U.D.C. 541.63 : 542.97

Stereochemistry of Certain Catalytic Reactions of Cyclic Hydrocarbons in the Presence of Group VIII Noble Metals

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The mechanisms of certain catalytic reactions in the presence of solid catalysts—mainly Group VIII noble metals—are discussed in the review. Attention has been concentrated on the stereochemistry of the reactions. It has been shown that the modern conformational hypotheses may be successfully employed to investigate the detailed mechanisms of a number of heterogeneous-catalytic reactions, in particular certain stereochemical reactions of cyclic hydrocarbons. The most widely adopted mechanisms of the hydrogenation of dialkylcyclo-olefins and also di- and poly-alkylbenzenes have been examined and discussed. Both types of reactions are genetically related and the proportions of the stereoisomers obtained serve in many cases as a definite criterion for the selection of a particular reaction mechanism. The configurational isomerisation of di- and poly-cycloalkanes—a reaction involving direct interconversion of the isomers—has been examined in detail. The direct involvement of hydrogen in this reaction, which at first sight appears to be unimolecular but is in fact bimolecular, has been demonstrated.
The bibliography includes 125 references.

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I. INTRODUCTION

This review is devoted to the mechanisms of certain catalytic reactions where stereochemical-factors play a very significant role. By combining and mutually supplementing the usual catalytic and stereochemical concepts, in particular those of conformational analysis, hypotheses of great promise for the understanding of the detailed mechanisms of heterogeneous catalytic reactions are obtained. This view is confirmed by certain studies quoted in a number of reviews[1-8], where the above approach is employed in some form.

The general concept of reaction mechanism is nowadays understood to involve collisions of reacting species, redistribution of electron density in the species, and other elementary stages, taking into account in each individual step in as great detail as possible the stereochemistry of the conversion of the reactants into products. This presupposes the knowledge of the so called activated complex or transition state, which entails not only the enumeration of the molecules or species involved in it but also geometrical factors (interatomic distances and angles). Therefore the problem of determining the mechanism of a particular reaction has become unusually complex. Bond and Wells[4] believe that the mechanism has been elucidated when sufficient information has been obtained on the following three questions: (a) the nature of all the species participating in the reaction; (b) the qualitative types of their interactions making a major contribution to the overall reaction; (c) the quantitative aspects of these interactions—relative rather than absolute. This view is probably correct.

Whereas in homogeneous reactions this problem is frequently simplified by the fact that the mechanisms of many such reactions are identical and their transition states are very similar, in heterogeneous catalytic reactions there arises a new specific factor, which is very difficult to take into account—the compound adsorbed on the surface. Indeed, the principal difficulty in the interpretation of the mechanism of a heterogeneous catalytic reaction consists in the fact that the surface itself is actively involved in the reaction and is essentially one of the reactants. The problem is complicated by the fact that it is virtually impossible to determine the concentration of the active surface at the instant of the reaction step. Nevertheless the information about the geometry of the distribution of the surface catalyst atoms, i.e. about the type of crystal lattice and its defects and also about the steric distribution of the reactants and products, is all the more important. The sum total of such knowledge may promote the understanding of the stereochemistry of the complex adsorbed on the surface, i.e. may provide certain more detailed hypotheses concerning the mechanism of heterogeneous catalytic reaction.

In the light of the considerations set out above, certain stereochemical reactions of cyclic hydrocarbons are discussed in this review. The first part reviews the studies on the hydrogenation of di- and poly-alkylcyclo-olefins, and the second deals with the stereochemistry of the hydrogenation of the benzene ring with two or three alkyl groups. The hydrogenation of dialkylcyclo-olefins and also di- and poly-alkylbenzenes results in the formation of stereoisomeric (in relation to the plane of the ring) cycloalkanes. The proportions of the steric isomers depend on the structures of the starting materials and on the hydrogenation conditions (pressure, temperature, catalyst, medium, etc.) and may serve as a definite criterion for the validity of a particular hypothetical reaction mechanism. Finally the last section is devoted to the direct interconversion of stereoisomeric di- and poly-alkylcycloalkanes. This reaction, which we have called configurational isomerisation, is, by virtue of its relative simplicity, a good model for the elucidation of the details of the structure of the activated complex adsorbed on the catalyst surface.

In this review, particular attention has been devoted to configurational isomerism also because there is virtually no review in the literature where it is discussed in any detail, although we believe that, because of a number of important characteristics discussed below, it merits special consideration.

II. HYDROGENATION OF CYCLO-OLEFINS

There is a fairly large literature on the hydrogenation of cyclo-olefins in the presence of Group VIII metals. The fundamental finding is that the hydrogenation of dialkylcyclo-olefins in the presence of heterogeneous catalysts leads not only to *cis*- but also to *trans*-isomers. Probably *cis*- addition of hydrogen is accompanied by *trans*-hydrogenation over various catalysts under different conditions.

The relative amounts of the *cis*- and *trans*-isomers depend on the structure and positions (relative to one another and the double bond) of the alkyl groups, on the nature of the catalyst, on hydrogen pressure, and, if the hydrogenation is carried out in a liquid phase, on the solvent and the pH. The formation of *trans*-products under these conditions is very important for the understanding of the hydrogenation mechanism. This reaction is one of the most typical examples of the use of stereochemistry for a more detailed investigation of the mechanism of heterogeneous catalytic reactions.

Before considering specific studies on the hydrogenation of substituted cyclo-olefins and the conclusions which follow from them, it is necessary to consider briefly various types of steric forms of substituted five- or six-membered cycloalkanes in order to comprehend better the possibilities in their interconversions and the nature of the energy barriers overcome in these processes.

Classical stereochemistry, which deals with the positions of atoms in space, takes into account only interatomic distances and valence angles. This already made it possible to understand many characteristics of the behaviour of cyclic molecules. However, a new enormous advance in this respect was made in modern stereochemistry after the introduction of conformational concepts.

The modern conformational concepts are based on the fact that the steric relations between neutral atoms not linked directly to one another are not determined by volumes depending on atomic radii but on effective or van der Waal's volumes. These volumes, which in recent years have come to be called conformational volumes, are much larger than the atomic volumes (for example the atomic radius of the hydrogen atom is 0.30 Å and its conformational radius is 1.2 Å) and these in fact determine the relative positions in space of the individual components of molecules, provided that their interrelations are not influenced by some other more powerful interactions. In particular, the steric distribution of atoms in alkane and cycloalkane molecules is largely determined by the conformational volumes of neighbouring, but not linked directly, hydrogen atoms. When these atoms approach one another to distances slightly exceeding the sum of their van der Waals radii, repulsion forces arise between them. When the distance between non-bonded atoms are equal to this sum, the repulsion forces increase sharply. Further mutual approach or overlapping of the van der Waals radii may lead to the instability or even the breakdown of the molecule. Under the influence of these forces, all the hydrogen atoms in the molecule tend to take up positions as far away from one another as possible.

In any organic molecule, except the simplest, there is a possibility of a multiplicity of relative positions of all its components (atoms or groups) with different distances between non-bonded atoms. If there is a possibility of interconversion of such distributions merely as a result of rotation about particular bonds without their dissociation, the states corresponding to each distribution are called conformations (conformations of molecules or groups).

Each conformation is characterised by its own set of distances between non-bonded atoms and consequently by its own sum of non-bonding interactions (repulsion of non-bonded atoms). Thus different conformations of any organic molecule are usually energetically non-equivalent even if none of the bond lengths and valence angles deviate from the normal values.

The molecule can pass from one conformation to another by internal rotation (for reasons which will become clear subsequently, this rotation can no longer be referred to as free). Certain conformations have an energy minimum in the sense that, whatever the direction of the internal rotation, the sum of the energies of non-bonding interactions increases, i.e. the potential energy of the molecule as a whole also increases. All conformations of this type have a certain stability, but the energy minima in different conformations of a single molecule may have unequal depths; for this reason, their stabilities also differ. The most favourable of these conformations of a molecule is frequently referred to as the usual conformation or simply as the conformation of the given molecule. On the other hand, other conformations are distinguished by energy maxima, i.e. internal rotation can only decrease their energy. Naturally, such conformations are unstable. Since the transitions from one favourable conformation to another by internal rotation necessarily proceed via conformations with maximum energies, such unfavourable conformations are frequently called rotational barriers. Thus one may say that the ease of transition from one favourable conformation to another is determined by the height of the barrier separating them. On rotation of one part of the molecule relative to another about a bond, a series of rotational barriers are overcome in succession. Therefore it would be incorrect to call such rotations free.

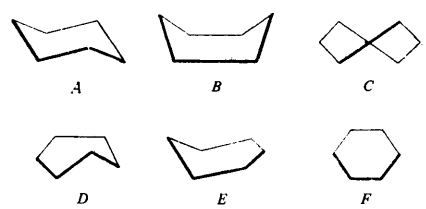


Figure 1. Conformations of cyclohexane: *A*) chair form; *B*) boat form; *C*) twist form; *D*) half-chair form; *E*) envelope form; *F*) planar form.

All that has been said above must be taken into account in one way or another in an experimental study and discussion of the stereochemistry of catalytic reactions. In particular, according to the concepts of classical stereochemistry, cyclohexane can exist in two states free from angular strain—the chair and boat forms (Figs. 1*A* and 1*B*). However, Raman[9] and infrared[10] spectra, electron diffraction[11], and other physical methods have shown that in fact it exists in virtually only one state. This finding was explained by conformational concepts.

It was found that cyclohexane can exist in six conformations (Figs. 1*A*–1*F*), which are energetically non-equivalent. In form *F* the conformational strain is greatest owing to the particular proximity of all six adjacent hydrogen atoms on either side of the ring. In addition there is

in this case also a considerable Baeyer strain. Hydrogen atoms assume the most favourable positions in form *A* and it is least strained. It is followed, as regards the amount of strain, by form *C* and then form *B*. All these factors can be traced on special Stuart–Briegleb models taking into account the conformational volumes of the atoms. The difference between the energies of forms *A* and *C* is 5–6 kcal mole^{-1} which is sufficiently large for the concentration of form *C* in real cyclohexane to be much less than 1%. Therefore cyclohexane normally consists of molecules in the chair form. The energy relations of the most interesting transitions between the three conformations of cyclohexane are presented in Fig. 2.

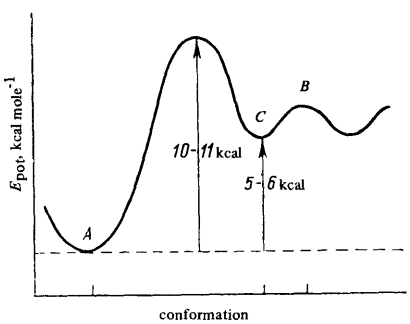


Figure 2. Potential curves for the interconversions of cyclohexane conformers (*A*, *B*, and *C*)—see Fig. 1.

When one of the hydrogen atoms in the cyclohexane molecule is replaced by a CH_3 group, the latter can be either in an equatorial (*e*) or an axial (*a*) position. However, in the *a*-form the non-bonding interactions between the methyl group and the hydrogen atoms in the 3- and 5-positions (the so called 1,3-interactions) prove to be fairly appreciable. On the other hand, in the *e*-form the CH_3 group is relatively remote from the ring and such interactions do not occur. The difference is 1.6–1.8 kcal mole^{-1}.[12] Thus methylcyclohexane is predominantly in the *e*-form. Thermodynamic calculations[12] and also electron diffraction data[11] confirm this conclusion. It has been shown experimentally[13] that at 25°C equilibrium is rapidly established between the *e*- and *a*-forms in which about 95% of the molecules are in the *e*-form and only 5% in the *a*-form. This does not of course mean that methylcyclohexane must react only in the *e*-form, since the energy barrier between the two conformations is lower than the activation energy for the majority of reactions.

When two hydrogen atoms in the cyclohexane molecule are replaced by substituents, for example in dimethylcyclohexane, a new type of stereoisomerism arises—the *cis–trans* isomerism of di- and poly-substituted cycloalkanes. According to conformational analysis, *cis*-1,2-, *trans*-1,3-, and *cis*-1,4-dimethyl-cyclohexanes each have one axial and one equatorial group. Only one conformation is possible for them, since ring inversion yields an identical structure, i.e. $ea \rightleftharpoons ae$. On the other hand, *trans*-1,2-, *cis*-1,3-, and *trans*-1,4-dimethylcyclohexanes might each consist of two forms—*ee* and *aa*. However, the powerful non-bonding 1,3-interaction of two axial CH_3 groups in dimethylcyclohexane and hydrogen atoms gives rise to an additional strain in the molecule. It is so great that the concentration of the diaxial form in the equilibrium mixture proved to be negligible.

It must be specially emphasised that conformational isomers, for example the diequatorial and diaxial forms of *trans*-1,2-dimethylcyclohexane, can be converted into one another as a result of rotation about single C–C bonds. This is a usual case of rotational isomerism and therefore on conversion of one chair-form into another the configuration of dialkylcyclohexane does not change. On the other hand, *cis*- and *trans*-dialkylcycloalkanes are configurational isomers, i.e. they differ by the steric distribution of groups about one of the asymmetric carbon atoms. Consequently the interconversion of the *cis*- and *trans*-isomers requires a rearrangement, i.e. a "jump" by the substituents at this asymmetric carbon atom from one position to another, which necessarily involves the dissociation of the old and the formation of a new bond and consequently a considerable energy expenditure.

Many of the points discussed above refer to a greater or lesser degree also to cyclopentane hydrocarbons. The stereochemistry of this class of hydrocarbons has now been investigated in fair detail.

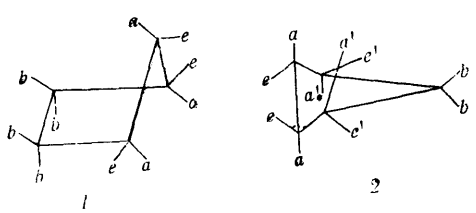


Figure 3. Conformations of cyclopentane: *1*) envelope form; *2*) half-chair form; (*a* and *a'*—axial and quasi-axial bonds respectively; *e* and *e'*—equatorial and quasi-equatorial bonds; *b*—bisectional bonds).

Experimental measurements of the entropy of gaseous cyclopentane[14,15] and calculated data[12] show that the cyclopentane ring is not coplanar. According to conformational considerations analogous to those for cyclohexane, the planar conformation of cyclopentane is highly strained. Therefore the ring bends in space owing to the internal strain and some distortion of the valence angles. In this process two conformations are produced: the envelope and half-chair forms (Fig. 3), similar to the corresponding conformations of cyclohexane. Their Baeyer strain is greater than in the planar form but this is compensated by an energy gain owing to the decrease of the conformational strain. The envelope form is slightly more favourable than the half-chair form. As in cyclohexane, the side bonds in cyclopentane are not identical. In the envelope form there are equatorial (*e*) and axial (*a*) bonds (Fig. 3), fully analogous to the corresponding positions in cyclohexane. In the half-chair form there exist also quasiequatorial (*e'*) and quasiaxial (*a'*) bonds with slightly different directions relative to the "plane of the ring" compared with the *e* and *a* bonds. In addition in both forms there exists also a special bisectional (*b*) bond position which is energetically intermediate between the *e*- and *a*-bonds. The energy differences between the *e*- and *a*-positions in cyclopentane are smaller than in cyclohexane: for the methyl group, the energy difference is 0.75–0.9 kcal mole^{-1}.[16–18]

In cyclopentane the site where the ring atom is displaced from the plane is not fixed; the system undergoes simultaneously vibrations about the most stable position and pseudohomogeneous rotation in which the site of the bend rotates about the ring.

Like cyclohexane hydrocarbons, di- and poly-alkylcyclopentanes exist in the form of *cis*- and *trans*-isomers. *Trans*-1,2-dimethylcyclopentane is thermodynamically more stable, like *trans*-1,2-dimethylcyclohexane. For the same reason, *cis*-1,3-dimethylcyclopentane is more stable than the *trans*-isomer.

Proceeding now to the discussion of specific studies on catalytic hydrogenation, account must be taken of the characteristics of the steric structures of the starting materials and the final products. In many cases this approach leads to new possibilities for the elucidation of reaction mechanisms.

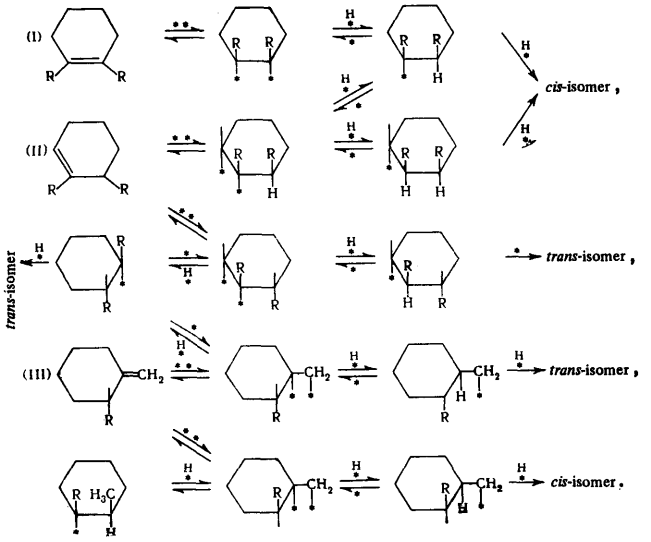


Figure 4. Mechanism of the hydrogenation of dialkylcyclo-olefins according to Siegel and Smith[20] (*—adsorption centre).

In a series of studies of Siegel and coworkers[2,7,19-22] and also in those of Burwell[1,23,24] and Sauvage and coworkers[25,26] certain definite generalisations have been made and certain considerations have been put forward concerning the mechanism of the hydrogenation of disubstituted cyclo-olefins in the presence of metal catalysts. However, one must not overestimate the information obtained in these studies, as there exist processes (for example the migration of the double bond in the ring) which must be taken into account for the concepts about the reaction mechanism to be adequately rigorous. For example, it is known that on a platinum catalyst there are differences in the rates and stereoselectivity of the hydrogenation of 1,2-dimethylcyclohexene and its 2,3-isomer. The structure of the first gives rise to its adsorption in the form of a π-complex or a σ-1,2-diadsorbed state, in which both CH_3 groups assume the *cis*-configuration on hydrogenation. On the other hand, in 2,3-dimethylcyclohexene the two sides of the ring are not identical. Therefore, when a substituent in the 3-position is directed away from the surface of the catalyst in the adsorption process, σ-1,2-diadsorbed *cis*-2,3-dimethylcyclohexane is formed as an intermediate, which is then desorbed as the *cis*-form. On the other hand, when the CH_3 group in the 3-position is directed towards the surface in the adsorption process, *trans*-1,2-dimethylcyclohexane is formed. To account for the observations made in the hydrogenation of cyclo-olefins, Siegel and Smith[20] proposed the mechanism shown schematically in Fig. 4.

The mechanism takes into account two important factors: (a) the simultaneous hydrogenation and migration of the double bond in the ring and (b) the effect of hydrogen on the hydrogenation and the relative rates of formation of the *cis*- and *trans*-isomers of 1,2-dimethylcyclohexanes.

Indeed it has been shown experimentally[20] that an increase of hydrogen pressure at 25°C over the initial 1,2-dimethylcyclohexene in acetic acid results in an increase of the amount of the *cis*-isomers of 1,2-dimethylcyclohexane in the catalytic reaction mixture (82% at atmospheric pressure and 93.5% at 150 atm H_2; see also Fig. 5).

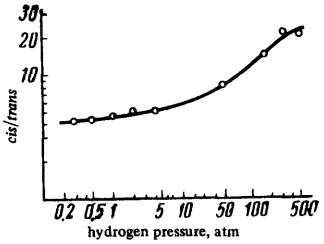
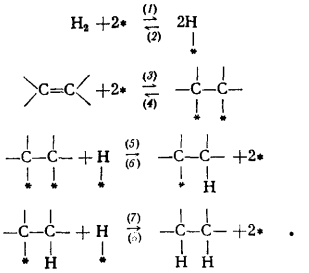


Figure 5. Variation of the stereoselectivity of the hydrogenation of 1,2-dimethylcyclohexene with hydrogen pressure[20].

According to Siegel and coworkers[7,20,21], the above mechanism of the hydrogenation of cyclo-olefins is consistent with the Horiuti–Polanyi mechanism[27] of the hydrogenation of unsaturated hydrocarbons:

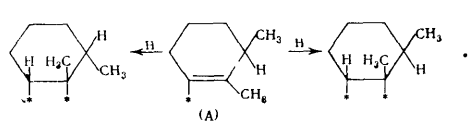


In their explanation of the increase of the concentration of *cis*-1,2-dimethylcyclohexane with increasing hydrogen pressure, the authors suggest that at sufficiently high hydrogen pressures the overall course of the reaction is determined by the formation of an $\alpha\beta$-diadsorbed state [reaction (3)]. On the other hand, at low hydrogen pressures the rate-limiting stage is the formation of the semi-hydrogenated state [reaction (5)]. According to Siegel[7],

examination of the individual stages shows that the rate of reaction (3) is independent of hydrogen pressure†, while the rates of reactions (5) and (7) are functions of the surface concentration of hydrogen and consequently its pressure. Then the rate of stage (7) depends in the first place on the concentration of the semihydrogenated state, which is itself a function of hydrogen pressure, and in the second place it depends directly on the concentration of adsorbed hydrogen. Therefore stage (7) should be accelerated by increasing hydrogen pressure to a greater extent than all others. The increase of the yield of *cis*-1,2-dimethylcyclohexane with increasing hydrogen pressure is probably associated with this factor (Fig. 5). It is specially noted that the structures of the species adsorbed on the catalyst and produced by reactions (3) and (5) are significantly different: the diadsorbed species largely retains the geometry of the olefin, while the semihydrogenated state has essentially a saturated structure.

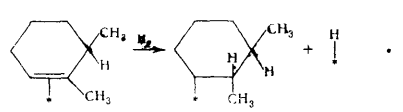
It is noteworthy that, although the mechanism proposed by Siegel and coworkers[20] (Fig. 4) is in fact consistent with the experimental data, it is by no means unique and has been criticised. Thus Bond and Wells[4] note that the reaction with such a mechanism should proceed towards the thermodynamically less stable cyclo-olefin—2,3-dimethylcyclohexene. Moreover, it appears unlikely that the latter would be desorbed to a sufficient extent.

Smith and Burwell[28] and also Sauvage and coworkers[25,26] proposed a different pathway for the formation of stereoisomeric cycloalkanes. These workers suggest that the intermediate stage in the hydrogenation may be the radical A disadsorbed by a dissociative mechanism, which then reacts with formation of both the *cis*- and *trans*-isomers:



(A)

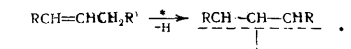
Yet another interpretation of the appearance of *trans*-isomers in the hydrogenation of cyclo-olefins is that of Gault et al.,[29] who suggest the possibility of a direct addition of hydrogen from the bulk phase to the π-complex adsorbed on the catalyst surface:



In this mechanism of hydrogenation the stage involving isomerisation to the corresponding 2,3-cyclo-olefins becomes obligatory for the formation of the *trans*-isomers from 1,2-dimethylcyclopentene and 1,2-dimethylcyclohexene. However, this as well as the preceding mechanism (in contrast to Siegel's work[7,20]) do not explain the experimental results obtained when the hydrogen pressure is altered (Fig. 5).

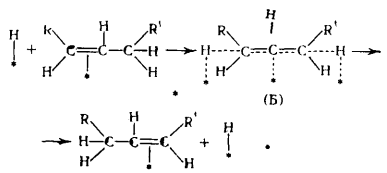
† Strictly speaking, the rate of reaction (3) depends on hydrogen pressure, since the number of free active centres on the catalyst surface on which the olefin may be adsorbed with formation of $\alpha\beta$-diadsorbed species depends on the amount of hydrogen in the system. When this factor is taken into account, Siegel's conclusion[7] becomes even more convincing, since at high pressures of H_2 an increase in its amount in the system lowers the rate of formation of $\alpha\beta$-diadsorbed species even more [reactions (3) and (6)].

It is also necessary to note that in recent years the concept of intermediate adsorbed compounds of the π-allyl type has been successfully employed to explain the mechanism of hydrogenation, deuterium exchange, and other reactions of hydrocarbons[30-40]. A π-allyl complex of one metal atom and three carbon atoms with a common electron cloud, produced as a result of the loss of one hydrogen atom by the initial olefin, is then considered as the intermediate surface compound:



It is postulated that the adsorbed π-allyl compound has a structure similar to those of the known π-allyl complexes of palladium[41]. In this connection the finding[20] that the migration of the double bond in the hydrogenation of substituted cyclo-olefins takes place only in the presence of hydrogen is of undoubted interest. This phenomenon has features in common with the analogous relation in the case of open-chain olefinic hydrocarbons[42-44] and also the relations which we discovered[45] in a study of the configurational isomerisation of di-alkylcycloalkanes, described in Section IV.

In a discussion of the stereochemistry of the hydrogenation of disubstituted cyclopentanes in the presence of many Group VIII noble metals, we proposed an associative version of double bond migration in olefins, in particular in cyclo-olefins, with participation of activated hydrogen. The double bond migrates via a transition state of the π-allyl type (B), which subsequently decomposes into the isomeric cyclo-olefin and adsorbed hydrogen:



(Б)

Within certain limits, this transition state (B) resembles the π-allyl complex described above, although in principle it differs from it by the fact that it is not a kinetically independent species and does not exist for any appreciable time on the catalyst surface. This last mechanism has the advantage, compared with the dissociative mechanism, in that it does not require the assumption of a complete dissociation of the C–H bond in the first reaction stage, which is known to require a considerable energy expenditure. Different versions of the adsorption of cyclo-olefins on the surface of various catalysts have been examined[46] and it has been concluded that the rate of migration of the double bond depends significantly on the geometry of the transition complex, determined by the nature of the catalyst.

Tables 1–3 present data on the stereoselectivity of the hydrogenation of various cyclo-olefinic hydrocarbons over platinum, palladium, and other Group VIII metal catalysts.

Examination of Table 1 reveals a considerable scope for the analysis and comparison of the data for the hydrogenation of cyclo-olefins of a very wide variety of structures and permits additional conclusions concerning the mechanism of this reaction. Table 1 shows that a definite relation obtains between the structures of the initial cyclo-olefins and the stereoselectivity of their hydrogenation on the same catalyst. For example, on PtO_2 the amount of the *cis*-isomer formed in the hydrogenation of the cyclo-olefins under consideration decreases in the sequence shown in Fig. 6.

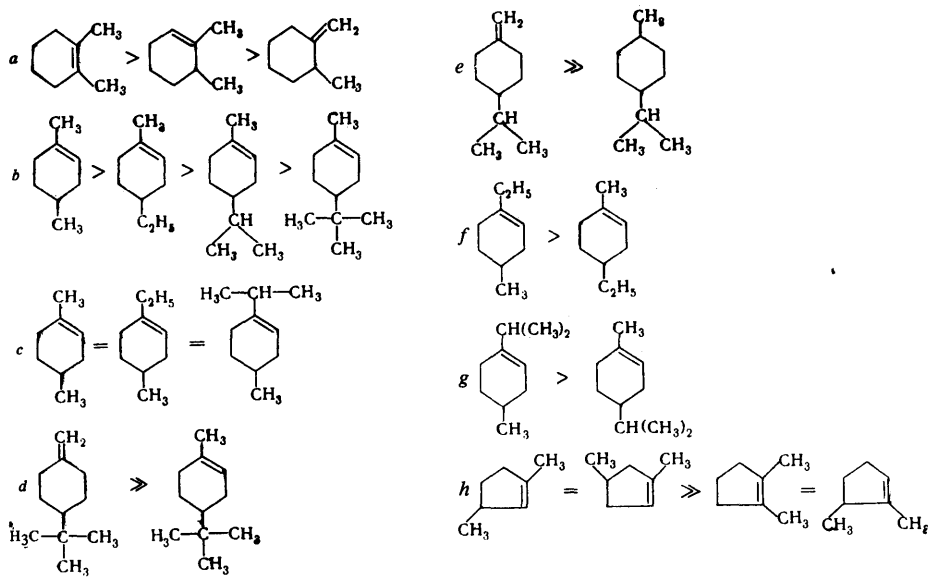


Figure 6. Relative decrease of the formation of the *cis*-isomer in hydrogenation over PtO_2.

Table 1. Stereoselectivity of the hydrogenation of certain dialkylcyclohexanes and alkylalkylenecyclohexanes in the presence of PtO_2 [19,25], Pd/C, [26] and Rh/C [47] at 25°C in acetic acid.

Initial hydrocarbon	*cis*-Isomer in hydrogenation products, %					
	1 atm. H_2, PtO_2		2.5 atm. H_2, PtO_2	1 atm. H_2, Pd/C		1 atm. H_2, Rh/C
	complete hydrogenation	partial hydrogenation		complete hydrogenation	partial hydrogenation	
1,2-Dimethylcyclohexene	82[a].83[b]	81[c]	78	—	25[d]	—
2,3-Dimethylcyclohexene	77[a].72[b], 77[c]	75[a]	70	—	23[d]	—
2-Methyl-1-methylenecyclohexane	70[a].70[c]	69[a]	64	—	28[d]	—
1,3-Dimethylcyclohexene	74	74	77	—	—	—
2,4-Dimethylcyclohexene	—	—	70	—	—	—
3-Methyl-1-methylenecyclohexane	—	—	68	—	—	—
1,4-Dimethylcyclohexene	57	57	55	28	31	61
4-Methyl-1-methylenecyclohexane	75	74	56	29	29	—
1-Ethyl-4-methylcyclohexene	58	58	—	27[e]	—	55
4-Ethyl-1-methylcyclohexene	48	47	—	24[e]	—	55
1,4-Diethylcyclohexene	—	49[e]	—	25[e]	—	54
4-Isopropyl-1-methylcyclohexene	43	43	—	26	21	52
1-Isopropyl-4-methylcyclohexene	58	50	—	21	—	54
4-Isopropyl-1-methylenecyclohexane	81	83	—	24	20	—
1-Isopropylidene-4-methylcyclohexane	36	—	—	18	—	—
4-t-Butyl-1-methylcyclohexene	37	36[f]	—	—	34[h]	—
4-t-Butyl-1-methylenecyclohexane	83	83[f].70[g]	—	—	33[h]	—

a) 1 atm H_2 (Ref. 20); b) 2 atm H_2 (Ref. 20); c) 0.5 atm H_2 (Ref. 20); d) Pd/Al_2O_3 (Ref. 20); e) Ref. 47; f) Ref. 21; g) Pt/Al_2O_3 (Ref. 21); h) Pd/Al_2O_3 (Ref. 21).

Table 2. Stereoselectivity of the hydrogenation of dialkylcyclopentenes and 2-methyl-1-methylenecyclopentanes on various Group VIII metals at 25°C and 1 atm of H_2 in n-hexane [46].

Initial cycloolefin	Catalyst	*cis*-Isomer in hydrogenation product, %	Initial cycloolefin	Catalyst	*cis*-Isomer in hydrogenation product, %
1,2-Dimethylcyclopentene	Pt/C	35[a]	1,2-Dimethylcyclopentene	Ir/C	90[a]
ditto	Pd/C	35[a]	2-Methyl-1-methylenecyclopentane	Pd/C	~25[b]
»	Rh/C	65[a]	2-Ethyl-1-methylcyclopentene	Rh/C	60[a]

a) The initial hydrocarbon contained 20% of the corresponding 2,3-dialkylcyclopentene.
b) In acetic acid solution [21].

For example row *a* shows the most favourable positions of the double bond in the six-membered cyclo-olefin for the *cis*-addition of hydrogen. On the other hand, the identical proportions of the *cis*- and *trans*-isomers obtained in the hydrogenation of 1,2- and 2,3-dimethylcyclopentenes (row *g*) suggest that, under the chosen conditions, the interconversion of these isomers is significantly faster than their hydrogenation. Row *c* shows that the length and bulk of the group located directly at the double bond do not in fact affect the stereoselectivity of the hydrogenation of cyclohexenes. This conclusion should probably still be regarded as preliminary, since the hydrocarbons investigated do not include 1-t-butyl-4-methylcyclohexene. The bulky substituent at the double bond can screen it to a certain extent, altering the stereoselectivity of the hydrogenation. At the same time examination of row *b* indicates a definite influence of the bulk of the substituent in the 4-position relative to the double bond: in the hydrogenation of 4-t-butyl-1-methylcyclohexene the amount of the *cis*-isomer formed is much less than in the case of 1,4-dimethylcyclohexene. Naturally, the above relations may be modified by altering the experimental conditions, in particular the catalyst, pressure, etc.

It follows from Table 1 that platinum and palladium catalysts exhibit different stereoselectivities in the hydrogenation of cyclohexenes. On a platinum catalyst in acetic acid solutions, the hydrogenation products are

mainly the *cis*-isomers, while on a palladium catalyst the products are the *trans*-isomers. According to the view of Gault et al.,[29] these facts can be accounted for by the different capacities of these metals for the formation of intermediate π-allyl complexes. While on palladium π-allyl complexes predominate, on platinum the reaction proceeds to a considerable degree also with participation of a σ-bonded intermediate compound.

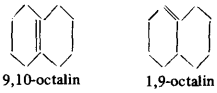
Table 3. Stereoselectivity of the hydrogenation of certain dialkylcyclopentenes in the presence of PtO_2 at 25°C in acetic acid[21] and under other conditions[48-50] (unless otherwise stated the figures refer to Ref. 21).

Initial hydrocarbon	*cis*-Isomer in hydrogenation product, %		Initial hydrocarbon	*cis*-Isomer in hydrogenation product, %	
	at 1 atm H_2	at 3 atm H_2		at 1 atm H_2	at 3 atm H_2
1,2-Dimethylcyclopentene	43; 49[a]	45	2-n-Butyl-1-methylcyclopentene	28[b,c]	—
2,3-Dimethylcyclopentene	44	41	1-Ethyl-2-n-propylcyclopentene	13[c,d]	—
2-Methyl-1-methylenecyclopentane	81	71	2-n-Butyl-1-ethylcyclopentene	14[c,d]	—
1,3-Dimethylcyclopentene	92	91	1,2-Dibutylcyclopentene	16[c,d]	—
2,4-Dimethylcyclopentene	91	91			

a) Pt black[48]. b) Pt/C (without solvent)[49]. c) The initial hydrocarbon contained 15–40% of the corresponding 2,3-dialkylcyclopentene. d) Pt/C (in alcohol)[50].

Table 1 shows that the stereospecificity of rhodium in the hydrogenation of cyclohexenes is very similar to that of platinum. The different stereoselectivities of various Group VIII noble metals in hydrogenation have been demonstrated by Bragin et al.,[46] for 1,2-dialkylcyclopentenes (Table 2). It was found (Fig. 7) that in a neutral n-hexane medium rhodium and particularly iridium catalysts form preferentially *cis*-dialkylcyclopentanes, while platinum and palladium catalysts give rise mainly to the *trans*-isomers.

Table 3 presents data on the hydrogenation of a number of dialkylcyclopentenes in the presence of various platinum catalysts. The specific effect of various catalysts (platinum, palladium, and rhodium) is also shown in the hydrogenation of octalins:



9,10-octalin 1,9-octalin

It might have been expected that 9,10-octalin would tend to undergo only *cis*-addition under the conditions of heterogeneous hydrogenation. However, as for 1,2-dimethylcyclopentene and 1,2-dimethylcyclohexene, the hydrogenation of 9,10-octalin on various catalysts results in the formation of both *cis*- and *trans*-decalins. The results are presented in Table 4.

It would appear that the relations obtained might be accounted for by the above considerations concerning the mechanism of the hydrogenation of 1,2-dimethylcyclohexene. However, it has been observed that the hydrogenation of 1,9-octalin catalysed by palladium yields more *cis*-decalin than the hydrogenation of 9,10-octalin. Therefore in this case the formation of *trans*-decalin from 9,10-octalin cannot be a result of the isomerisation of the latter to 1,9-octalin. The data in Table 4 as well as the results given previously show that, among the three metals discussed, the rhodium catalyst favours most the *cis*-addition of hydrogen.

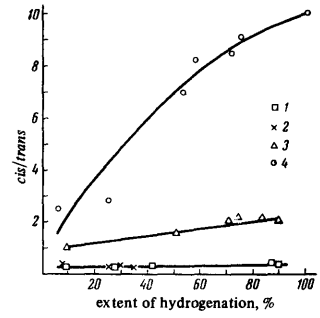


Figure 7. Stereoselectivity of the hydrogenation of 1,2-dimethylcyclopentene on Group VIII metals[46]: *1*) Pt/C; *2*) Pd/C; *3*) Rh/C; *4*) Ir/C.

The solvent and in particular the pH have a great influence on the stereoselectivity of liquid-phase hydrogenation. Thus Skita[53] and Auwers[54] showed that the hydrogenation of cyclo-olefins in an acid medium takes place mainly with formation of *cis*-isomers and in a neutral medium with formation of *trans*-isomers. Later this was also noted by Kazanskii and coworkers[55,56].

Table 4. Stereoselectivity of the hydrogenation of octalins in the presence of a number of Group VIII metals at 20°C at atmospheric pressure in acetic acid.

Octalin hydrogenated	Catalyst	*cis*-Isomer in hydrogenation products, %	References
9,10-Octalin	Pd/C	10; 7[a]	26
ditto	$Pd/BaSO_4$	12	26
»	PtO_2	51; 50	25; 51
»	Pt black	66; 50[b]	52
»	Rh/C	74; 67[a]	24
1,9-Octalin	Pd/C	21	26
ditto	$Pd/BaSO_4$	23	26

a) In ethyl alcohol. b) In ether.

The stereoselectivity of the hydrogenation of a triple bond in a cyclic hydrocarbon is also of definite interest. Partial hydrogenation of a cyclononyne, cyclodecyne, and cycloundecyne over various palladium catalysts results as a rule in the formation of a *cis*-olefin, i.e. *cis*-addition of hydrogen takes place[57-62]. Table 5 presents the conditions and results of the hydrogenation of the above cyclic acetylenic hydrocarbons in the presence of various palladium catalysts.

Turner and Meador[63] obtained data on the heat of hydrogenation of the *cis*- and *trans*-isomers of cyclo-octene, cyclononene, and cyclodecene and found that in acetic acid solution in the presence of PtO_2 the heat of hydrogenation of the *trans*-isomers is greater than that of the corresponding *cis*-isomers.

Examination of the above versions of the hydrogenation mechanism leads to the conclusion that none of them can account for all the experimental data available. Probably there is as yet no general mechanism for the hydrogenation of cyclo-olefins. It may be that, as the system (initial hydrocarbon, catalyst, and solvent) and the hydrogenation conditions are altered, there is also an appreciable change also in the reaction mechanism. Whereas under conditions of liquid-phase hydrogenation at room temperature and atmospheric pressure π-complexes and compounds of the π-allyl type may predominate as intermediates, under more severe conditions the reaction may proceed also via some other mechanism. Then in many cases factors such as the nature of the catalyst, the geometry of the active surface, the polarity of the medium, the structure of the initial cyclo-olefin, etc., play a decisive role. A significant role must be attributed in this case also to intramolecular isomerisation—the migration of the double bond in the ring. This process is undoubtedly fairly significant in all the reactions examined above and itself depends greatly on the nature of the primary adsorption of the initial compounds on the surface of the catalyst.

Table 5. Stereoselectivity of the hydrogenation at 25°C of cyclic C_9–C_{11} hydrocarbons containing a triple bond.

Initial hydrocarbon	Catalyst	Solvent	Reaction product	References
Cyclononyne	$Pd/BaCO_3$	ethyl acetate	*cis*-cyclononene	57
ditto	Pd/norite	methanol with admixture of pyridine	ditto	58
Cyclodecyne	$Pd/CaCO_3$	methanol	*cis*-cyclodecene	59
ditto	$Pd/BaCO_3$	ethyl acetate	ditto	60
	$Pd/CaCO_3$	petroleum ether (b.p.60-70°) with admixture of quinoline	»	61
	Pd/norite	methanol with admixture of pyridine	»	58
Cycloundecyne	$Pd/CaCO_3$	methanol	*cis*-cycloundecene	62
ditto	Pd/norite	methanol with admixture of pyridine	93% *cis*- and 7% *trans*-cycloundecene	58

According to the literature[34-36], the hydrogenation of cyclohexenes may be regarded to some extent as one of the stages of the hydrogenation of aromatic hydrocarbons. Therefore the data in the present section constitute to an appreciable degree an introduction to the next. Both sections are related and supplement one another.

III. HYDROGENATION OF AROMATIC HYDROCARBONS

The study of the stereoselectivity of the hydrogenation of di- and poly-substituted aromatic hydrocarbons can greatly expand the existing concepts concerning the mechanism of the hydrogenation of benzene and its derivatives. The conclusions arrived at in many studies are largely the same as those obtained in the hydrogenation of di- and poly-substituted cyclohexenes, although in many cases the specific characteristics of the initial substances hydrogenated are shown to some extent.

The hydrogenation of aromatic hydrocarbons has been investigated by many workers on different catalysts under different conditions (solvent, temperature, pressure). However, the stereochemical aspect of this reaction has as yet been inadequately examined, since the majority of studies have been of a purely preparative type. In the main the hydrogenation of di- and poly-alkyl benzenes has been studied on platinum and nickel catalysts. It was found that on both catalysts a certain amount of *trans*-isomers was formed as well as the *cis*-isomers. Nevertheless it would appear that simple addition of six hydrogen atoms to the aromatic ring when the latter undergoes planar adsorption should lead exclusively to the *cis*-form. Therefore here the following questions are mainly of interest: in what way are the *trans*-isomers of the cyclohexane series formed and via what intermediate stages, and whether these intermediate compounds are desorbed (at least partially) with subsequent readsorption on the catalysts or do all stages take place directly in the adsorption layer? The amount of *trans*-isomer formed depends on the nature of the catalyst and the hydrogenation conditions. Table 6 demonstrates the most typical results for

Table 6. Stereoselectivity of the hydrogenation of certain aromatic hydrocarbons on Group VIII metals[a].

Initial hydrocarbon	Catalyst	Hydrogenation temp., °C	*cis*-Isomer in hydrogenation products, %	References
1	2	3	4	5
o-Xylene	PtO_2	25[b]	95	19
ditto	PtO_2	25	92	64
»	PtO_2	25[c]	93	64
»	Pt black	25	~91	65
»	PtO_2	85	87.3	66
»	Os/asbestos	50—70	*cis*[d]	67
»	Rh/C	100[e]	89.2	68
»	Ru/C	100[e]	92.6	68
»	(2.5%Rh + 2.5%Pt)/C	100[e]	91.4	68
»	Ni	175	*trans*[d]	67
»	Ni	180	~50	65
m-Xylene	PtO_2	25	86	19
ditto	PtO_2	25	77	64
»	PtO_2	25[c]	85	64
»	PtO_2	25[f]	77	69
»	PtO_2	84	81	66
»	Rh/C	100[e]	73.7	68
»	Ru/C	100[e]	84.5	68
»	(2.5%Rh + 2.5Pt)/C	100[e]	77.4	68
p-Xylene	PtO_2	25[b]	74	19
ditto	PtO_2	25	73	64
»	PtO_2	25[c]	82	64
»	Os/asbestos	50—70	*cis*[d]	67
»	PtO_2	85	66.6	66
»	Rh/C	100[e]	63.6	68
»	Ru/C	100[e]	69.7	68
»	Pd/C	160[e]	47.3	68
»	(2.5%Rh + 2.5%Ru)/C	100[e]	55.4	68
»	(2.5%Rh + 2.5%Pt)/C	100[e]	64.5	68
»	(2.5%Rh + 2.5%Pd)/C	100[e]	65.0	68
»	Pt black	200	20	65
»	Ni	175	*trans*[d]	67
»	Ni	180	20	65
o-Ethyltoluene	PtO_2	25[b]	77	70
p-t-Butyltoluene	»	25	61	64
ditto	»	25[c]	71	64
p-Di-isopropylbenzene	Raney Ni (dehydrated)	190[d]	~50	71
Tetralin	PtO_2	25[f]	91	69
Naphthalene	PtO_2	25[f]	77	69
1,3,5-Trimethylbenzene	Pt, Ni	175	90	72
1,3,5-Triethylbenzene	»	175	97	72

a) Unless otherwise stated, the dehydrogenation was carried out at atmospheric pressure.
b) Hydrogenation at 2.5 atm H_2.
c) Hydrogenation at 300 atm H_2.
d) Predominantly the isomer specified.
e) Hydrogenation at 70 atm H_2.
f) Hydrogenation at 120 atm H_2.

the stereoselectivity of the hydrogenation of *o*-, *m*-, and *p*-xylenes and also certain other di- and tri-alkylbenzenes over various heterogeneous catalysts.

Analysis of Table 6 leads to the isolation of a number of relations.

1. Under mild hydrogenation conditions, a mixture of the *cis*- and *trans*-isomers is obtained, but the former as a rule predominates.

2. In the hydrogenation of 1,2- and 1,4-dialkylbenzenes, the relative amount of the *trans*-isomer increases and becomes dominant as the temperature is raised from 25° to 180°C. In the hydrogenation of *m*-xylene in the same temperature range, constant preferential formation of the *cis*-isomer is observed. One should remember that in the 1,2- and 1,4-series the *trans*-isomers are energetically more favoured (*ee*-substituents) than the *cis*-isomers (*ae*-substituents), while in the 1,3-series the *cis*-isomers are diequatorial and therefore energetically more favoured.

3. The relative amounts of the *cis*- and *trans*-isomers obtained in the hydrogenation of each of the three xylenes are related to the relative positions of the substituents. In the hydrogenation of xylenes under similar conditions the content of the *cis*-isomer in the reaction product diminishes in the sequence *ortho* > *meta* > *para* (for example in the hydrogenation over PtO_2 at 25°C in acetic acid or over Rh/C and Ru/C at 100°C).

4. Tetralin and naphthalene‡ behave under similar hydrogenation conditions like 1,2-dialkylbenzenes and 1,3,5-trialkylbenzenes behave like 1,3-dialkylbenzenes. Not only the nature of the metal employed but also its relative content in the catalyst has a considerable influence on the stereoselectivity of the hydrogenation. It has been found that in the hydrogenation of *o*- and *p*-xylenes on Rh/C the content of the *trans*-form of the corresponding dimethylcyclohexane increases with the concentration of the metal in the catalyst; on the other hand, in the hydrogenation of *m*-xylene the content of the *trans*-form of 1,3-dimethylcyclohexane diminishes somewhat. The relevant data are presented in Table 7.

The study of the effect of the carrier is very important in an examination of the stereoselectivity of the hydrogenation of the aromatic ring. Table 8 presents the results of the hydrogenation of all three xylenes on 5% rhodium, and ruthenium catalysts deposited on different carriers. It has been shown that, among the six carriers investigated, activated charcoal leads to preferential *cis*-addition of hydrogen; moreover, it has been discovered that as a rule more *cis*-isomers are formed on the ruthenium catalyst than on rhodium.

The mechanism of the hydrogenation of aromatic hydrocarbons has been discussed by many investigators, but the problem is very complex and there is as yet no generally accepted view on this subject. According to the multiplet theory, the hydrogenation of aromatic compounds on the surface of metal catalysts takes place with planar adsorption of the aromatic ring on the metal surface (platinum, nickel, cobalt, copper, ruthenium, iridium, palladium, rhodium, osmium, and rhenium). This mechanism has been discussed in a number of papers by Balandin[73] and many Soviet and non-Soviet investigators have shown that the above metals, which have a face-centred cubic or hexagonal lattice with interatomic distances in the range up to 2.49 Å for nickel and 2.77 Å for platinum, are indeed hydrogenation–dehydrogenation catalysts. According to the multiplet theory, when an aromatic ring undergoes planar adsorption, it does not leave the active centre until six hydrogen atoms have added either in succession or all at once. The problem of the formation of *trans*-substituted cyclohexanes remains open.

‡ The stereochemistry of the hydrogenation of these hydrocarbons and their homologues in the presence of metal catalysts has been described in detail in a recently published review by Weitkamp[8].

Table 7. Stereoselectivity of the hydrogenation of xylenes on various Rh/C* catalysts[68].

Catalyst (wt.g)	Initial xylene	*trans*-Dimethylcyclohexane in hydrogenation products, %	Catalyst (wt.g)	Initial xylene	*trans*-Dimethylcyclohexane in hydrogenation products, %
5%Rh/C (0.3)	*ortho*-	10.8	5%Rh/C (0.3)	*para*-	36.4
30%Rh/C (0.3)	*ortho*-	18.7	30%Rh/C (0.3)	*para*-	48.9
5%Rh/C (0.3)	*meta*-	26.3	30%Rh/C (0.05)	*para*-	47.0
30%Rh/C (0.3)	*meta*-	23.0			

* All the experiments were carried out at 100°C and an initial pressure of 70 atm H_2.

In their discussion of the mechanism of the hydrogenation of benzene, Farkas and Farkas[74] suggested that the rate-limiting stage of this reaction is the interaction of the adsorbed benzene with two adsorbed hydrogen atoms:

$$C_6H_6(\text{ads.}) + 2H(\text{ads.}) \underset{\text{slow}}{\longrightarrow} C_6H_8(\text{ads.}) \xrightarrow[\text{fast}]{2H_2} C_6H_{12} + \text{catalyst (Ct)}.$$

Table 8. Effect of the carrier on the stereoselectivity of the hydrogenation of three individual xylenes on rhodium and ruthenium catalysts[68]*.

Catalyst	*trans*-Forms of dimethylcyclohexanes in hydrogenation products, %		
	1.2-	1.3-	1.4-
Rh/C	6.5	15.6	22.7
Ru/C	3.0	9.3	23.8
Rh/kieselguhr	7.1	19.7	31.9
Ru/kieselguhr	6.0	—	27.0
$Rh/SrCO_3$	8.0	23.8	25.0
$Ru/SrCO_3$	4.3	11.8	31.8
$Rh/BaCO_3$	15.8	30.3	30.3
$Ru/BaCO_3$	3.6	15.7	27.6
$Rh/BaSO_4$	14.2	18.2	34.5
$Ru/BaSO_4$	5.2	14.4	—
Rh/Al_2O_3	8.0	27.8	29.5
Ru/Al_2O_3	9.7	14.7	29.4

* All the experiments were carried out at 20°C and an initial pressure of 3.5 atm H_2; all the catalysts contained 5 wt.% of the metal.

At the same time according to these authors, deuterium exchange involving benzene takes place via a dissociative mechanism:

$$C_6H_6 + Ct \rightarrow C_6H_5(\text{ads.}) + H(\text{ads.})$$

and further

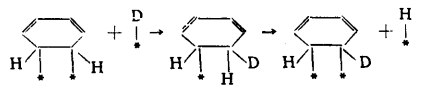
$$C_6H_5(\text{ads.}) + D(\text{ads.}) \rightarrow C_6H_5D + Ct.$$

According to Horiuti and Polanyi[27], both reactions (hydrogenation and deuterium exchange) involve an associative mechanism and in the first case the two hydrogen atoms are added consecutively:

Hydrogenation:

$$C_6H_6(ads.) + 2H(ads.) \rightarrow C_6H_7(ads.) + H(ads.) \xrightarrow[slow]{} C_6H_8(ads.) \xrightarrow[fast]{2H_2} C_6H_{12} + Ct\,.$$

Deuterium exchange:



Later Greenhalgh and Polanyi[75] showed that, if in deuterium exchange via the dissociative mechanisms the rate-determining stage is the interaction of the adsorbed phenyl radicals with a deuterium atom, then both mechanisms (dissociative and associative) are described by the same kinetic equation.

In a number of studies[76-78] of the hydrogenation of benzene on a nickel catalyst and of xylenes on ruthenium, rhodium, nickel, and PtO_2 catalysts, the formation of a small amount of the corresponding cyclo-olefins was observed. Thus in the hydrogenation of *p*-xylene[77] the formation of 1,4-dimethylcyclohexene was discovered and in the hydrogenation of *m*-xylene that of 1,3- and 2,4-dimethylcyclohexenes, although the rates of hydrogenation of cyclo-olefins are significantly higher than those of the corresponding aromatic hydrocarbons[79]. On this basis, Siegel and coworkers[78] suggest that the hydrogenation of aromatic hydrocarbons in the presence of heterogeneous catalysts proceeds via the intermediate formation of cyclo-olefins, which are then very rapidly hydrogenated further in accordance with the mechanism described previously (Fig. 4).

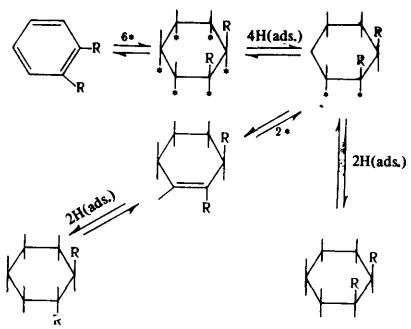
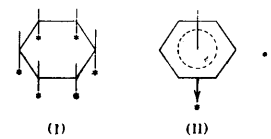


Figure 8. Mechanism of the hydrogenation of *o*-xylene according to Siegel et al.[64]

The mechanism proposed by Siegel and coworkers[64] is presented below in Figs. 8, which shows the possible pathways in the formation of the *cis*- and *trans*-isomers of 1,2-dimethylcyclohexane from *o*-xylene. In the same study the authors investigated the relative amounts of the *cis*- and *trans*-isomers as a function of hydrogen pressure. It was found that for aromatic hydrocarbons, as for cyclo-olefins, this ratio increases with hydrogen pressure. However, it follows from the work of Siegel and coworkers[19,20,64] that the hydrogenation of xylenes gives an appreciably greater amount of the *cis*-isomers than the hydrogenation of the corresponding cyclo-olefins. Therefore the considerations adduced above concerning the hydrogenation mechanism do not appear very convincing.

The most widely held view, which has been reflected in a number of investigations[34,35,64] in recent years, is that the hydrogenation reactions of aromatic hydrocarbons and cyclo-olefins have a number of stages in common. Therefore both can involve common partially hydrogenated intermediates adsorbed on the surface of the catalyst. One can easily imagine two versions of the adsorption of the aromatic ring on the catalyst: (I) the formation of six new σ bonds[64] and (II) the formation of a π complex of benzene with the catalyst[35]:



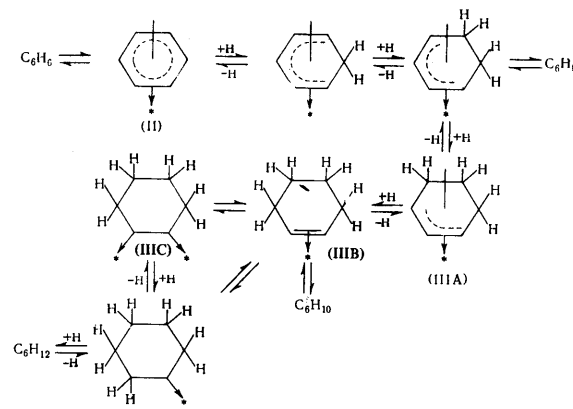


Figure 9. Mechanism of the hydrogenation of benzene according to Rooney[35].

We believe that model (II) is energetically more favoured and hence more probable. Rooney[35] represents the hydrogenation of benzene as a process involving the transformation of (II) via a series of intermediates into cyclohexene and further into cyclohexane. Then the cyclohexene adsorbed on the catalyst surface is represented either as a π-allyl adsorbed structure (IIIA) or as a π-complex (IIIB) (see the mechanism in Fig. 9). Probably the stereoselectivity of the hydrogenation of dialkylbenzenes depends primarily on the last step in the transformation of structure (IIIA) or (IIIB) [or their σ-diadsorbed analogue (IIIC)] into the corresponding dialkylcyclohexane. In turn, the similarity (or the difference) in the stereoselectivity of the hydrogenation of disubstituted aromatic compounds and the corresponding cyclohexenes can serve as a criterion of the similarity of the mechanisms of the hydrogenation of the hydrocarbons in these classes. It is noteworthy that, according to Rooney, the structures (IIIA) and (IIIB) represented in the above mechanism may be hydrogenated not only by adsorbed hydrogen but also by the hydrogen in the bulk phase. Thus, these concepts may account for the formation of *cis*- and *trans*-cyclohexanes in the hydrogenation of aromatic compounds.

In conclusion of this section it must be emphasised that, under mild hydrogenation conditions (Table 6), *cis*-addition of hydrogen with the formation of the *cis*-isomer predominates. Under more severe conditions, the situation changes: as mentioned above, with increase of temperature, the amount of the *trans*-isomer rises appreciably. We believe that this phenomenon is largely caused by the configurational isomerisation of the *cis*-isomer formed in the hydrogenation process. Indeed, it has now been shown that in the presence of many Group VIII metals the *cis*- and *trans*-isomers of di- and poly-alkylcycloalkanes are interconverted at a high rate (see Section IV). However, in none of the studies quoted above is the possibility of such direct interconversions of stereoisomers under severe hydrogenation conditions of aromatic hydrocarbons in any way discussed. Nevertheless, as shown in the next section, such possibility must be taken into account. At the same time, it should be specially noted that under mild conditions (particularly at room temperature), configurational isomerisation does not take place. Therefore, it cannot be used to explain the formation of *trans*-isomers under these conditions. Indeed, at room temperature the mixture of the stereoisomeric 1,3-dimethylcyclohexanes in thermodynamic equilibrium should contain, according to calculation, only about 5% of the *trans*-isomers, but in the hydrogenation of *m*-xylene under these conditions 14–23% of *trans*-1,3-dimethylcyclohexane is formed (Table 6). Thus, in order to explain the formation of the *trans*-isomers in the hydrogenation of aromatic compounds, it is necessary to resort to a special mechanism. In this sense, Rooney's mechanism[35] is supported by insufficient evidence.

IV. CONFIGURATIONAL ISOMERISATION OF STEREOISOMERIC DI- AND POLY-ALKYLCYCLOALKANES

As already mentioned in the preceding section, until recently the mechanism and characteristics of the direct interconversion of the stereoisomeric di- and poly-alkylcycloalkanes were hardly discussed in the literature. However, these reactions have a direct bearing on the composition of the reaction products formed as a result of the hydrogenation of both cyclo-olefins and aromatic hydrocarbons. The mechanism below (Fig. 10) represents the reversible interconversion of the *cis*- and *trans*-forms of di-alkylcycloalkanes, which takes place readily in the presence of many Group VIII metals. In this process there is at least formally no addition of atoms to or their abstraction from the initial molecule, the molecular skeleton remaining unchanged, and only one of the alkyl groups migrates from one side of the ring to the other, i.e. the configuration of one of the ring carbon atoms changes. In this connection the reaction discussed received a special name—configurational isomerisation[80]. Below it will be shown why the term *cis–trans* isomerisation encountered in the literature should not be employed in this case. These interesting and at first sight simple reactions constitute a convenient model which may yield important information about the detailed mechanism of heterogeneous catalysis and about the intermediate activated complex, the formation and decomposition of which govern the course of this reaction.

Configurational isomerism was described for the first time by Zelinskii and Margolis[67] in 1932 for the stereoisomeric 1,2- and 1,4-dimethylcyclohexanes. These workers observed that the *cis*-forms of the above hydrocarbons are converted into the corresponding *trans*-forms under the influence of a nickel catalyst. Subsequent investigation showed that these reactions do not result in the formation of the individual stereoisomers but their mixtures, the composition of which approaches to some extent the composition of mixtures at thermodynamic equilibrium.

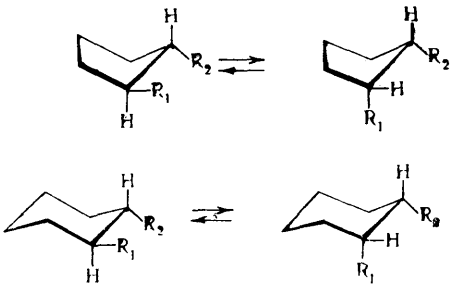
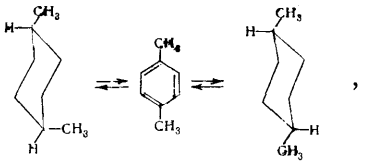


Figure 10. Configurational isomerisation of stereoisomeric 1,2-dialkylcycloalkanes.

Whereas in the series of cyclohexane homologues the mechanism of the interconversion of the stereoisomeric forms could be readily represented in terms of the intermediate formation of aromatic hydrocarbons,



for other ring compounds (in particular cyclopentane homologues) such possibility is excluded. Therefore the work of Kazanskii et al.,[81] in which they observed for the first time configurational isomerism in the cyclopentane series, is extremely unexpected and interesting. It was shown that the hydrogenolysis of stereoisomeric 1,2,3-trimethylcyclopentane on a platinum catalyst is accompanied by configurational isomerisation. For any initial stereoisomer, the thermodynamically most stable $1^c,2^t,3^c$-form predominates in the catalytic reaction mixture, the amount of the $1^c,2^c,3^t$-isomer is significantly less, and the $1^c,2^c,3^c$-stereoisomer is present in an altogether negligible amount.

After this first publication on the configurational isomerisation of stereoisomeric trimethylcyclopentanes, this reaction was not discussed in the literature for about 15 years. Only at the beginning of the 1960's, after the work of Gault et al.[29] and the first publications by the present authors[82,83], configurational isomerisation of cyclopentane homologues became the subject of discussion by a number of Soviet and non-Soviet investigators. We showed[82] that in the presence of platinised charcoal stereoisomeric 1,2-dimethylcyclopentanes are readily interconverted over a wide temperature range (150–280°C). The configurational isomerisation takes place at a significantly higher rate than the accompanying hydrogenolysis of the five-numbered ring. Later we showed[83] that, together with platinum, rhodium, osmium, iridium, and palladium are

also active catalysts promoting configurational isomerisation. Subsequently this range of catalysts was extended to include ruthenium[80] and cobalt[84].

Deuterium exchange in polymethylcyclopentanes on the surface of metallic films (platinum, palladium, nickel, and rhodium) was investigated[29]. Together with D–H exchange, a study was made of the configurational isomerisation of the *cis*- and *trans*-forms of 1,1,3,4-tetramethylcyclopentane and also *cis*-1,2-dimethylcyclopentane. Having investigated the kinetics of deuterium exchange and configurational isomerisation, Gault and coworkers concluded that the rates of both reactions are described by an equation for a first-order process and can be expressed as follows:

deuterium exchange:

$$-d(d_0)/dt = k_H[(d_0) - (d_0)_\infty]/[100 - (d_0)_\infty]\ ; \qquad (I)$$

configurational isomerisation:

$$-dx/dt = k_1(x - x_\infty)/(100 - x_\infty)\ , \qquad (II)$$

where k_H and k_I are the rate constants for reactions (I) and (II) respectively, d_0 is the concentration of the initial hydrocarbon not containing deuterium at time t, $(d_0)_\infty$ the equilibrium concentration of the initial hydrocarbon not containing deuterium, x the concentration of the initial *cis*- or *trans*-isomer at time t, and x_∞ the equilibrium concentration of the initial *cis*- or *trans*-isomer.

After simple rearrangement, these equations can be put in the form

$$\lg\frac{x - x_\infty}{x_0 - x_\infty} = \frac{k_I}{k_H}\cdot\frac{100}{100 - x_\infty}\lg\frac{(d_0)}{100} \qquad (III)$$

where x_0 is the concentration of the initial *cis*- or *trans*-isomer at time $t = 0$.

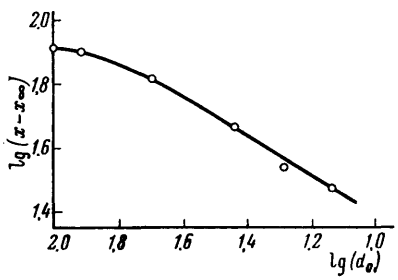
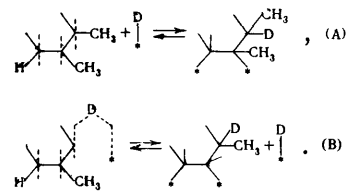


Figure 11. Relation between the configurational isomerisation and deuterium exchange of *cis*-1,1,3,4-tetramethylcyclopentane on a palladium catalyst[29].

It follows from Eqn. (III) that the relation between $\lg(x - x_\infty)$ and $\lg(d_0)$ should be linear, which the authors indeed observed (Fig. 11) for the configurational isomerisation and deuterium exchange of *cis*-1,1,3,4-tetramethylcyclopentane on a palladium catalyst at 65°C in the above range of values of $\lg(d_0)$.

These data show that both reactions are definitely related: the greater the extent of deuterium exchange the more far-reaching is the configurational isomerisation. The authors explain certain deviations of the experimental points from the straight line by the fact that the reactions investigated do not obey the equation for a first-order process altogether rigorously over the entire range of concentrations of the initial hydrocarbon.

The slope of the straight line (0.51) shows that the rate of deuterium exchange is approximately twice as high as that of configurational isomerisation. Probably the ratio of the rates of these two reactions depends primarily on the nature of the catalyst and not on the experimental temperature, since the results obtained in the presence of the same palladium catalyst at 87° and 146°C are very close to those at 65°C described above. In the presence of other catalysts investigated the rate of deuterium exchange predominates over that of configurational isomerisation to an even greater extent. On the basis of the data obtained, the authors conclude that these two reactions have a common mechanism and that they both take place with formation on the surface of the catalyst of transition complexes of the π-allyl type. They believe that the first reaction stage consists in the formation of this type of adsorption complex, located in a single plane which also contains all the methyl groups of the initial molecule. The second stage is the interaction of the adsorbed π-complex with the atom or molecule of hydrogen (deuterium) adsorbed on the catalyst surface. For 1,2-dimethylcyclopentane, the addition of hydrogen or deuterium to this type of adsorbed π-complex can be represented by the following two reversible processes:



They show that the adsorbed π-complex arises in the reaction of the catalyst with the p orbital of the carbon atom, which is shown by dashed lines. In mechanism (A) the adsorbed deuterium atom attacks the ring from below, adding to the p orbital of the carbon atom bound to the methyl group. In mechanism (B) deuterium adds to the p orbital of the carbon atom after attacking the ring from above. After the addition of deuterium or hydrogen to the adsorbed π-complex and after the desorption of 1,2-dimethylcyclopentane, the sp^3 hybridisation of carbon atoms in the latter is restored with formation of *cis*-1,2-dimethylcyclopentane [mechanism (A)] or the *trans*-form [mechanism (B)] respectively. The authors of this mechanism suggest that the first stage—the step involving the dissociative chemisorption of the initial hydrocarbon with formation of an adsorbed π-complex of the allyl type—is rate-determining. Thus in their analysis of studies on the configurational isomerisation of dialkylcycloalkanes, Bragin et al. noted that in previous investigations this reaction was always accompanied by other processes (hydrogenolysis, deuterium exchange, dehydrogenation). After a large-scale study of the conditions under which configurational isomerisation takes place, we demonstrated[84] the possibility of a smoother course of this reaction, without any side and secondary processes. It was found that the configurational isomerisation of 1,2-dimethylcyclopentane on platinum and palladium catalysts below 200°C at space velocities of 1.4–21.6 h^{-1} takes place quite successfully without being complicated by side processes. At the same time on other Group VIII noble metals (osmium, ruthenium, rhodium, and iridium) at 200°C hydrogenolysis products were formed (particularly vigorously on the Ru/C catalyst). However, at 150°C and below there were virtually no side reactions on these metals either and the rate of configurational isomerisation

remained appreciable. Comparison of the relative activities of the metals enumerated above, deposited on activated charcoal, showed that their catalytic activities are extremely varied. In all cases Pt/C and Rh/C showed the greatest activity and the remaining four catalysts were significantly less active. Comparative data on the configurational isomerisation of *trans*-1,2-dimethyl- and *trans*-2-ethyl-1-methyl-cyclopentanes, obtained on six of the above catalysts, are presented in Fig. 12. The results for the corresponding *cis*-isomers of the cyclopentane and the stereoisomeric cyclohexane hydrocarbons were similar.

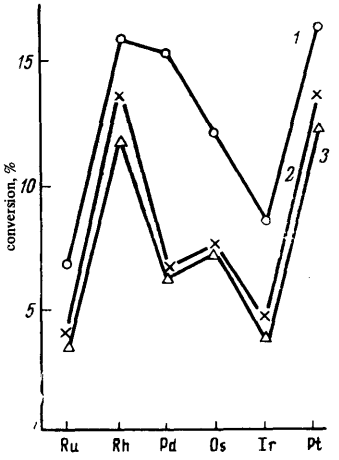


Figure 12. Relative activities of Group VIII metals in configurational isomerisation[84]: *1*) and *2*) *trans*-1,2-dimethylcyclopentane at 300° and 200° respectively; *3*) *trans*-2-ethyl-1-methylcyclopentane at 200°C.

In a study of the kinetics of the configurational isomerisation of stereoisomeric 1,2-dialkylcyclopentanes we showed[80,85] that, under the conditions investigated, this reaction is of zero (or nearly zero) order with respect to the hydrocarbons. The conversion of the energetically more stable *trans*-forms of 1,2-dimethyl-, 2-ethyl-1-methyl-, and 1-methyl-2-n-propyl-cyclopentanes into the *cis*-isomers requires a somewhat greater activation energy than the reverse process. The activation energies found on platinum, rhodium, and cobalt catalysts are similar and are listed in Table 9.

Kalechits and coworkers[86] carried out the configurational isomerisation of 1,3-dialkylcyclopentanes. The conversion of *cis*-1,3-dimethylcyclopentane into the *trans*-form over an iron–platinum catalyst takes place up to concentrations close to equilibrium; the reverse transformation occurs to a relatively low extent.

In the studies of Petrov and coworkers[87] the configurational isomerisation of stereoisomeric di- and poly-alkylcyclopentanes was employed to establish thermodynamic equilibrium between them and to calculate a number of thermodynamic functions.

In all the studies on configurational isomerisation quoted above hydrogen or deuterium was always present to some extent in the reaction zone. In one of our early investigations[83] we suggested that hydrogen chemisorbed on the surface of the catalyst may enter into the composition of the transition complex and thereby may play a significant role in the reaction. Subsequently this hypothesis was tested and confirmed experimentally. Thus in one of our investigations[45] we considered a number of possible mechanisms of configurational isomerisation, the essential feature of which consists in the application to this reaction of various modifications of the dissociative and associative modes of adsorption of the initial hydrocarbon. The adsorption of the latter by a dissociative mechanism can lead to the formation of either ions or radicals. In this case the formation of carbonium ions can probably be excluded, since it would have to be accompanied by a more profound skeletal isomerisation (the formation of a six-membered ring), which was not observed either in experiments in a flow system or under pulse conditions. The second possibility is the intermediate formation of radicals adsorbed on the surface of the catalyst. This process should take place in at least two stages: (a) chemisorption of the hydrocarbon with formation of radicals (monomolecular reaction) and (b) addition of hydrogen to these radicals from the side opposite to that from which it had been abstracted (bimolecular reaction). In the second stage the attack of hydrogen on the mono- or di-adsorbed (chemisorbed) complex, results in the formation of the hydrocarbon stereoisomeric with the initial compound and the free catalyst. For instance, the two stages can be represented schematically in the following way:

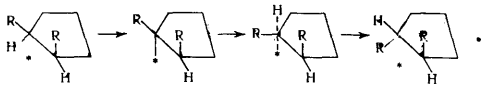


Table 9. Activation energies for the configurational isomerisation of stereoisomeric 1,2-dialkylcyclopentanes[80,85].

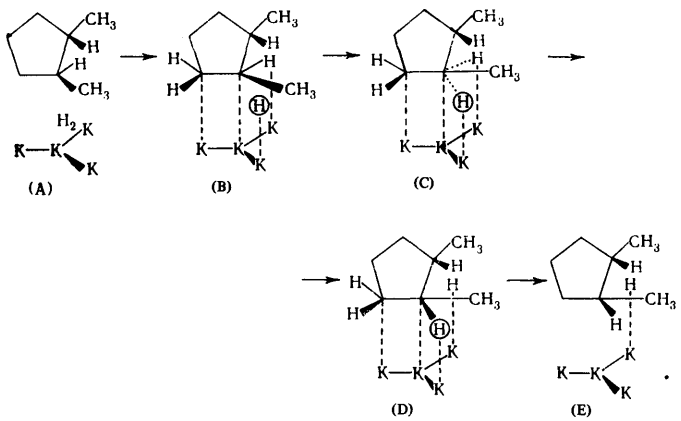
Initial hydrocarbon	Activation energy Q, kcal mole^{-1}		Initial hydrocarbon	Activation energy Q, kcal mole^{-1}	
	Pt/C	Rh/C		Pt/C	Rh/C
trans-1,2-Dimethylcyclopentane	12	14.5	*trans*-1-Methyl-2-n-propyl-cyclopentane	9	—
cis-1,2-Dimethylcyclopentane	10	9.5			
trans-2-Ethyl-1-methylcyclopentane	16.5	—	*cis*-1-Methyl-2-n-propylcyclopentane*	5	—
cis-2-Ethyl-1-methylcyclopentane	7.5	—			

* In the presence of 18% Co/C, the activation energy for the conversion of *cis*-1-methyl-2-n-propylcyclopentane into the *trans*-form was 7.5 kcal mole^{-1}.

In this version the rate of reaction is determined by either the first or the second stage. Further studies excluded the first stage—the formation of the adsorbed complex—from the rate-limiting steps.

Nevertheless, we believe it likely that the intermediate transition complex is formed by an associative mechanism. The data quoted below on the participation of hydrogen as a second reactant in configurational isomerisation, the absence of dehydrogenation and skeletal isomerisation products under mild reaction conditions, and also kinetic results are consistent with this view. The kinetic results demonstrate a comparatively low activation energy for configurational isomerisation, whereas the dissociation of the C–H bond (the first stage in the formation of the transition

complex by the dissociative mechanism) requires a significantly greater energy expenditure. The transition complex formed by the associative mechanism probably includes the reacting hydrocarbon molecule, the active catalyst surface, and a hydrogen species. The formation and breakdown of this activated complex proceed by a mechanism identical or formally similar to the S_N2 Walden inversion:



The mechanism presents the stages in the conversion of *trans*-1,2-dimethylcyclopentane into the *cis*-form. The initial *trans*-1,2-dimethylcyclopentane (A) is adsorbed via two carbon atoms and one hydrogen atom on three adsorption centres of the catalyst with formation of (B). The hydrogen atom adsorbed in an adjacent position attacks the hydrocarbon molecule and the transition complex (C) is formed. The latter then breaks down with incorporation of the attacking hydrogen atoms in the hydrocarbon molecule and with simultaneous loss by the molecule of another hydrogen atom [stage (D)]. This results in the formation of *cis*-1,2-dimethylcyclopentane adsorbed on the catalyst surface, which is then desorbed [stage (E)].

It should be noted that the available data do not as yet provide sufficient grounds to decide whether the mechanism proposed is truly of S_N2 type or only bears a formal resemblance to it. A reaction involving an S_N2 mechanism requires attack by either an anion or a negatively polarised group. In the case discussed this could be a negatively polarised hydrogen atom, the hydride ion, or an H_2^- ion. The existence of the last two species on films of a number of Group VIII metals was demonstrated by Krasil'shchikov and Antonova[88]. However, there is as yet no direct evidence for the presence of such species under the conditions of configurational isomerisation. Nevertheless, it is noteworthy that a number of studies have shown[88,94] that hydrogen may be chemisorbed on the surface of certain metals (including platinum) in the form of species other than neutral atoms. In the adsorption layer hydrogen atoms may be polarised by the conductivity electrons of the metal, forming with the atoms of the latter dipoles, the properties of which resemble those of hydride ions.

The above considerations demonstrate the important role which hydrogen plays in configurational isomerisation. For this reason, special series of experiments were performed in which the effects of the concentration and the space velocity of hydrogen on the rate of configurational isomerisation were elucidated.

In experiments where stereoisomeric 1,2-dimethylcyclopentanes mixed with inert gases (helium, argon, and nitrogen) and also with methane were passed over a platinum catalyst, we discovered that under these conditions the reaction does not take place at all. However, when the carrier gas contains quite a low concentration of hydrogen (about 3%), the reaction begins at an appreciable rate; on further increase of the hydrogen concentration in the gas, the rate of reaction rises and, beyond a certain hydrogen concentration, reaches a constant value and no longer alters (Fig. 13).

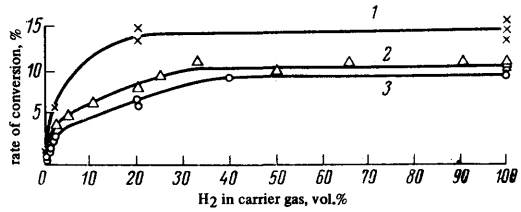


Figure 13. Variation of the rate of the configurational isomerisation of *cis*- and *trans*-1-2-dimethylcyclopentanes on Pt/C with the ratio of H_2 and N_2 (or He) in the carrier gas[45]: *1*) *cis*-isomer at 110°C (H_2 + N_2); *2*) and *3*) *trans*-isomer at 220°C (H_2 + He) and 150°C (H_2 + N_2) respectively.

The study of the effect of the space velocity of hydrogen on the rate of configurational isomerisation led to similar results. This is shown in Fig. 14, where the ascending sections of the curves are indeed similar to the corresponding sections in Fig. 13. They show that at low hydrogen flow rates, i.e. at low hydrogen concentrations in the mixtures of hydrocarbons, the rate of reaction depends significantly on the hydrogen concentration and tends to zero when the latter is reduced. The subsequent decrease of the rate of reaction (the descending sections in Fig. 14) can be explained by the fact that, at a certain instant, the increase of the rate of supply of hydrogen leads to an appreciable decrease of the duration of contact of the mixture as a whole. In the experiments presented in Fig. 13 this phenomenon was not observed, since, whatever the mixture composition, the duration of contact was kept constant from the beginning to the end of the experiment.

The above relations are very similar to those observed for bimolecular reactions and suggest that in the presence of platinum hydrogen does not behave as a simple carrier gas but as a second reactant in configurational isomerisation. The principal relations remain the same on other Group VIII metals[45]. In an atmosphere of hydrogen these metals activate configurational isomerisation, while in the absence of hydrogen the isomerisation does not occur. However, a more detailed study revealed certain specific features of particular metals, but the decisive role of hydrogen, demonstrated previously on platinum, was found to apply also to palladium, rhodium, ruthenium, osmium, and iridium.

Thus we believe that the associative mechanism of configurational isomerisation[45], of the S_N2 Walden inversion type, may be extended also to the other Group VIII metals investigated.

The mechanisms discussed above emphasise the fundamental role of hydrogen in configurational isomerisation. The relations obtained are not exceptional and have a number of analogies in other reactions. Thus it was noted earlier that the *cis–trans* isomerisation of olefins on Group VIII metals also takes only in the presence of hydrogen or deuterium[42-44]. In this connection, the work of Siegel and coworkers[20,21] quoted above, in which it was noted that the hydrogenation of cyclo-olefins on platinum and palladium catalysts is accompanied by isomerisation with migration of the double bond in the ring while in the absence of hydrogen the isomerisation does not occur, is of definite interest. Probably the mode of action of these catalysts has certain features in common in the above reactions, although their specific mechanisms may in fact be different.

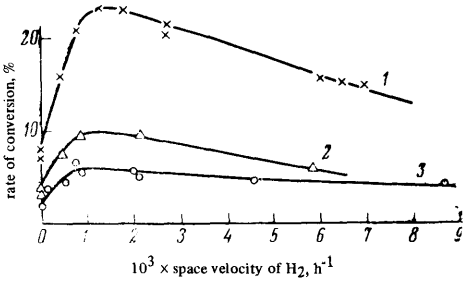


Figure 14. Variation of the rate of the configurational isomerisation of *cis*- and *trans*-1,2-dimethylcyclopentanes on Pt/C with the space velocity of hydrogen[45]: *1*) *cis*-isomer at 110°C; *2*) and *3*) *trans*-isomer at 150° and 130°C respectively.

Almost all the papers quoted above, in which the configurational isomerisation is discussed, refer to hydrocarbons of the cyclopentane series. However, there are indications in the literature that configurational isomerisation takes place also in other cyclic systems. Thus Gault, Maire, and coworkers[39,95,96] investigated the simultaneous hydrogenolysis, deuterium exchange, and configurational isomerisation of stereoisomeric 1,2-dimethylcyclobutanes on platinum, palladium, rhodium, and nickel catalysts. According to these authors, the above reactions of cyclobutane homologues have identical or similar mechanisms with formation of intermediate complexes of the π-allyl type.

Allinger and coworkers widely employed configurational isomerisation for the attainment of thermodynamic equilibrium between stereoisomers and for the calculation of the thermodynamic functions of stereoisomeric 1,3-dimethylcyclo-octanes[97], decalins[98], bicyclo[5,2,0]nonanes[99] and bicyclo[5,3,0]decanes[100].

The reaction has been widely investigated in the cyclohexane series, but not in quite such detail as for cyclopentane hydrocarbons. This is probably due to the complications which arise due to the accompanying dehydrogenation reaction and possibly also the somewhat lower rate of the configurational isomerisation of cyclohexane homologues compared with cyclopentanes[84]. The rate of attainment of thermodynamic equilibrium in the series of cyclohexane homologues depends on the nature and activity of the catalyst employed, the experimental conditions, and the properties of the initial isomers. Thus Waterman and coworkers[101] showed that, in the presence of a nickel/kieselguhr catalyst at 170–180°C and a hydrogen pressure of 7–8 atm, *cis*- and *trans*-1,3- and 1,4-dimethylcyclohexanes reached thermodynamic equilibrium more rapidly than 1,2-dimethylcyclohexanes. Under the influence of Raney nickel, *trans*-1,2-dimethylcyclohexane attains equilibrium faster than the corresponding *cis*-isomer. Allinger and coworkers[102-107] carried out a series of studies on the conformational analysis of the stereoisomeric cyclohexane homologues, which in the presence of a palladium catalyst can be reversibly interconverted by configurational isomerisation. The composition of the thermodynamic equilibrium mixtures formed in this process enabled the authors to calculate the equilibrium constants, a number of thermodynamic functions, and also the energies of the interconversion of a number of conformers.

Petrov, Zakharenko, and coworkers[108,109] also determined the equilibrium ratios of stereoisomeric di- and poly-alkylcyclohexanes with the aid of configurational isomerisation. The work of Eliel[110-112], who investigated the configurational isomerisation of stereoisomeric mono- and di-alkylcyclohexanols, is of interest too. These studies yielded information about the relative rates of interconversion, esterification, and oxidation of stereoisomeric alkylcyclohexanols and also yielded the conformational energies of various axial alkyl groups in stereoisomeric 1,3- and 1,4-dialkylcyclohexanols.

In these and certain other studies the term epimerisation (and correspondingly the terms epimerisation conditions and rate of epimerisation) is applied to configurational isomerisation but, from our point of view, it is non-rigorous and may lead to an incorrect understanding of the essential features of the reaction. Indeed, the term epimerisation is usually applied to a racemisation process involving one asymmetric centre (of the several present) in the molecule of an optically active substance. For example, the conversion of D-*trans*-1,2-dimethylcyclopentane, which has two asymmetric centres, into the L-*trans*-stereoisomer can be legitimately called epimerisation, but the conversion of the *trans*-form into the *cis*-form is a completely different reaction. In configurational isomerisation stereoisomeric dialkylcycloalkanes are not as a rule optically active and, for example, the interconversion of *cis*-1,2-dimethylcyclohexane and its *trans*-form is the interconversion of two racemates. We believe that the mechanism of the interconversions of stereoisomeric dialkylcycloalkanes is fundamentally different also from the mechanism of the *cis–trans* isomerisation of olefins and this is why we propose a special name for the former reaction, i.e. configurational isomerisation.

Shopov and Andreev[113] showed that the rate of dehydrogenation of stereoisomeric dialkylcyclohexanes depends on the nature of the catalyst. Thus on a platinum catalyst the *cis*- and *trans*-forms of 1,2-dimethylcyclohexane are dehydrogenated to xylene at the same rate, while on palladium and nickel the *trans*-form is dehydrogenated at an appreciably lower rate. This is probably associated in some way with the different relative rates of the configurational isomerisation of the *cis*- and *trans*-isomers of dimethylcyclohexane in the presence of various catalysts. Indeed, in the configurational isomerisation of the *cis*- and *trans*-isomers of 1,3-dimethylcyclohexane we found that[84] platinum and rhodium catalysts are more active than other Group VIII noble metals.

Our finding[45] that on all Group VIII noble metals the configurational isomerisation of cyclohexane homologues takes place only in the presence of hydrogen§, as in the cyclopentane series, is extremely important. The study of the kinetics of the configurational isomerisation of *cis*-1,2- and *trans*-1,3-dimethylcyclohexane showed[115] that the activation energies for the conversion of these hydrocarbons into the corresponding stereoisomers are 7.5 and 6 kcal mole^{-1}. These and other facts obtained in the study of the configurational isomerisation of cyclohexane hydrocarbons indicate a number of similar features of these reactions in the cyclopentane and cyclohexane series. In the first place these include the direct participation of hydrogen in the reaction, the absence of cyclo-olefins and aromatic hydrocarbons under mild conditions of configurational isomerisation, fairly close activation energies, etc. All these findings suggest that the configurational isomerisation of cyclohexane homologues takes place by an S_N2 mechanism identical with or similar to the mechanism described above for stereoisomeric dialkylcyclopentanes.

It may be supposed that such an S_N2 mechanism plays a role not only in the reactions of the classes of compounds discussed above, but also in many others. This hypothesis is based on the exo $\rightleftharpoons$ endo isomerisation of alkyl substituents in the series of bridged bicyclic hydrocarbons described by Plate and coworkers[116,117].

In conclusion, it should be noted that at the present time the stereochemical approach to certain catalytic reactions, in particular hydrogenation or hydrogenolysis, is comparatively widely employed. The studies of the hydrogenolysis of optically active compounds began by Bonner[118] and continued by Japanese investigators[119-122] are very promising in this connection. The structure of the initial compounds, the nature of the metal, its concentration in the catalyst, and sometimes the carrier employed influence the mechanism of hydrogenolysis, which, depending on these factors, can proceed via S_N1, S_N2, or S_i mechanisms. These studies have been analysed in Klabunovskii's review[5]. In this connection, the series of investigations by Balandin, Klabunovskii, and coworkers[123-125] of the structure of the active catalyst surface by the hydrogenation of molecules with a rigid steric configuration are also of undoubted interest.

The study of model reactions in which the starting materials undergo minimal changes (ortho–para conversion of hydrogen, configurational isomerisation, etc.) and the use for investigation of optically active and labelled compounds in combination with the latest physical techniques for the study of the catalyst itself constitutes new and promising approaches to the elucidation of the fine details of reactions on the surface of the catalyst.

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§ The special role of hydrogen as a non-stoichiometric reactant in a number of processes (configurational isomerisation, double bond migration in olefins, and others) has been discussed by Eidus and Ershov[114].

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