium–copper alloys[56]. A more detailed description of the characteristic features of the reactions in the presence of alloys would be outside the framework of the present review; some additional information can be found in other reviews[166–170].

* * *

Significant progress has been achieved in recent years in the understanding of the mechanisms of catalytic reactions of hydrocarbons on metals. These advances are associated with the application of model compounds in catalysis, in particular those labelled with ^{13}C and ^{14}C, in combination with careful kinetic investigations. An important contribution to the understanding of the mechanisms of the above reactions in the presence of metal-containing catalysts undoubtedly came from a series of studies involving the participation of hydrogen in these reactions (see Section IV). A series of investigations of the influence of the structure of metallic catalysts on the mechanisms of different reactions is of fundamental importance (Section V).

However, in most cases the available information about the transition state in the key stages of the reactions of hydrocarbons is clearly inadequate and the structure of the catalytic centres and the relative positions of the orbitals of the surface metal atoms and the orbitals of the reacting atoms of the adsorbed molecules have not been elucidated. An important problem in the study of mechanism involves the investigation of the effect arising when the surface of the metal is acted upon by the reactants and products of the reaction in the course of its occurrence.

Studies carried out with the aid of a set of new physical methods whereby one can obtain information about the geometry of the adsorbed molecular fragments and the structure of the most active sections of the surface of the metal and the elucidation of the nature of the cluster and ligand effects in monometallic and polymetallic systems are at present the most important trends in the establishment of the mechanisms of the action of metal-containing catalysts.

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