has clarified the distinction between daltonides and berthollides, azeotropes, eutectics, cryohydrates, etc.

We cannot overemphasise the importance of the work of Kurnakov and his students in rationalising pyrometallurgical processes, preparing a large number of important alloys, and exploiting the mineral (particularly salt) resources of our country.

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THE TRANSFORMATION OF HYDROCARBONS WITH MEDIUM-SIZED RINGS IN THE PRESENCE OF PLATINUM CATALYSTS

B.A.Kazanskii, E.S.Balenkova, and S.I.Khromov

The chemistry of cyclic compounds with rings of medium dimensions, containing 8–12 carbon atoms in the molecule, has developed considerably in recent years. The interest in these compounds results from the important part which they played in theoretical organic chemistry, due to a number of unique features characteristic of this class of compound. These features include the unique geometric shape of the molecule and the consequent possibility of interaction between atoms of the same molecule, not directly joined to one another. This interaction in medium-sized rings may take place through the ring (transannular interaction) and may be produced between hydrogen atoms attached to neighbouring carbon atoms (vicinal interaction). Both of these factors lead to an increased energy content in medium-sized rings; this has been called "non-classical" conformational strain and is responsible for a number of characteristic features in the chemical and physical properties.

Transannular reactions not only are characteristic of functional derivatives of medium-sized rings but also take place in the catalytic transformation of hydrocarbons with rings of medium dimensions over hydrogenation–dehydrogenation catalysts. In 1955, Prelog and coworkers [1] observed for the first time the transformation of hydrocarbons containing 9–18 carbon atoms in the ring, over a palladium catalyst at 400°C. Depending on the number of

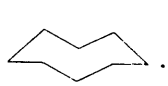
carbon atoms in the ring, removal of hydrogen gave various polycyclic, aromatic, and pseudo-aromatic hydrocarbons (indene, azulene, naphthalene, phenanthrene, etc. up to triphenylene). The hydrocarbons studied were divided into four groups, according to the nature of the transformations and the number of carbon atoms in the original ring:

(I) $C_5 + 4n$ C_9H_{18}; $C_{13}H_{26}$; $C_{17}H_{34}$
(II) $C_6 + 4n$ $C_{10}H_{20}$; $C_{14}H_{28}$; $C_{18}H_{36}$
(III) $C_7 + 4n$ $C_{11}H_{22}$; $C_{15}H_{30}$
(IV) $C_8 + 4n$ $C_{12}H_{24}$; $C_{16}H_{32}$

Hydrocarbons of group (I) are transformed into condensed systems with five-membered rings (for example, cyclononane forms indene). Of the hydrocarbons in group (II), cyclodecane gives azulene and naphthalene, and the others are converted into condensed compounds containing six-membered rings. Hydrocarbons of groups (III) and (IV) are converted into more complex condensed systems. For example, acenaphthene and acenaphthylene were found in the catalysate from cyclododecane.

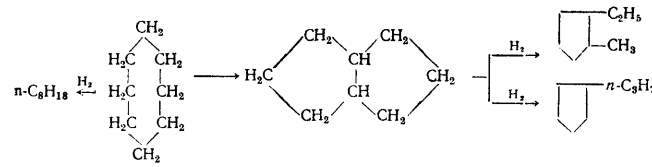
Prelog found only aromatic hydrocarbons in the reaction products. There is no doubt that by carrying out the reaction under different conditions, it is possible to find among them both primary and intermediate transformation products. The first stage of transannular dehydrocyclisation in alicyclic hydrocarbons with a medium-sized ring is probably C_5- or C_6-dehydrocyclisation[2] inside the ring. In this instance it would be expected that platinised carbon, which is a more specific dehydrocyclisation catalyst than palladised carbon, would be a more suitable catalyst for such transformations and that by carrying out the reaction at temperatures lower than those used in Prelog's work it would be possible to trap the products of the first stage of the transannular dehydrocyclisation, namely, such bicyclic hydrocarbons as hydrindane, decalin, perhydroazulene, etc.

As early as 1930, Zelinskii and Freiman[3] studied the behaviour of cyclo-octane in the presence of platinised carbon at 300°C and suggested that it is converted into bicyclo[3,3,0]octane (pentalane) and methylcycloheptane. From the modern viewpoint, the suggestion that pentalane is formed from cyclo-octane under these conditions is quite well-founded. In actual fact, according to modern conformational theories, cyclo-octane has the shape of a crown[4], in which four quasi-axial hydrogen atoms lie above the central plane of the eight-membered ring, and four lie below it: the atoms of each group of four are moved closer to one another towards the centre of the molecule; this on the one hand creates additional internal conformational strain and on the other hand facilitates the removal of the 1,5 hydrogen atoms when cyclo-octane is adsorbed on a catalyst surface at elevated temperature, as a result of which a transannular 1,5 C–C bond may be produced, with the formation of pentalane



In 1960 it was shown that on the surface of platinised carbon at 310°C cyclo-octane is almost completely converted into *cis*-pentalane, which then undergoes hydrogenolysis[5]. On a specially selected catalyst the yield of *cis*-pentalane can be increased to 70%.[6]

The reaction scheme is:



A small quantity of n-octane was found in the products of the transformation of cyclo-octane, so that the eight-membered ring undergoes direct hydrogenolysis, albeit to a very slight extent.

It might be assumed that the conformational characteristics of other multi-unit hydrocarbons would also play an important part in their transformations. Here, however, it must be borne in mind that the conditions of the reaction—elevated temperature and the presence of a catalyst—may lead to certain conformational changes in these cyclanes and the appearance of reaction products which do not come from their most stable conformations.

In 1960 an X-ray diffraction study was made of the structures of nine-, ten-, and twelve-membered rings[7-11]. The X-ray diffraction data were used to calculate the C–C–C valency angles, the torsion angles, and the length of the C–C bonds; this made it possible to obtain a picture of the most stable conformations of these rings and the position of the hydrogen atoms in the rings. It was found that the carbon framework of the cyclononane molecule is completely asymmetric, so that all 18 hydrogen atoms in it are non-equivalent. For practical purposes, however, Dunitz and Prelog[12] proposed their division into two groups: six intra-annular hydrogen atoms, directed into the ring, and twelve extra-annular Each of the six intra-annular hydrogen atoms approaches two others in space so that the shortest distance between them is about 1.8 Å (Fig. 1). This close positioning of the intra-annular hydrogen atoms facilitates their removal when the hydrocarbon molecule is adsorbed on a catalyst surface.

The ability of platinised carbon to catalyst the reactions of C_5- and C_6-dehydrocyclisation with the formation of five- and six-membered cyclanes and also condensed hydrocarbons with five- and six-membered rings suggests that when cyclononane is adsorbed on a catalyst surface, removal of the intra-annular hydrogen atoms on the first and fifth or third and eighth carbon atoms will take place readily, leading to the formation of hydrindane as chief reaction product.

In actual fact, the chief primary product of the transformations of cyclononane on platinised carbon at 300°C is

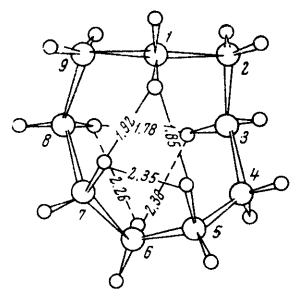
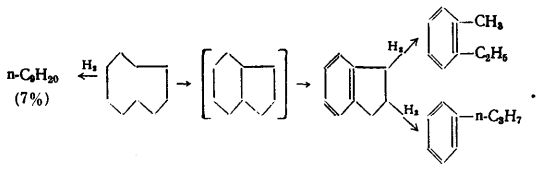


Fig. 1. Conformation of cyclononane.

hydrindane, which under the conditions of the experiment is immediately converted into indane. Hydrogenolysis of the five-membered ring in indane gives *o*-ethyltoluene and n-propylbenzene. For cyclononane a greater part is played by the second direction of the reaction—direct hydrogenolysis of the ring. The yield of n-nonane amounts to 7%.[13]

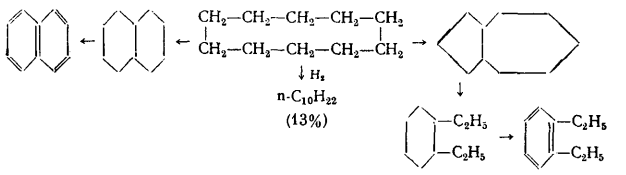
The cyclononane reacted according to the scheme:



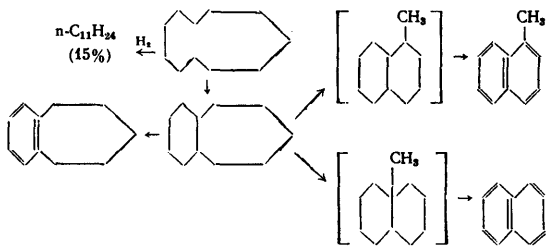
The cyclodecane molecule (Fig. 2) also has six intra-annular hydrogen atoms directed into the ring, and in this sense the geometries of the nine- and ten-membered rings show considerable similarity. Among the intra-annular hydrogen atoms, two pairs of atoms are moved together in the 1,5 position, and their removal under the reaction conditions should lead to the formation of decahydroazulene.

The products of the catalytic transformations of cyclodecane consisted of *cis*-decahydroazulene, 1,2-diethylcyclohexane, and 1,2-diethylbenzene, small quantities of *trans*-decalin and naphthalene, and n-decane. The formation of 1,2-diethylcyclohexane and 1,2-diethylbenzene can apparently be attributed to hydrogenolysis of the five-membered ring to decahydroazulene, with subsequent isomerisation of the seven-membered ring.

As expected from the conformational characteristics of cyclodecane, the chief direction of its transformations proved to be the transannular C_5-dehydrocyclisation into decahydroazulene. n-Decane—the product of the direct hydrogenolysis of the ten-membered ring—made up 13% of the weight of the catalysate[14]:

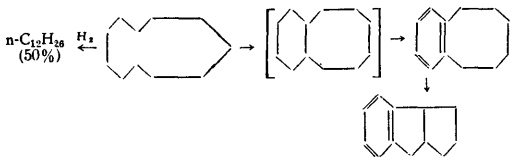


There are no published data on the conformational characteristics of an eleven-membered ring. Transannular reactions are characteristic of cycloundecane compounds, however, just as they are for 8–10-membered cyclic compounds[15]. Therefore cycloundecane apparently has transannular hydrogen atoms close to one another, so that for this compound, as for the cyclanes examined above, transannular dehydrocyclisation should take place readily. In contact with platinised carbon at 300°C, cycloundecane reacted to give 15% direct hydrogenolysis of the ring with the formation of n-undecane and dehydrocyclisation into *trans*-bicyclo[5,4,0]undecane, which under the conditions of the experiment was then converted into benzosuberane. The appearance of small quantities of α-methylnaphthalene and naphthalene in the catalysate can be attributed to isomerisation of the seven-membered ring into bicyclo[5,4,0]undecane with the formation of 1-methyldecalin and 9-methyldecalin, which then undergoes dehydrogenation under the conditions of the experiment:



Study of the structure of cyclododecane (Fig. 3) showed that there is no significant transannular interaction between opposite hydrogen atoms, and that the shortest distance between the hydrogen atoms is 2.1 Å. If it is assumed that transannular dehydrocyclisation takes place with the removal of the hydrogen atoms closest to one another, increase in the dimensions of the ring and increase in the distance between the transannular hydrogen atoms should decrease the ability of the cyclane to undergo transannular dehydrocyclisation.

In actual fact, it was found that the dehydrocyclisation of cyclododecane takes place to the extent of only 50%, with the formation of bicyclo[6,4,0]dodecane, which on dehydrogenation is converted into benzocyclo-octane; the latter, like cyclo-octane[5,6], is then converted into benzopentalane, the yield of n-dodecane amounting to 50%.[16]



Thus the catalytic transformations of hydrocarbons containing rings of medium dimensions in the present of platinised carbon at 300°C take place in two main directions:

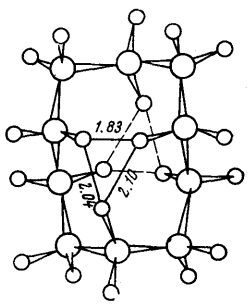


Fig. 2. Conformation of cyclodecane.

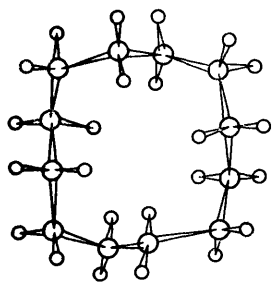


Fig. 3. Conformation of cyclododecane.

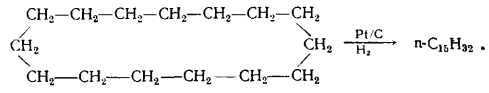
transannular dehydrocyclisation with the formation of condensed aromatic and non-aromatic hydrocarbons, and direct hydrogenolysis of the ring with the formation of normal paraffinic hydrocarbons. This last observation is of fundamental importance, since until recently hydrogenolysis in the presence of platinised carbon was known only for rings containing not more than five carbon atoms.

In 1962 it was shown that the products of the transformations of cycloheptane in the presence of platinised carbon at 300°C include n-heptane, from which it follows that the seven-membered ring also undergoes direct hydrogenolysis [17]. Liberman and coworkers [18] showed that cyclohexane does not undergo ring opening in the presence of a platinum catalyst, but hydrogenation of the six-membered ring is observed with ruthenium, iridium, and osmium, deposited on carbon.

The ability of the cyclane with a ring of medium dimensions to undergo hydrogenolysis in the presence of a platinum catalyst increases from cyclo-octane to cyclododecane; with the twelve-membered ring, the degree of hydrogenolysis increases sharply and the yield of normal alkane reaches 50%. The ability of the cyclane to undergo transannular dehydrocyclisation changes in the opposite sequence: the transannular dehydrocyclisation of cyclo-octane takes place to the extent of almost 100%, that of cycloundecane to the extent of 85%. and that of cyclododecane to the extent of only 50%. The structures of the resulting bicyclic hydrocarbons are determined by the conformational characteristics of the original cyclanes.

The hydrogenolysis and transannular dehydrocyclisation which take place in a number of medium-sized rings in the presence of a platinum catalyst are apparently competing reactions: for 8–10-membered cyclanes, because of their conformational characteristics, dehydrocyclisation takes place readily, and the rate of dehydrocyclisation is greater than the rate of hydrogenolysis, whereas with cyclododecane, which does not have such a favourable structure for dehydrocyclisation, the rates of the two reactions become commensurate. With large rings, the appreciable dimensions of the ring and the fact that there are no opposed hydrogen atoms at a short distance from one another should hinder intramolecular dehydrocyclisation, and hydrogenolysis may become the chief reaction.

As a representative of hydrocarbons containing rings with large dimensions, we took cyclopentadecane. It was found that cyclopentadecane in the presence of platinised carbon at 300°C in fact undergoes only hydrogenolysis of the ring with the formation of n-pentadecane as the only reaction product [19].



The dependence of the degree of hydrogenolysis on the number of units in the ring is shown in Fig. 4.

Usually, in the discussion of the reactivity of cyclic compounds containing rings with medium dimensions, allowance is made for the change in the strain, in addition to other factors characteristic of the given reaction. The problem of the strain in medium-sized rings is extremely complex. In its examination, allowance must be made for three factors: the distortion of the valency angles, producing Bayer strain, the energy of the torsion angles—Pitzer strain—and the transannular interaction of atoms which are not joined to one another.

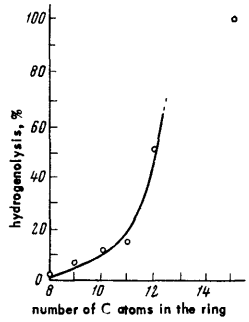


Fig.4. Dependence of the degree of hydrogenolysis on the number of C atoms in the ring.

X-Ray diffraction study of the structures of 8-, 9-, 10-, and 12-membered rings has provided a picture of the strain in these rings. The structure of the eight-membered ring has been described in less detail, but for the others, as already noted, the values of the C–C–C valency angles, the torsion angles, and the shortest distance between the transannular hydrogen atoms have been calculated.

From these data it may be concluded that among the medium-sized rings, the greatest strain should be shown by cyclononane and cyclo-octane, since they are characterised by considerable Bayer and Pitzer strain, and also by strain due to transannular interaction. Cyclodecane has almost no Pitzer strain, but its valency angles are much greater than tetrahedral, indicating appreciable Bayer strain. Cyclodecane is also characterised by strain due to transannular interaction. Unfortunately, the structure of cycloundecane has not been studied, but on the basis of the heat of combustion [20], which may give information on the strain in cyclic compounds, it may be concluded that cycloundecane is not free from strain, and that, like cyclodecane, it is apparently characterised by strain due to transannular interaction. X-Ray diffraction study shows that in cyclododecane there is no Pitzer or Bayer strain, nor significant transannular interaction. Cyclopentadecane is free from all forms of strain.

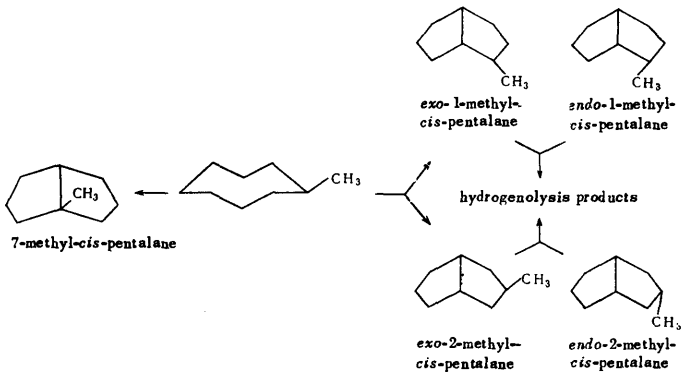
Examination of the above material in the light of modern views on ring strain indicates that the formation of a bicyclic hydrocarbon by intramolecular dehydrocyclisation removes the transannular strain produced as a result of the repulsion of opposite hydrogen atoms and hence is energetically favourable for 8–11-membered cyclanes. For cyclododecane, in which there is no significant transannular interaction, dehydrocyclisation will not be so energetically favourable as for the other cyclanes with medium-sized rings. In actual fact, cyclo-octane undergoes dehydrocyclisation to the extent of almost 100%, cyclononane to the extent of 93%, and cyclododecane to the extent of only 50%.

In hydrogenolysis, the chief role is apparently played not by the strain in the original molecule but by the strain produced in the transition complex when the cyclane molecule is adsorbed on the catalyst surface.

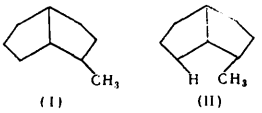
To investigate the influence of an alkyl substituent on the direction of the transformation of hydrocarbons with medium-sized rings, a study was made of the behaviour of methylcyclo-octane, methylcyclononane, and methylcyclodecane in the presence of platinum catalysts [21,22].

On platinised carbon at 300°C, methylcyclo-octane, like cyclo-octane itself, shows only slight (~ 1%) direct hydrogenolysis of the ring with the formation of isomeric methyloctanes. The chief reaction undergone by methylcyclo-octane under the above conditions is C_5-dehydrocyclisation, leading to the formation of all isomeric methyl-*cis*-pentalanes. Of these, 1-methyl-*cis*-pentalane is formed preferentially, and 2-methyl-*cis*-pentalane and 7-methyl-*cis*-pentalane are formed in smaller quantities. The catalysate also contains products of the hydrogenolysis of the methylpentalanes; to decrease the amount, the methylcyclo-octane was subjected to catalysis on a specially selected platinum catalyst containing 2% iron[23]. An interesting feature is that in this instance the formation of isomeric methylpentalanes in the same proportions as on platinised carbon is observed.

The ratio of methyl-*cis*-pentalanes formed by the transannular dehydrocyclisation of methylcyclo-octane does not depend on the nature of the platinum catalysts studied and is apparently determined by the conformational characteristics of the methylcyclo-octane molecule.

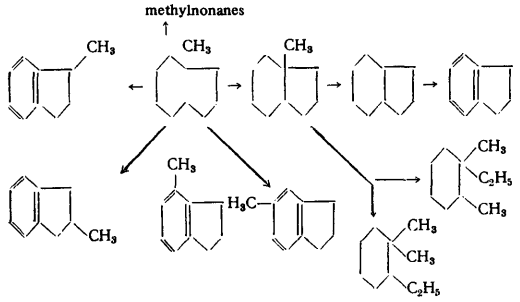


Another noteworthy feature is that, of the *exo*- and *endo*-1-methyl-*cis*-pentalanes formed, the *exo*-isomer predominates, whereas *exo*- and *endo*-2-methyl-*cis*-pentalanes are formed in comparable quantities. The preferential formation of the *exo*-form of 1-methyl-*cis*-pentalanes (I) relative to the *endo*-form (II) is apparently due to the characteristic features of the three-dimensional structure of this hydrocarbon. In the *endo*-form the methyl group and the hydrogen attached to the sixth carbon atom come so close together that the forces of repulsion between them make this form of the molecule more strained than the *exo*-form. In 2-methyl-*cis*-pentalane the *endo*- and *exo*-forms of the molecule have equally favourable arrangements of the methyl group, so that these isomers are apparently equally stable, and the *exo*- and *endo*-forms of 2-methyl-*cis*-pentalane are formed in almost equal quantities.



The chief primary product of the transformations of methylcyclononane in the presence of a platinum catalyst was *cis*-8-methylhydrindane; this hydrocarbon and the products of its secondary transformations made up ~ 50% of the weight of catalysate. 8-Methylhydrindane could be formed by the transannular dehydrocyclisation of methylcyclononane only if the methyl group is attached to a carbon atom with an intra-annular hydrogen atom which is moved closer, in the 1,5 position, to an intra-annular hydrogen atom of the opposite carbon atom. The removal of a methyl group in 8-methylhydrindane leads to the formation of hydrindane, and the dehydrogenation of the six-membered ring in hydrindane produces indane. Ethyldimethylcyclohexanes are formed as a result of the hydrogenolysis of the five-membered ring in 8-methylhydrindane.

Thus methylcyclononane is characterised by a type of transannular dehydrocyclisation which takes place preferentially with the participation of the hydrogen attached to the carbon atom of the ring carrying the substituent. The presence of 1-, 2-, 4-, and 5-methylindanes in the catalysate, however, indicates that other intra-annular hydrogen atoms, brought closer together in the 1,5 position, may also take part in this reaction. The catalysate contained isomeric methylnonanes, formed by the direct hydrogenolysis of the nine-membered ring in the same amounts as the n-nonane in the catalytic transformations of cyclononane.



The chief primary reaction of methylcyclodecane in the presence of platinised carbon is transannular dehydrocyclisation, which takes place in two directions: firstly, C_5-dehydrocyclisation takes place with the formation of methyldecahydroazulenes, and secondly, C_6-dehydrocyclisation takes place, producing methyldecalins and methylnaphthalenes. Like cyclodecane, methylcyclodecane is characterised to a greater extent by C_5-dehydrocyclisation than by C_6-dehydrocyclisation, since the products formed by the first reaction make up more than 70% of the total weight of transformation products.

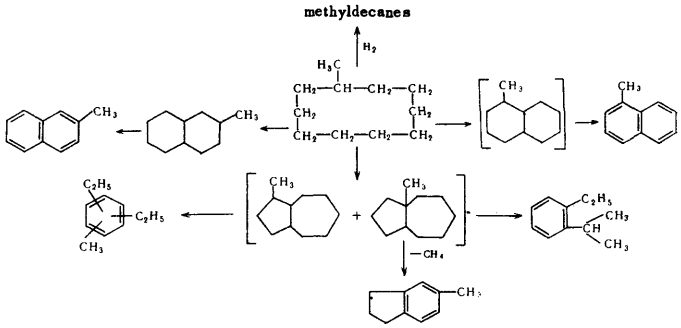
Methyldecahydroazulenes are unstable under the conditions of the experiment and undergo further transformation. Secondary transformations of the methyldecahydroazulenes

TABLE. Composition of the products of the transformation of methylcyclo-octane at 800°C.

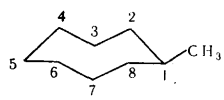
Hydrocarbons	Percentage concentration	
	Pt/C	Pt/Fe/C
Methyloctanes	1	>1
7-Methyl-*cis*-pentalane	8	13
endo-1-Methyl-*cis*-pentalane	6	8
exo-1-Methyl-*cis*-pentalane	34	35
endo-2-Methyl-*cis*-pentalane	11	15
exo-2-Methyl-*cis*-pentalane	17	18
Products of the hydrogenation of methyl-*cis*-pentalanes		
I- and 2-Methylpentalanes	12	11
7-Methylpentalane	11	

apparently lead to the formation of 1-ethyl-2-isopropylbenzene, which makes up almost half of the weight of the methylcyclodecane transformation products. Of all the possible isomers of methyldecahydroazulene, only 9-methyldecahydroazulene and 1-methyldecahydroazulene can lead to the formation of 1-ethyl-2-isopropylbenzene as a result of hydrogenolysis of the five-membered ring and isomerisation of the seven-membered ring. Secondary transformations of these hydrocarbons may also explain the presence of diethylmethylbenzene and 5-methylindane in the catalysate.

Thus the final products of the transformations of methylcyclodecane indicate that on transannular C_5-dehydrocyclisation of this hydrocarbon not all the isomeric methyldecahydroazulenes are formed to equal extents, and that 9-methyldecahydroazulene and 1-methyldecahydroazulene apparently predominate. The presence of isomeric methyldecanes in the catalysate indicates direct hydrogenolysis of the ten-membered ring. Comparison of the degrees of hydrogenolysis of cyclodecane and methylcyclodecane indicates that cyclodecane itself undergoes hydrogenolysis more readily than its homologue: the yield of paraffinic hydrocarbons for methylcyclodecane amounts to only 2% of the weight of transformation products, whereas for cyclodecane under the same conditions, 13% n-decane is formed:



Transannular dehydrocyclisation in the series of alkylcyclanes with medium-sized rings is directed in character: the preferential direction of this process is not determined by the hydrogen atom attached to the tertiary carbon atom of the ring but is apparently related to the conformational characteristics of the cyclanes. In fact, in the dehydrocyclisation of methylcyclo-octane, the formation of 1-methylpentalane predominates, whereas from methylcyclononane under the same conditions, the bicyclic hydrocarbon with angular arrangement of the methyl group is formed preferentially, and the dehydrocyclisation of methylcyclodecane apparently produces chiefly 9- and 1-methyldecahydroazulenes. In the transannular dehydrocyclisation of methylcyclo-octane



there are two possibilities for the formation of 1-methylpentalane: by the removal of two quasi-axial hydrogen atoms attached to $C_{(2)}$ and $C_{(6)}$ or $C_{(4)}$ and $C_{(8)}$, and one possibility each for the formation of 2- and 7-methylpentalane (removal of the hydrogen on $C_{(3)}$ and $C_{(7)}$ for 2-methylpentalane and on $C_{(1)}$ and $C_{(5)}$ for 7-methylpentalane). If it is assumed that these possibilities for the formation of methylpentalanes are equally probable, the quantity of 1-methylpentalane in the methylcyclo-octane catalysate should have been double the quantities of 2- or 7-methylpentalane. In fact, 1-methylpentalane predominates in the catalysate for this reaction.

In cyclononane (see Fig. 1) the substituents probably can occupy only the extra-annular positions. Data obtained by X-ray diffraction studies show that substituents are preferred among the extra-annular positions. An example is the position of the substituent on $C_{(1)}$. The preferential positioning of the methyl group in the nine-membered ring also apparently explains the preferential formation of 8-methylhydrindane in the transannular dehydrocyclisation of methylcyclononane. The methyl group is attached to the carbon atom carrying an intra-annular hydrogen atom which has been brought closer to the intra-annular hydrogen atom of the opposite carbon atom of the ring. The transannular dehydrocyclisation apparently takes place with the removal of the intra-annular hydrogen atoms which have been brought together with the production of a new C–C bond.

Analogous reasoning can be applied to methylcyclodecane, in which directed transannular dehydrocyclisation is also observed, with the preferential formation of 9- and 1-methyldecahydroazulenes as primary reaction products.

The transformations of hydrocarbons with medium-sized rings in the presence of a platinum catalyst take place in two independent directions: transannular dehydrocyclisation and direct hydrogenolysis of the ring. The first stage of the transannular dehydrocyclisation leads to the formation of a bicyclic hydrocarbon, whose nature is determined chiefly by the conformational characteristics of the original cyclane. Under the conditions of the experiment, bicyclic hydrocarbons undergo further transformations: aromatisation, hydrogenolysis of five-membered rings, and isomerisation of seven-membered rings, to give reaction mixtures with extremely complex compositions. For methylcyclanes with 8–10-membered rings, transannular dehydrocyclisation is directed in character; the preferential direction of the catalytic process is determined by the conformation of the original hydrocarbon.

With increase in the dimensions of the ring there is a decrease in the extent to which transannular dehydrocyclisation takes place and an increase in the extent to which hydrogenolysis takes place; for large rings, hydrogenolysis becomes the main direction of the transformations. These data show that hydrogenolysis is general in the chemistry of cyclic hydrocarbons: hydrogenolysis is the only direction of the transformations for rings containing not more than five carbon atoms, and takes place in addition to dehydrocyclisation in medium-sized rings.

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TEMPERATURE DEPENDENCE OF THE RATE OF GAS-PHASE REACTIONS

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1. INTRODUCTION

The rate constant of an elementary chemical reaction is usually expressed in the form of the Arrhenius equation:

$$k=A\exp(-E_0/kT) \qquad (1.1)$$

(where A and E_0 are constants) or of the formula

$$k = A_0T^{1/2}\exp(-E_0/kT), \qquad (1.2)$$

which follows from kinetic theory for when the activation energy is provided by the component of the kinetic energy of the relative motion of the interacting particles lying along the line of their centres[1]. Formula (1.2) can be obtained also in the more general example by assuming a particular dependence of the reaction cross-section upon the energy of relative motion[2]. Kassel[3] proposed also an empirical formula of the type:

$$k = CT^m\exp(-E_0/kT) \qquad (1.3)$$

($m > 0$), and gave some theoretical justification for it.

The dissociation rate constant is also frequently expressed in the form

$$k_d = A_0T^{-n}\exp(-D/kT), \qquad (1.4)$$

which takes account of the contribution of internal degrees of freedom to the activation of the molecule undergoing dissociation[1].

The rate constant of the recombination process, which is the reverse of the dissociation process, is most often described by the formula:

$$k_r = A_0T^{-m}. \qquad (1.5)$$

Whereas the formulae describing the rate constants of the dissociation and recombination processes have recently achieved some—but far from complete—theoretical justification, as discussed below, exchange processes on the other hand have hardly been investigated at all in spite of the fact that they are the commonest type of elementary reaction. Yet, it is possible to introduce some significant advances into the quantitative kinetics of exchange processes on the basis of the (still imperfect) theory of the transition state alone, and also on the basis of quantum statistics.

The main problem in the theoretical calculation of the rate constant is to evaluate the contribution of the various degrees of freedom and to make allowance for the perturbation of the equilibrium distribution brought about by the reaction itself. The transition state method avoids both these difficulties by assuming that the complicated energy exchange process can be described by the motion of the representative point along some reaction coordinate q_r whose choice is not strictly unique, whilst completely ignoring the perturbation of the equilibrium distribution of the reactants over the states. To some extent, correct allowance for these two factors can be made independently. First, we calculate the reaction cross-section σ_r as a function of the dynamic parameters of the partners during a collision—the initial vibrational states n_i and rotational states j, and also the relative velocity v of the colliding molecules. As a second step, the reaction rate R is calculated by averaging σ_r over all the n, j, v initial states by means of the expression

$$R = \int \sigma_r(n, j, v)\, v f(n, j, v)\, d\Gamma. \qquad (1.6)$$

Here $f(n, j, v)$ is the distribution function (in general, non-equilibrium) of the colliding molecules, normalised for the total number of reacting molecules. If the concentrations of the initial molecules are taken out of f as common factors, the reaction rate R can be expressed in the form

$$R = k(C_A)^\alpha(C_B)^\beta \qquad (1.7)$$

where k now has the significance of the rate constant of a reaction of order α with respect to reactant A, of order β with respect to reactant B, etc. The calculation of the