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STUDIES OF THE CHEMISTRY OF HYDROCARBONS AND THEIR CATALYTIC CONVERSIONS†

A. L. Liberman

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I. INTRODUCTION

In recent decades hydrocarbons have become more and more widely used in the chemical industry as most valuable raw materials and the petroleum industry has added the supply of such raw materials to its production of liquid fuels, the two developments giving rise to the petrochemical industry, based on much organic chemical research on various hydrocarbons and their reactions, as well as on an investigation of the composition of various types of petroleum. Russian scientists have played an enormous part in this research, so that petrochemistry has justifiably become traditional in Soviet chemical science. Soviet chemists and B.A.Kazanskii in particular, have contributed much new knowledge in this field.

The chief components of crude oil are paraffins, cyclopentanes, cyclohexanes, and aromatic hydrocarbons. Mutual transformations of cyclopentane hydrocarbons into paraffin ones and of paraffins into aromatic or cyclopentane hydrocarbons have been discovered in the past 25–30 years. A study has been made of the conditions favouring the conversion of paraffins into the industrially important unsaturated hydrocarbons as well as of the hydrogenation of diene and aromatic hydrocarbons under ordinary and high pressures. The laws governing the conversion of gem-substituted cyclohexanes in the presence of various catalysts have been elucidated and new ways found for the preparation of paraffins from carbon dioxide and hydrogen. Some of these reactions were discovered and studied in detail by Kazanskii and his school, who also made numerous new and original contributions to the study of the other reactions concerned. Recently much interest has been shown in the hydrocarbons with three- and four-membered rings as well as those with more than six-carbon atoms in the ring. Here the contribution of Kazanskii and his followers has also been very important. One of the analytical methods (the so-called combined

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method) developed for the determination of the composition of the petroleum part of crude oil was devised with the active participation of Kazanskii and his colleagues and was based on many years' work on the synthesis of some 200 individual hydrocarbons of high purity and the study of their Raman spectra. This method is widely used in Soviet laboratories and in some of the People's Democracies.

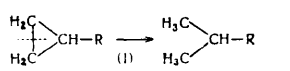
This article is a current review of some of the problems of the chemistry and catalytic reactions of hydrocarbons with particular reference to the work of Kazanskii and his school.

II. CATALYTIC HYDROGENATION OF CYCLIC HYDROCARBONS

Reactions in which catalytic hydrogenation of cyclanes led to the formation of paraffins attracted attention many years ago. These reactions have been known for some time in the case of three- and four-membered rings: in an atmosphere of hydrogen cyclopropane is converted to propane at 180° in the presence of nickel on pumice[1], at 0° in the presence of nickel on kieselguhr[2], and at 25° in the presence of platinum[3]. The same reaction occurs with the homologues of cyclopropane[4,5,6]. Cyclobutane and its homologues also undergo hydrogenation in the presence of nickel and platinum, giving paraffin hydrocarbons[1,7,8]. These reactions were long thought to be associated with the considerable Bayer's strain in three- and four-membered rings and have even been regarded as proof of Bayer's hypotheses. However, it was subsequently shown that cyclopentanes, free of Bayer's strain, underwent hydrogenation relatively readily, and quite recently cyclanes with an even larger number of carbon atoms in the ring (from 8 to 10 at any rate) have been found to undergo this reaction.

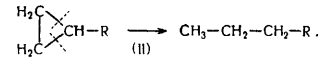
Kazanskii first discovered hydrogenation of the five-membered ring as a student in N. D. Zelinskii's laboratory, where extensive work was carried out on the various catalytic reactions of hydrocarbons. He and his own students then studied this reaction in detail using cyclopentane and its homologues; they also discovered the hydrogenation of cyclanes with still larger numbers of carbon atoms in the rings. Kazanskii also reinvestigated the previously discovered analogous reactions of small rings, establishing new and important facts and finding explanations for some of the very contradictory data provided by earlier workers.

Cyclopropanes. Hydrogenation of cyclopropane shows a noteworthy feature in the wide variation of the requisite experimental conditions, depending on the catalyst used (complete conversion at 0° with kieselguhr and at 180° with nickel on pumice). Other data are equally contradictory. According to some authors hydrogenation of cyclopropane requires a higher temperature than that of its homologues[9], whereas other authors claim the exact reverse[4,5,6]. Some authors state that the hydrogen adds on to the ring carbon atoms carrying the most hydrogen atoms[4,6]:



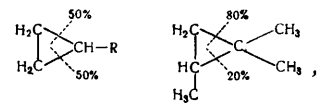
(I)

whereas others consider that the ring opens at the least hydrogenated carbon atoms[10]:

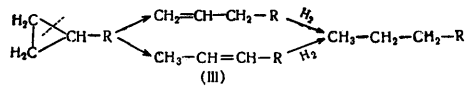


(II)

Kazanskii, Lukina, *et al.* have shown that these contradictions are only apparent, since two different reactions can take place under the conditions of hydrogenation. Hydrogenation itself occurs[11,12] with opening of the ring in accordance with scheme (I); this is especially clear-cut when platinised charcoal is used. With catalysts such as palladised charcoal or platinised kieselguhr some paraffins are always obtained which would appear to be formed in accordance with scheme (II)[13,14]. Kazanskii and his co-workers, however, showed that the process was more complex, the alkyl cyclopropanes undergoing isomerisation to open-chain olefines[15,16,17] when the following catalysts are employed: silica gel (~50°), aluminosilicates (~50°), kieselguhr (120°), pumice (170°–200°) and activated charcoal (~200°), the ring always opening at the bonds next to the least hydrogenated carbon atom in the ring:



the bond between the most hydrogenated carbon atoms remaining intact. If there is a double bond next to the ring the initial isomerisation is considerably more intense and is accompanied by immediate polymerisation of the resulting dienes[18]. The polymer which is deposited on the catalyst poisons it rapidly and completely, thus preventing further isomerisation. The list of catalysts above indicates that not all the carriers used for the catalysts are inert, and therefore they may induce isomerisation themselves. The olefines thus formed add on hydrogen to give the appropriate paraffins:



(III)

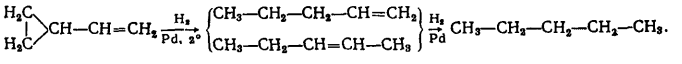
which are in fact the paraffins which are suggested by scheme (II). Thus the apparent contradictions mentioned above are resolved by competition between reactions (I) and (III). Platinised charcoal is so highly selective for cyclopropane hydrogenation because the rate of hydrogenation is particularly high in the presence of platinum, whereas the rate of isomerisation on activated charcoal is very low. In the case of platinised kieselguhr the carrier favours a relatively higher rate of isomerisation, and so the yield of scheme (III) products becomes appreciable. The ratio is shifted still further towards scheme (III) when the other catalysts mentioned are used.

Particularly important in the work of Kazanskii's school are the studies of the hydrogenation of the cyclopropane hydrocarbons with a double bond or a benzene ring adjacent to the three-membered ring[19-22].

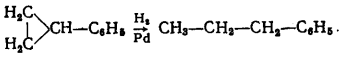
Modern theories claim that the structure of a three-membered ring allows some semblance of a π-electron cloud in the plane of the ring along its perimeter[23,24]; consequently the π-electron cloud of the adjacent double bond or benzene ring can interact with that of the three-membered ring. Spectroscopic investigation of such

compounds has repeatedly confirmed the resemblance of these systems to conjugated ones, being close to π-π- than to σ-π-conjugation. For conjugation to occur, the axes of the π-clouds should be parallel or almost parallel.

One of the characteristic properties of such systems is the ease of their hydrogenation with ring opening under conditions which leave the three-membered ring of the alkyl cyclopropanes intact, the specific catalyst for this reaction being palladium black. This catalyst gives smooth hydrogenation of vinyl- and isopropenyl-cyclopropanes with the addition of two moles of hydrogen; experiments with incomplete hydrogenation have shown that the hydrogen adds initially not to the double bond but to the C–C bond in the ring adjacent to the substituent:



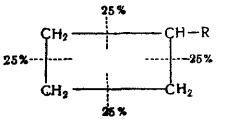
Such hydrogenation occurs when an unsaturated group, including the carbonyl group, is adjacent to the ring. In this case, as in that of the phenylcyclopropanes, the hydrogen adds on to the three-membered ring:



The properties of diphenylcyclopropanes indicate that the extent of conjugation of the phenyl and cyclopropyl rings depends on steric factors: conjugation is more marked in the case of *trans*-1,2-diphenylcyclopropane than in the *cis*-isomer, where steric hindrance displaces the phenyl substituent from the position most advantageous for conjugation. No conjugation can take place in 1,1-diphenylcyclopropane, where the axes of the π-electron clouds of the three-membered and the phenyl rings cannot be parallel. This has been substantiated by Raman spectra and by the fact that this substance does not add on hydrogen in the presence of palladium [25,26,27].

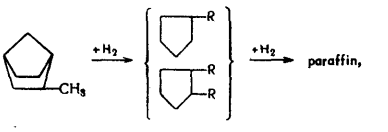
Cyclobutanes. Until recently little had appeared on the hydrogenolysis of the cyclobutane series of hydrocarbons, with total absence of comparative data on the hydrogenation of these compounds and cyclopropanes and cyclopentanes. This gap has been substantially filled by Kazanskii's school: it was shown [28] that under strictly comparable conditions, and using the same amount of catalyst, the three C_5H_{10} hydrocarbons with different rings — ethylcyclopropane, methylcyclobutane, and cyclopentane — undergo hydrogenation at different rates. Whereas at 260° cyclopentane only begins to undergo hydrogenation, methylcyclobutane is completely hydrogenated. The hydrogenation of ethylcyclopropane is complete even at 60°.

The orientation of hydrogenation was not as specific for alkylcyclobutanes as for alkylcyclopropanes, the former undergoing fission in all four ways with equal ease [28,29]:

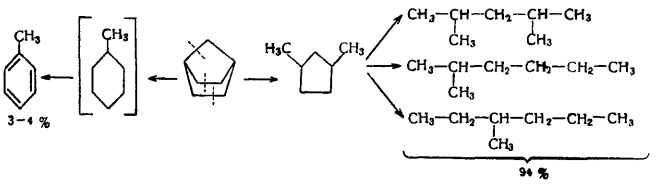


Alkylcyclobutanes are very stable to isomerisation catalysts, yielding only traces of cyclopentane hydrocarbons at ~250°, with aluminosilicates. This stability declines sharply, however, if there is a double bond adjacent to the ring. Kazanskii and his coworkers [30,31] showed that isopropenyl- and isopropylidene-cyclobutanes could isomerise in the presence of silica gel and kieselguhr with almost the same ease as alkylcyclopropanes. Despite this similarity, alkenylcyclobutanes give no evidence of conjugation, either during the specific hydrogenation reaction in the presence of palladium, or in their Raman spectra.

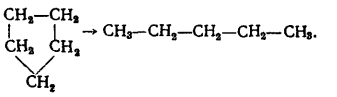
Cyclopentanes. Hydrogenation of cyclopentanes was first discovered in 1934 during an attempt to find out whether the six-membered ring of 2-methylbicyclo[2,2,1]-heptane could be dehydrogenated [32]. It was found that at 300°, with platinised charcoal, hydrogen was not split out, but added on. The authors suggested cleavage of the five-membered ring according to the scheme:



which was later confirmed by Kazanskii *et al.* [33] by fractional analysis of the hydrogenation products from bicyclo[2,2,1]heptane:

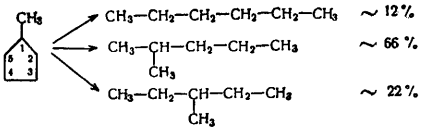


This scheme was subsequently confirmed with cyclopentane which was converted to n-pentane under the same conditions:

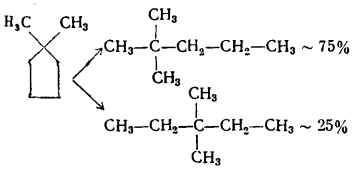


This led to a series of studies in which the hydrogenation of the five-membered ring was fully confirmed. At first only the fact of hydrogenation was established without detailed investigation of the reaction products and therefore without discovering which bonds underwent preferential cleavage. Hydrogenation of the five-membered ring was shown to occur in methyl-, ethyl-, and n-propyl-cyclopentanes [34], in n-butyl-, s-butyl-, and isoamyl-cyclopentanes [35,36], in n-hexylcyclopentane [36], and in n-nonylcyclopentane [38].

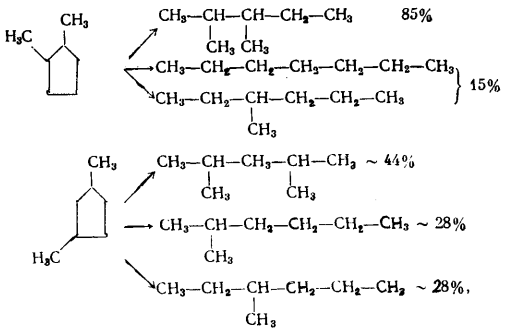
The orientation and kinetics of cyclopentane hydrogenation could be investigated more precisely with the help of Raman spectra and accurate fractionation. This enabled Kazanskii *et al.* [39] to show as early as 1941 that hydrogenation of ethyl- and n-propyl-cyclopentanes involved all the five bonds in the ring but with varying ease. The lowest yield was that of normal paraffins, indicating that the ring bond adjacent to the substituent is the most stable. Even more conclusive results were obtained with methylcyclopentane [40]:



Thus the 2–3 and 4–5 bonds rupture most easily, the 3–4 bond with rather more difficulty (it must be borne in mind that there is only one of these bonds in the molecule, so that the probability of finding products of its fission is half that expected in the case of the 2–3 and 4–5 bonds), the bonds adjacent to the methyl group being still more difficult to break. It is even more difficult to break bonds 1–2 or 1–5 in 1,1-dimethylcyclopentane[41], the other bonds behaving similarly to the previous case:

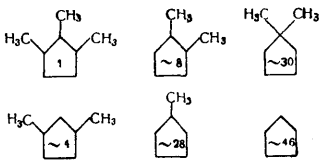


This was also confirmed for 1,2- and 1,3-dimethylcyclopentanes[42],



as well as for 1,2,3-trimethylcyclopentane[43], which yielded mainly 2,3,4-trimethylpentane.

These already fairly precise studies showed that the rates of hydrogenation of these hydrocarbons were closely related to their molecular structure, decreasing with an increase in the number of ring bonds screened by methyl groups. To verify this, Kazanskii *et al.* investigated the rates of hydrogenation of a number of hydrocarbons of the cyclopentane series under comparable conditions[42]. If the rate of hydrogenation of 1,2,3-trimethylcyclopentane is taken as unity, the rates for the other compounds are given by the values marked within their rings in the following figure:



Kinetic studies on the hydrogenation of cyclopentane on platinised charcoal[44] showed that the catalyst's activity at first declines fairly appreciably until a certain value is reached and then remains constant, suggesting that the most active centres of the catalyst are also the least stable. Once they become poisoned the catalyst surface becomes sufficiently constant to allow kinetic measurements. Kazanskii and Bulanova found that the energy of activation of cyclopentane hydrogenation was 35 kcal mole^{-1}.

Attempts made by Kazanskii and his coworkers to find other catalysts for the reaction at atmospheric pressure failed. Palladised charcoal was quite inactive[45,46]; nickel on alumina or kieselguhr did open the five-membered ring, but at the same time caused considerable destructive hydrogenation, both of the initial hydrocarbon and the reaction products, with the formation of methane and other low-molecular hydrocarbons[36,40,46], and so far platinum is the only known selective catalyst for cyclopentane hydrogenation.

Two hypotheses have been proposed for the reaction mechanism. The earlier one[47] was based on Balandin's multiplet theory, according to which cyclopentane is adsorbed on the surface of the catalyst and the interaction with hydrogen occurs as a typical doublet reaction. This, however, fails to explain the failure of n-pentane or cyclohexane to undergo hydrogenation, since they also can be adsorbed on the surface of the platinum catalyst and could then react by the same doublet mechanism. Kazanskii, Liberman, and Plate[48] suggested a different scheme, also based on the multiplet theory. It is feasible that the hydrocarbon molecules could become attached on the platinum surface by more than two carbon atoms, which in the case of n-pentane and cyclopentane could be all five. If it is assumed that the carbon atoms are adsorbed on the lattice sites preferred by platinum during crystal growth, then the distances between all the carbon atoms in the n-pentane molecule will remain unchanged when they are all involved in adsorption, and only the valency angles will increase to 120°. Distortion of the cyclopentane molecule in such an adsorption process would be much more marked and one of the five C–C bonds would necessarily be stretched. Rupture of this extended (and therefore weakened) bond and the addition of hydrogen follow the doublet scheme of the multiplet theory, but in order to achieve the ncessary molecular deformation, the latter must first be adsorbed at an active centre forming a complete sextet. For this reason the theory is called the sextet–doublet mechanism.

Further details of the studies of Kazanskii and his coworkers on the hydrogenation of the five-membered ring are given in a review article[49].

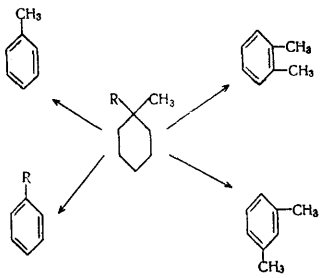
Cyclohexanes. The six-membered ring of the cyclohexane hydrocarbons cannot undergo hydrogenation in the presence of platinised charcoal. This had been supposed to be caused by purely kinetic factors, the rate of dehydrogenation of the cyclohexanes to aromatic hydrocarbons under the conditions employed being much higher than the rate of hydrogenation. However, Kazanskii and Liberman[50] refuted this suggestion. They placed 1,1-dimethylcyclohexane in contact with platinised charcoal in a large excess of hydrogen at 300°. This hydrocarbon is not as readily dehydrogenated as cyclohexanes without the geminal grouping, and under the conditions described it was converted into aromatic hydrocarbons with great difficulty. Nevertheless, although over 70% of the hydrocarbon remained unchanged, no signs of any products of hydrogenation were found in the product. The inability of cyclohexane hydrocarbons to undergo hydrogenation is thus connected with peculiarities of their structure.

Cycloheptanes, etc. Hydrogenation has not so far been observed in the case of cycloheptanes, nor in cyclanes with 8–10 carbon atoms in the ring until Kazanskii *et al.*[51] found that in the presence of nickel on kieselguhr at the relatively low temperature of 200° cyclo-octane gave a considerable yield of n-octane. They have also shown[52,53] that cyclononane and cyclodecane undergo hydrogenation to a greater or lesser degree in the presence of platinised charcoal at ~300°, yielding the corresponding normal paraffins.

III. CATALYTIC CONVERSIONS OF GEMINAL--DISUBSTITUTED CYCLOHEXANES USING PLATINUM AND ALUMINIUM SILICATE CATALYSTS

In 1947 Kazanskii and Liberman[50] showed that 1,1-dimethylcyclohexane, previously believed[54] to be chemically too stable to undergo aromatisation by catalytic dehydrogenation over platinum, could be converted to toluene and *o*- and *m*-xylenes using platinised charcoal at 300°. This reaction was then studied more widely[55,56,57] with a number of 1-methyl-1-alkyl- (or cycloalkyl-)cyclohexanes, using platinised charcoal at 320°, and the relative stability of the 1,1-dialkylcyclohexane series of compounds to catalytic action of platinum was confirmed, most of the hydrocarbons involved undergoing conversion to the extent of only 40–60%.

The catalytic reaction of these compounds occurs by splitting off of one alkyl group, usually the smaller one, to form monoalkylbenzenes, the tendency to split off diminishing with increasing length of the carbon chain in the radicals in the case of the longer straight chains. Small amounts of *o*- and *m*-xylenes are also formed, evidently as the result of toluene methylation:



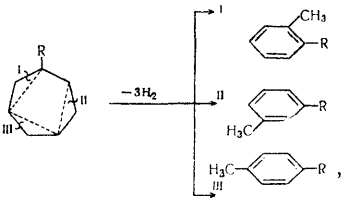
where R = C_2H_5; C_3H_7; C_4H_9.

The nature of the radical attached to the ring carbon atom also plays a considerable part in this catalytic aromatisation[58,59,60]. 1,1-Disubstituted cyclohexanes with two adjacent quaternary carbon atoms, of which one or both is in the six-membered ring (*e.g.* 1,1′-dimethyldicyclohexyl, 1-methyl-1-t-butylcyclohexane, 1,1′-diethyldicyclohexyl), undergo aromatisation readily and almost completely; the bond between the quaternary carbon atoms breaks with the greatest ease, giving toluene as the main reaction product in the case of the first two hydrocarbons, and ethylbenzene in the case of 1,1′-diethyldicyclohexyl.

The catalytic conversions of a series of 1-methyl-1--alkylcyclohexanes have been studied[61-65] using aluminosilicate catalyst at 500°. The reactions include hydro--cracking, methylation, dehydrogenation, isomerisation of the six-membered ring to a five-membered one, and disproportionation of hydrogen. The main reaction products are aromatic hydrocarbons (benzene, toluene, xylenes, and trimethylbenzenes), together with smaller amounts of naphthenes with five- and six-membered rings. The catalytic conversion increases with increasing number of carbon atoms in the alkyl substituent, rising from 42% in the case of 1,1-dimethylcyclohexane to 84% in that of 1-methyl-1-butylcyclohexane. 1-Methyl-1-phenylcyclohexane undergoes this type of catalytic conversion very readily, giving a considerable amount of a mixture of aromatic hydrocarbons (benzene, toluene) and naphthenes (predominantly mono- and di-alkylcyclopentanes), even at 350°.

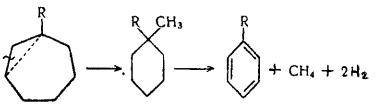
IV. CATALYTIC CONVERSIONS OF SEVEN- TO TEN--MEMBERED CYCLANES OVER PLATINISED CHARCOAL

Although the catalytic conversions of seven- to ten--membered cyclanes under hydrodehydrogenation catalysis conditions are of interest in connection with the special chemical properties of compounds with 8–12 carbon atoms in the ring (transannular reactions), until recently they have not been studied extensively. Prelog and Schenker investigated the behaviour of a series of such cyclanes in the presence of palladised charcoal and showed that transannular cyclisation gave aromatic hydrocarbons with condensed rings, *e.g.* cyclodecane yielded naphthalene and azulene[66]. However, they only examined the aromatic reaction products. Kazanskii and his school made much fuller studies on the contact conversions of cycloalkanes with larger than six-membered rings, using platinised charcoal and certain other catalysts. The hydrogenation of these rings has already been mentioned, but other reactions were found to occur in the course of these investigations[67-69] on a series of alkyl-, cycloalkyl-, and aryl--cycloheptanes. When methyl-, ethyl-, n-propyl-, or n-butyl-cycloheptanes are passed over platinised charcoal at 320° the seven-membered ring is isomerised to a six--membered one with the formation of isomeric methylalkylcyclohexanes and then a mixture of *o*-, *m*-, and *p*-methylalkylbenzenes (chiefly the *o*-isomer) as the result of dehydrogenation:



where R = CH_3; C_2H_5; C_3H_7; C_4H_9.

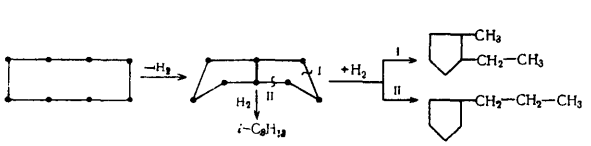
An interesting new observation is that under these conditions 1-methyl-1-alkylcyclohexanes are formed; they undergo partial conversion to alkylbenzenes, but the main bulk remains unchanged and they can be isolated from the products:



The yield of the corresponding 1-methyl-1-alkylcyclohexanes increases (from 21 to 29% of catalyst weight) as the radical becomes more complex (from C_1 to C_4) which is connected with the increasing stability of 1-methyl-1--alkylcyclohexanes to the catalytic action of platinum with increasing complexity of the alkyl substituents.

Kazanskii, Khromov, and Shokova studied the behaviour of cyclo-octane in the presence of such hydro- and dehydro--genation catalysts as platinised or palladised charcoal[70], nickel deposited on kieselguhr[51], and alumina-chromite catalyst[71]. The main reaction over platinised charcoal at 310° (without a carrier gas) is transannular C_5-dehydrocyclisation (*i.e.* dehydrocyclisation with the formation of a five-membered ring, *vide infra*, section on dehydrocyclisation) of cyclo-octane, with the formation of *cis*--bicyclo[3,3,0]octane (*cis*-pentalane), the yield of the products of hydrogenation of one and two five-membered rings

in pentalane being smaller. The yield of the latter rises sharply when the reaction is carried out in a stream of hydrogen:

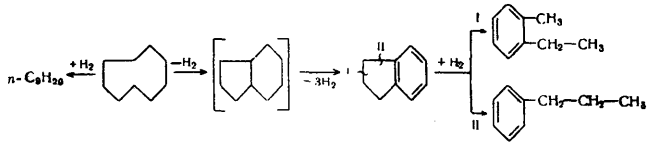


Hydrogenation of the pentalane formed was inhibited by using an iron-platinum catalyst increasing the pentalane yield to 75%, making it a practicable preparative method for this relatively inaccessible hydrocarbon.

When cyclo-octane is passed over 50% nickel on kieselguhr at 200° in a stream of hydrogen it reacts in three main directions: (1) hydrogenation to n-octane; (2) transannular C_5-dehydrocyclisation giving *cis*-pentalane; (3) stepwise isomerisation to hydrocarbons with seven-, six-, and five-membered rings. The quantitative ratio of the reaction products is affected substantially by the experimental temperature: at 200° reaction (1) predominates, whereas at 250° reaction (2) is most conspicuous.

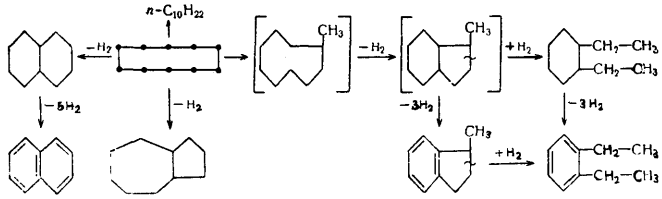
When cyclo-octane is passed over an alumina-chromite catalyst at 420° in a stream of hydrogen, the reaction products are *cis*-pentalane, ethyl benzene, and *o*-, *m*-, and *p*-xylenes, all of which are, in the authors' view, connected with transannular dehydrocyclisation of cyclo-octane.

Cyclononane undergoes transannular dehydrocyclisation over platinised charcoal at 300° to form perhydroindane[52], which is then dehydrogenated to indane, and the latter is partially converted by hydrogenation of the five-membered ring to *o*-methylethylbenzene and n-propylbenzene. Moreover, as already mentioned, the nine-membered ring undergoes direct hydrogenation to n-nonane (7% of catalyst weight).



Kazanskii *et al.*[53] found that under similar experimental conditions cyclodecane also shows dehydrogenation, hydrogenation, and ring isomerisation during its catalytic conversions. As a result of transannular C_6-dehydrocyclisation of cyclodecane, which passes through the initial stage of decalene formation, naphthalene is obtained as one of the main products of catalysis. Transannular C_5-dehydrocyclisation leads to *cis*-perhydroazulene — a bicyclic hydrocarbon with a five- and a seven-membered ring. n-Decane is formed by direct hydrogenation of cyclodecane. Part of the latter apparently isomerises to methylcyclononane, which is converted by transannular dehydrocyclisation first to 1-methylhydrindane and then to 1-methylindane. The five-membered ring in the greater part of the 1-methylhydrindane and 1-methylindane formed undergoes further hydrogenolysis, giving 1,2-diethylcyclohexane and *o*-diethylbenzene, which constitute a substantial part of the catalysate. No azulene is formed in the presence of platinised charcoal within this temperature range.

The above data on the conversions of cyclodecane can be represented by the following scheme:

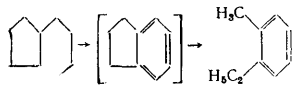


V. HYDROCARBON DEHYDROCYCLISATION REACTIONS

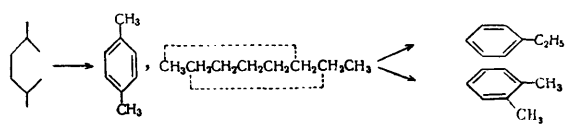
At present two types of dehydrocyclisation of hydrocarbons with catalytic closure of their open chain through dehydrogenation are known. The open chain may either belong to an aliphatic hydrocarbon or be a sufficiently long side chain of a cyclic hydrocarbon such as an alkylbenzene. Chronologically, the first type of dehydrocyclisation is the aromatisation of aliphatic hydrocarbons (or cyclic ones with a sufficiently long side chain) designated by Kazanskii and Liberman[72,73] as C_6-dehydrocyclisation from the number of carbon atoms constituting the newly-formed ring. The second type is C_5-dehydrocyclisation (using the same authors' terminology) giving rise to hydrocarbons with a five-membered ring, *e.g.* cyclopentane hydrocarbons from paraffins.

1. C_6-Dehydrocyclisation

Aromatisation of paraffin hydrocarbons on platinised charcoal discovered concurrently and independently a quarter of a century ago in three Soviet laboratories[74-76], immediately stirred the interest of chemists abroad, and was later the subject of numerous investigations both at home and abroad. This discovery stemmed from the studies of the hydrogenation of cyclopentane hydrocarbons, where aromatic hydrocarbons, which are not formed in similar reactions undergone by the lower homologues of cyclopentane, were found by Kazanskii and Plate[74] in the products of butylcyclopentane hydrogenolysis. Analysis of all the data suggested that under the experimental conditions used closure of a six-membered ring occurred to give a benzene ring:



The possibility of ring closure was verified by passing di-isobutyl and n-octane over platinised charcoal. The first gave *p*-xylene and the second ethylbenzene and *o*-xylene, two ways of ring closure being possible:



Later a series of other paraffins[77,78] of normal- and iso-structure was subjected to aromatisation over platinised charcoal at 260°–315°.

Aromatisation of paraffin hydrocarbons on chromic oxide at 450°–470° was discovered by Moldavskii and Kamusher[75] and on a chrome-copper-phosphate catalyst at 500°–550° by Karzhev *et al.*[76] Aromatisation with oxide catalysts is accompanied by side reactions, such as cracking and coking. Since no destruction occurs during reactions on platinum catalyst, it has become a useful means of investigating the mechanism of catalytic conversions of hydrocarbons, including their dehydrocyclisation, which was studied later by Kazanskii and Liberman. Work on di-isobutyl[79] showed that on platinised charcoal the energy of activation of C_6-dehydrocyclisation and dehydrogenation of cyclohexane was practically identical (16.3 and 16.1 kcal mole^{-1} respectively). However, the rate of the second reaction is considerably higher than could have been explained by a larger number of active centres on which this reaction takes place. Further studies of the mechanism of dehydrocyclisation[80] showed that on platinised charcoal dehydrocyclisation occurs in two stages:

paraffin hydrocarbon → cyclohexane hydrocarbon → aromatic hydrocarbon.

This is confirmed by the occurrence of 1,1-dimethylcyclohexane in the products of aromatisation of 3,3-dimethylhexane; this product undergoes further conversions, previously investigated[50].

The practical and industrial implications of the aromatisation of hydrocarbons became apparent at a very early stage, and during 1938–1939 Kazanskii and his collaborators undertook an extensive survey of over 30 oxide catalysts (chromium, vanadium, uranium, thorium, aluminium, and others). They obtained considerable yields of aromatic hydrocarbons[81–86] from the aliphatic hydrocarbon fractions of Syntholǂ. This work laid the foundations for the selection of catalysts for aromatisation and clarified the action of individual oxides and the marked influence of the carriers (aluminium oxide, silica gel, activated charcoal, calcined chromic oxide) on the formation of a dehydrocyclising catalyst. In thorium catalysts (on aluminium oxide and activated charcoal) a product of catalytic conversion during coking was found to activate the heterogeneous catalyst. In all the other cases, both in this work and in later investigations, the more usual poisoning of dehydrocyclisation catalysts by surface coking was encountered. This phenomenon was studied in greater detail[87] during investigation of the effect of the pressure used in the preparation of aluminomolybdenum catalyst on its properties; when this pressure was increased from 2000 to 20 000 atm the efficiency of the catalyst (yield of aromatic products per unit volume of catalyst per hour) increased slightly, although the specific activity (yield of aromatic products per unit weight) dropped since the density of the dry catalyst had increased. The same was observed in dehydrogenation of cyclohexane. Coke poisoning of catalyst during dehydrocyclisation diminishes as the catalyst compacting pressure is increased.

Recently active aluminochromate catalysts have been reinvestigated in detail. It was found[88] that with an active catalyst giving up to 70% aromatic products from heptane at 515° and able to work without regeneration for up to 24 h, the dehydrocyclisation occurs outside the kinetic region. Introduction of various alkali and alkaline-earth elements into the catalyst revealed appreciable differences in the activity of different samples[89,90]. Most of these elements (excluding lithium, beryllium, and magnesium) activate the aluminochromite catalyst in dehydrogenation of cyclohexane and dehydrocyclisation of n-heptane. Maximum activating action in dehydrocyclisation is exhibited by rubidium among the alkali elements and by strontium among the alkaline-earth ones. Addition of potassium to pure chromic oxide catalyst had the opposite effect[91]: addition of 0.23 wt.% K_2O inhibited the dehydrocyclisation of n-heptane and dehydrogenation of cyclohexane, but only reduced the yield of aromatic products from hept-1-ene to two-fifths. The same effect occurred on addition of an equivalent amount of phosphoric acid. These findings suggest that the addition of these substances to the chromium catalyst affects the first stage of the catalytic process — the chemisorption of the saturated hydrocarbons on chromic oxide.

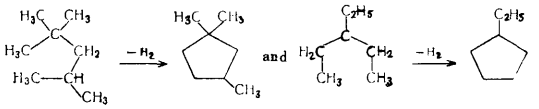
The growing requirements of the petrochemical industry for benzene and the presence of large deposits of n-hexane in the oil-bearing regions of the Soviet Union have made the preparation of benzene by dehydrocyclisation of petroleum hexane a project of practical interest, which has been studied by Kazanskii *et al.*[92] Like heptane, pure n-hexane at 550° gives a high yield of benzene during 24 h of continuous catalysis (without regeneration). The aromatisation of petroleum fractions was complicated by the presence of isohexanes and methylcyclopentane, which lowered the yield of benzene and increased coking. The role of the individual components in the process of aromatisation of narrow fractions isolated from petroleum was investigated, and revealed the practicability of obtaining benzene from hexane fractions of rectified petroleum using aluminochromite catalyst. Additional information was also gained about the dehydrocyclisation reaction; thus, for a given catalyst, a constant ratio was found to exist between the yields of benzene and of coke over a wide range of temperature and rates of passage of hexane.

2. C_5-Dehydrocyclisation

This reaction of paraffin hydrocarbons in the presence of platinised charcoal was discovered by Kazanskii, Liberman, and their coworkers in 1953 during investigations of a combined method of analysis of petroleum (to be mentioned in greater detail later), which required a catalyst which would dehydrogenate selectively cyclohexane hydrocarbons to aromatic ones. Platinised charcoal with certain additives to suppress the hydrogenation of cyclopentanes was proposed, but it was feared that this catalyst might be insufficiently selective, and in fact, as early as 1937 n-octane was found to be converted into a mixture of iso-octanes when it was passed in an atmosphere of hydrogen over platinised charcoal at 310°.[93] Kazanskii *et al.*[94] checked this and found that under combined method conditions n-heptane and n-octane remained unchanged but underwent conversion under more drastic conditions (310°, volume rate 0.2 h^{-1}), with homologues of cyclopentane among the conversion products. Before this work very little published material was available on the possibility of cyclising paraffins to cyclopentane. Cyclisation of n-pentane to cyclopentane on alumino-chromo-magnesium catalyst was suggested[95], but was confirmed experimentally only much later. Cyclopentane was found[96] in an extremely

ǂ In Russian: *sintin*. A colourless to dark yellow liquid produced by catalysed reaction of CO_2 and H_2 at medium pressures. It is available in two grades (nominal boiling ranges 100°–230° and 100°–300°) and is used in the automobile industry for case-hardening parts by a gas-phase process (Ed. of Translation).

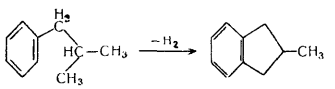
complex mixture obtained from n-heptane at pressure of up to 300 atm and at 450°–480°, but the complexity of the mixture made it impossible to assert that cyclopentane was a primary product. More reliable confirmation of Kazanskii's observation mentioned above was obtained by him with Liberman and others using 2,2,4-trimethylpentane [97,98] and 3-ethylpentane [99] which are particularly convenient, since each can give only one product of cyclisation:



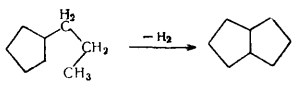
The reaction products could therefore be identified not only spectroscopically but also by actually isolating them.

These and subsequent studies on normal [100,101] and branched-chain paraffins [12] showed that n-pentane was the most difficult to cyclise, the other n-alkanes being rather less difficult and the extensively branched paraffins, especially 2,2,4-trimethylpentane, being the easiest. In all cases only those cyclopentanes were formed which would have been expected with no isomerisation of the carbon skeleton.

Later Kazanskii, Liberman, and Bragin showed that alkylbenzenes could also undergo C_5-dehydrocyclisation to yield indane and its homologues [102,103]:

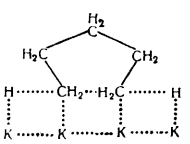


Alkylcyclopentanes were found to behave similarly [101,104]:



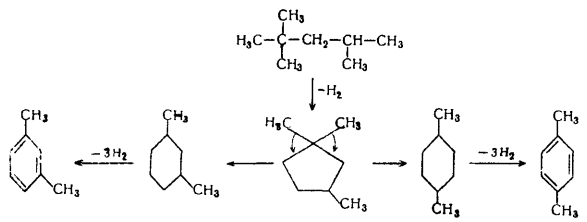
It was shown that C_5-dehydrocyclisation is a zero-order reaction [105] and its energy of activation for paraffins of any structure, whether normal or extensively branched, is the same and amounts to 20 kcal mole^{-1}. It is 7.5 kcal mole^{-1} higher for alkyl benzenes.

All these facts led Kazanskii and Liberman [73] to a number of speculations concerning the mechanism of the C_5-dehydrocyclisation reaction. Firstly, the reaction occurs most readily with hydrocarbons which need the least energy to undergo the transition from the more stable conformation to that most favourable for C_5-dehydrocyclisation, *i.e.* in practice those with the least number of energetically unfavourable rotations. Thus in 3-ethylpentane rotation through 120° at only one bond is necessary, and in 2,2,4-trimethylpentane it is only through 60°, whereas in n-alkanes two simultaneous rotations through 120° are needed, and the yields of cyclopentane (under identical conditions) rise on transition from n-alkanes (3–4%) to 3-ethylpentane (12%) and 2,2,4-trimethylpentane (40%). Secondly, these authors consider that C_5-dehydrocyclisation passes through a peculiar cyclic transitional state in which the catalyst atoms take part:

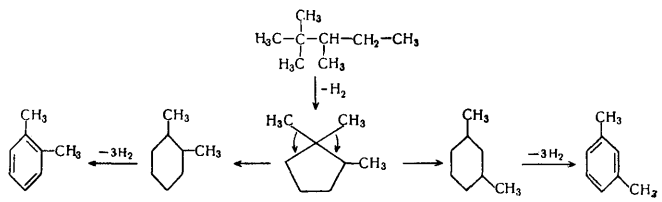


All the five carbon atoms of the ring arrange themselves on the sextet of the platinum catalyst. The reaction, as in hydrogenation of cyclopentane, thus follows a sextet–doublet scheme.

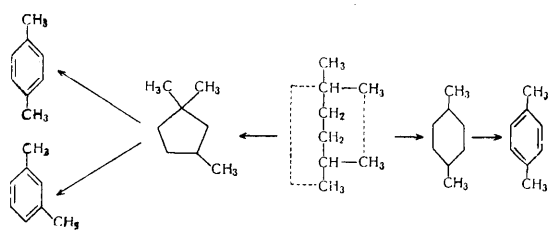
When paraffins containing five carbon atoms in the longest chain are cyclised in the presence of platinised charcoal, some aromatic hydrocarbons are always formed [72] by extension of the cyclopentane ring by means of geminal methyl groups and subsequent dehydrogenation. Thus, 2,2,4-trimethylpentane and 1,1,3-trimethylcyclopentane give approximately equal yields of *m*- and *p*-xylenes:



and 2,2,3-trimethylpentane gives *o*- and *m*-xylenes:



These findings indicate that with a six-carbon chain the aromatic products are formed by direct C_6-dehydrocyclisation and not through an intermediate formation of a five-membered ring: in the former case, di-isobutyl should yield *p*-xylene and in the latter approximately equal amounts of *m*- and *p*-xylenes:



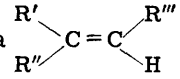
In fact, the aromatic products given by di-isobutyl consisted of 96% *p*-xylene and 4% *m*-xylene. The C_5- and C_6-dehydrocyclisation reactions thus occur independently and in parallel.

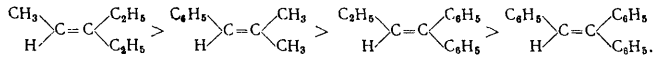
VI. SOME HYDROGENATION AND DEHYDROGENATION REACTIONS

The investigations in this field are too many for even a concise review to be included in this article, so that only some of the more important contributions of Kazanskii and his school will be mentioned here.

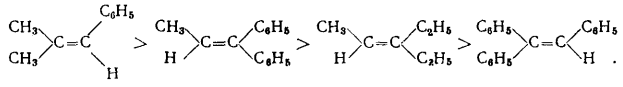
1. Catalytic Hydrogenation of Unsaturated Hydrocarbons

Over the last 20 years Kazanskii has given much attention to catalytic hydrogenation of mono- and poly-unsaturated hydrocarbons in the liquid phase at atmospheric pressure and room temperature, with emphasis on the structure of the initial hydrocarbon and the effect of the nature of the catalyst on the rate and selectivity of hydrogenation.

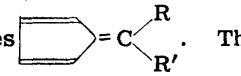
Four olefines of the general formula  were hydrogenated in the presence of platinum black and palladium black. In the presence of platinum[106] the rate of hydrogenation falls in the series:

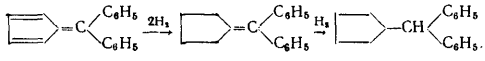


In the presence of palladium[107], on the other hand, the mono- and di-phenylated ethylenes are hydrogenated more rapidly than methyldiethylethylene; however, here an accumulation of phenyl groups also lowers the rate of hydrogenation:

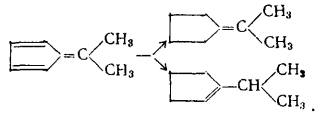


Nickel behaves similarly to palladium[106].

The effect of the nature of the substituents at the double bond and of the catalyst was also clearly seen in hydrogenation of fulvenes . Thus, in the presence of platinum, and especially of palladium[109] and nickel[110], diphenylfulvene rapidly adds on two molecules of hydrogen to two double bonds of the five-membered ring, the third molecule being added on much more slowly, permitting the isolation of the intermediate reaction product:



With alkyl substituents hydrogenation occurs less selectively and when two molecules of hydrogen add on to dimethylfulvene, two reaction products are formed[111]:

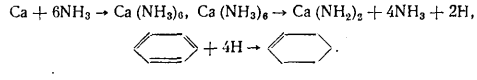


The mechanism of the addition of hydrogen to a conjugated system of double bonds has long been a controversial subject. Lebedev[112] suggested four types of addition of the first molecule of hydrogen depending on the structure of the dienes: (1) selective 1,4-addition; (2) non-selective 1,2-, 3,4-, or 1,4-addition; (3) non-selective addition to both double bonds at once; and (4) 1,2- or 3,4-addition, without 1,4-addition. All the compounds studied in detail by Lebedev belonged to type (2).

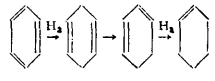
Kazanskii and Popova[113,114,115] showed by hydrogenation with platinum, palladium, and nickel that the dienes tentatively classified by Lebedev as belonging to type (1) (2,5-dimethylhexa-2,4-diene) or type (4) (hexa-2,4-diene and 2-methylhexa-2,4-diene) in fact belong to type (2). Moreover, two moles of hydrogen are also always added on. The structure of the dienes has a marked effect on the quantitative ratio of the different additions; it depends on the catalyst used[113-117], platinum being the least selective. In the presence of palladium the double bond in the intermediate mono-olefines can migrate, giving a mixture of mono-olefines with the addition of only one mole of hydrogen[118]. Such isomerisation is negligible with nickel[119] and totally absent with platinum[120]. All this indicates that the migration of the double bond in the presence of palladium undoubtedly affects the composition of the products and the kinetics of hydrogenation, so that any conclusions on the relation between the structure of the compound undergoing hydrogenation and the direction and rate of the reaction must take into account these possible complications.

2. Reduction of Aromatic and Olefinic Hydrocarbons with Nascent Hydrogen

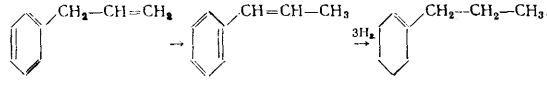
It had long been considered that nascent hydrogen only combined with polycyclic aromatic hydrocarbons but not with benzene and its homologues, and that it did not reduce the isolated double bond in unsaturated hydrocarbons. Kazanskii and his followers contributed a great deal to this subject. In 1916 it was noted[121] that when ammonia acts on metallic calcium in benzene, the latter adds on hydrogen to give "dihydrobenzene". Kazanskii and Smirnova found[122] that benzene and toluene readily added on two molecules of hydrogen evolved on decomposition of calcium ammine to give cyclenes:



Later a detailed study was made of the reduction of ethylbenzene, *o*-, *m*-, and *p*-xylenes, tetralin, mesitylene, styrene, propylbenzene, and allylbenzene with calcium hexammine and strontium, barium, and lithium ammines[123-125]. The corresponding cyclenes were found to be the main reaction products in all cases. The mechanism of the reaction[124] involves the transposition of the even bonds in the diolefine hydrocarbons with the formation of a conjugated system which adds on the hydrogen in positions 1,4:



The migration of even bonds was investigated in many aliphatic and cyclic compounds with isolated double bonds which behaved as compounds with conjugated double bonds when reduced by calcium hexammine. An identical reaction product was obtained on reduction of propenyl- and allyl-benzenes, namely 1-propylcyclohex-1-ene:



Further experiments with nascent hydrogen and diene hydrocarbons with conjugated double bonds[126-128] revealed that in the presence of calcium hexammine, hydrogen was

added on in positions 1,2 and 3,4 as well as 1,4, as in the case of other reducing systems[128-130]. The isomerising agent was found to be calcium amide, a product of calcium hexammine decomposition[131], which readily isomerises not only diene but also mono-olefinic hydrocarbons[131-135]. This reaction is catalytic in the vapour phase and the mechanism suggested for it[12,133,134] envisaged acid–base character with intermediate carbanion formation:

$$\underset{\text{acid.}}{CH_3-CH_2-CH=CH_2} + MNH_2 \rightarrow \underset{\text{base}}{[CH_3-\bar{C}H-CH=CH_2]}\,\overset{+}{M}NH_3 \rightarrow$$

$$\rightarrow [CH_3-CH=CH-CH_2]\,\overset{+}{M}NH_3 \rightarrow CH_3-CH=CH-CH_3 + MNH_2.$$

Later[136-139] repeated reduction of mono-olefines with calcium hexammine was found to result in partial formation of paraffin hydrocarbons and a multi-stage ionic mechanism was proposed for the reduction of unsaturated compounds with nascent hydrogen. In an alkaline medium the first stage consists of the addition of electrons to the carbon–carbon bond and the second one of proton addition; formation of free hydrogen is a parallel reaction which competes with the reduction:

$$>C=C< + 2\bar{e} \rightarrow >\bar{C}-\bar{C}<$$

$$>\bar{C}-\bar{C}< + 2H^+ \rightarrow >CH-CH<$$

$$H^+ + \bar{e} \rightarrow H,\quad 2H \rightarrow H_2.$$

Mono-olefines with various molecular weights and positions of the double bond were reduced with alkali metals (K, Na, and Li) in the presence of methyl, ethyl, and t-butyl alcohols in liquid ammonia, and it was shown that the activity of these metals with respect to the evolution of nascent hydrogen decreased in the order K > Li > Na, whereas their reducing capacity followed the reverse order. The acidity of the alcohol also affects the rate of the competing reactions, the amount of free hydrogen being directly related to the acidity of the alcohol: $(CH_3)_3COH < C_2H_5OH < CH_3OH$, the rate of reduction increasing in the reverse order. These results substantiate the proposed scheme for reduction with nascent hydrogen.

3. Dehydrogenation of Paraffins to Olefines

This line of research, directly connected with the requirements of the Soviet chemical industry, was prompted by the need for a reliable, active, and stable catalyst for the conversion of isopentane into amylenes, intermediates in the production of isoprene. Such an alumino-chromo-potassium catalyst was developed in 1957.[140] Under fixed conditions the process is carried out at 550° with a wide range of volume rates, and the liquid dehydrogenated product contains up to 58% of unsaturated compounds, chiefly isoamylenes. The olefine yield is 45–59% of the isopentane throughput; the selectivity of the catalyst reaching 70–90%. Since side reactions, such as isomerisation and cracking, are inevitable at such high temperatures, it was essential to develop accurate analytical methods for the complex polycomponent catalysts. This was achieved by means of vapour-phase chromatography[141].

VII. CATALYTIC POLYMERISATION REACTIONS

As in the previous section only some of Kazanskii's work in this field will be reviewed. It is interesting that his first research project was related to this subject, when, under the direction of N. D. Zelinskii, he found[142] that acetylene was converted into aromatic hydrocarbons in the presence of activated charcoal at 650°, with benzene as the main reaction product (approximately 70% of the initial acetylene):

$$3CH{\equiv}CH \rightarrow$$ 

He also worked on the polymerisation of olefinic hydrocarbons such as isobutylene, butylene, and ethylene, showing[143] that in the presence of hydroaluminosilicate catalysts isobutylene is polymerised to dimers and higher polymers, the maximum yield of the former being obtained at 200° and of the latter at room temperature. A rise in temperature also favours isomerisation, so that not only 2,4,4-trimethylpentene but also its structural isomers are formed. When but-1-ene is polymerised it is isomerised to isobutylene and but-2-ene, which then combines to 2,3,4-trimethylpentene.

Polymerisation of ethylene with a series of catalysts (nickelous oxide on aluminosilicates)[144] showed that it could be dimerised to but-2-ene at atmospheric pressure and temperatures of 275°–300°. In the studies of the catalytic synthesis of hydrocarbons from carbon dioxide and hydrogen[145], particular attention was paid to the selection of active catalysts and effective carriers from Soviet raw materials. Additives were found which lowered very considerably the temperature of catalyst regeneration.

VIII. HIGH-PRESSURE REACTIONS

In the last decade the investigation of the effect of pressure on the rate and nature of a reaction has often served to elucidate its mechanism. Kazanskii and his coworkers[146] examined the effect of pressure on the rate of thermal cracking of n-hexane and n-heptane. At pressures of 300–3000 atm the rate diminished with increasing pressure; published data, however, stated that at lower pressures (up to 10–20 atm) the opposite was true. This discrepancy was reconciled on the basis of a chain mechanism for the decomposition of paraffin hydrocarbons[147]; at low pressures the reaction chains are terminated predominantly by interaction of shorter (compared to the initial hydrocarbon) radicals; at high pressure this occurs predominantly with "long" radicals; hence the observed reversal of the effect of pressure.

Isomerisation of n-hexane[148] and methylcyclopentane[149] in the presence of aluminium chloride under pressure showed that the rate of isomerisation diminished with increasing hydrostatic pressure (or pressure of nitrogen). This suggested that the isomerisation included a stage involving a considerable increase in volume, and that the equilibrium at this stage of the reaction determined the rate of the overall process. As suggested[150] in 1932, such a stage could be dehydrogenation of the initial hydrocarbon. If this were so, the reaction would be inhibited most when the pressure was created by hydrogen with the dehydrogenation equilibrium particularly strongly displaced towards the initial hydrocarbon. This was fully confirmed experimentally, and subsequent studies[151,152] showed that such a mechanism also very probably operates in the presence of heterogeneous catalysts.

Studies in destructive dehydrogenation are of great theoretical and practical interest. Kazanskii and his co-workers[153] investigated the thermal conversions of various classes of hydrocarbons under high hydrogen pressure and put forward a radical-chain reaction mechanism for homogeneous destructive hydrogenation of alkylarenes, which includes the reaction of a hydrogen atom with the hydrocarbon molecule and splitting off the whole alkyl radical from the aromatic ring. The presumed mechanism of this substitution reaction is the addition of the hydrogen atom to the carbon atom in the aromatic ring which bears the alkyl group and subsequent stabilisation of the radical formed by splitting off the alkyl group. This is substantiated by the fact that increasing the hydrogen pressure markedly accelerated the splitting off of the alkyl group from the alkyl aromatic hydrocarbon, and is further supported by the fact that in methylcyclopentane, where it is impossible to add a hydrogen atom to the molecule, the splitting off of the methyl group is not accelerated by increasing the hydrogen pressure[154].

IX. SYNTHESIS OF HYDROCARBONS

Kazanskii and his school have, in the course of their general work on catalytic conversions of hydrocarbons and the composition of natural petroleums, synthesised many hydrocarbons of various classes, either to study their behaviour, as mentioned in previous sections, or to discover their physical properties (molecular constants, their relation to structure, spectral characteristics). These problems were often tackled in parallel. In the case of spectroscopic studies, the synthesis of hydrocarbons had a dual purpose: first, in collaboration with Landsberg and his school, the accumulation of a large collection of Raman spectra of pure hydrocarbons (some not previously described and many well-known ones) provided a means of their identification and quantitative estimation even in relatively complex mixtures, such as petroleum fractions; second, correlation of spectroscopic properties with a particular structural feature.

The synthetic work begun in 1939 (producing ~ 200 hydrocarbons of high purity) is still continuing. They form the foundation of a spectroscopic atlas of almost 160 spectra[155], the remaining ones appearing in later publications[101,156-158]. A combined method of determination of individual hydrocarbon constituents of petroleum was developed on the basis of this enormous work[155]. The search for spectroscopic correlation with chemical structure was also in some cases successful, as, for instance, in the case of differentiating *cis*-1,2- and *cis*-1,4-dialkylcyclohexanes from their *trans*-isomers[156].

The high purity requirements for hydrocarbon standards initiated a number of methodological studies on the separation and purification of hydrocarbons[159-162], which also entailed elaboration of known methods of preparation or devising of new ones.

In this article it is impossible to list even the most important of the hydrocarbons synthesised and the methods used. The preparation of individual *cis*- and *trans*-isomers of di- and tri-alkylcyclanes is very important. Among the substances prepared were diphenyl- and phenyl-cyclopropylcyclopropanes[25-27]; 1,2-dimethyl-, 1,3-dimethyl-, methyl-ethyl-, and methyl-n-propyl-cyclobutanes[163] (the first dialkylcyclobutanes to be separated into their isomers); 1,2,3-trimethyl- and 1,4-dimethyl-2-ethylcyclopentanes[164-166] (the first trialkylcyclopentanes to be separated into their stereoisomers) and a series of 1,2- and 1,4-dialkylcyclohexanes[167] among which 1,4-di-isopropylcyclohexanes are particularly noteworthy as the first representatives of 1,4-disubstituted cyclohexanes in which the boiling points do not obey the Auwers–Skita rule.

Kazanskii and his school can be confidently credited with having prepared for the first time about half the individual stereoisomeric hydrocarbons known in world literature.

X. INVESTIGATION OF THE COMPOSITION OF PETROLEUM

Among the various methods available in the Soviet Union the one that has gained great importance is the combined one[155] based on chromatographic separation of aromatic from naphthene and paraffin hydrocarbons, subsequent analytical dehydrogenation of the de-aromatised part and chromatographing of the catalysate followed finally by accurate fractionation. Highly efficient fractionating columns separate narrow fractions of primary and secondary aromatic and paraffincyclopentane components of petroleum. The individual fractions usually contain from two to four hydrocarbons which can be easily identified by Raman spectra.

This method was developed through the collaboration of Kazanskii and Landsberg and their schools, combining the synthetic and spectroscopic research mentioned above. The first investigation which showed the possibility of combining successfully accurate fractionation, dehydrogenation catalysis, and optic measurements was the analysis of Kalinskii petroleum[168]. The same but somewhat more refined method was used during the Second World War for the analysis of a number of German and American aviation fuels and high-octane additives[169]. In 1948 the method was supplemented by silica-gel chromatography for the isolation of aromatic hydrocarbons and the use of a new dehydrogenation catalyst which acted selectively for cyclohexanes without opening the ring in the cyclopentane hydrocarbons. This combined method permits identification of up to 90 wt.% of the hydrocarbon constituents of petroleum, while in the case of Karami petroleum (KNR) the figure is even higher (93%)[170].

The method is used in various institutes and the individual hydrocarbon composition of 36 petroleums[170-188] from the directly refined crude oils from the Azerbaidzhan, Bashkir, Kazakh, Tartar, Turkmen, Uzbek, and Chinese People's Republics, Maikop, and Sakhalin has been determined. In addition, a simplified version of the method has been applied to 15 petroleums from Azerbaidzhan[189].

The combined method also proved applicable to the analysis of petroleum obtained by thermal and catalytic cracking[190-193] and of other oil fractions of secondary origin[194,195], containing unsaturated hydrocarbons, which were separated and identified. When suitably modified, the method can also be used for analysis of the higher boiling fractions (ligroins and kerosenes)[177,196-198], but the identification of the individual constituents of the isolated ligroin fractions from their Raman spectra is difficult in the absence of standard hydrocarbons; their synthesis would require an enormous expenditure of time and effort. An attempt was therefore made to limit this to group-identification within the narrow fractions of ligroin from Koschagyl oil[196] (b.p. 150°–250°) from lines in the molecular spectra characteristic for certain structural features

e.g. characteristic of rings, number and position of side-chains, or the presence of individual structural groups (tertiary, quaternary carbon atoms, etc.). Thus for mono-, di-, tri-, and tetra-alkylbenzenes there are lines characteristic of a certain type of substitution in the benzene ring, regardless of the structure of the alkyl group. Since such lines proved to be more reliable and precise for aromatic hydrocarbons, 70% of the aromatic part of the ligroin was identified and 50% of the hexahydroaromatic part.

Work on the Raman spectra of hydrocarbons with boiling points of the ligroin and kerosene fractions is still going on.

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On 25th April, 1961 Academician Boris Aleksandrovich Kazanskii, full of creative energy and projects, celebrated the 70th anniversary of his birth.

Kazanskii graduated from the Moscow State University in 1918 and was retained by N. D. Zelinskii in the Department of Organic and Analytical Chemistry. In 1930 he was appointed Reader; in 1935 he obtained his doctorate in Chemical Sciences and was appointed Professor. From 1945 until 1960 Kazanskii was first Deputy and then Head of the Department of Petrochemistry at Moscow State University.

Kazanskii has worked at the Institute of Organic Chemistry of the Academy of Sciences of the USSR practically since its inception — since 1935; he heads the Laboratory of Catalytic Synthesis, created by him. In 1943 Kazanskii was elected Corresponding Member and in 1946 an Academician of the Academy of Sciences of the USSR. He has been Director of the N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR since 1954.

Kazanskii took part as Editor-in-Chief in the publication of the classical works of such Soviet chemists as A. M. Butlerov, N. D. Zelinskii, and A. E. Arbuzov. He has edited a number of books and monographs.

Kazanskii has been an active organiser and participant of many chemical meetings, conferences, and congresses. He is a member of the Bureau of the International Union of Pure and Applied Chemistry.

Always very exacting towards his own experimental work and conclusions, Kazanskii inculcated this attitude into his followers; much of his attention is devoted to the training of highly qualified scientific workers, including those from the Socialist countries.

Kazanskii has been awarded the Order of the Red Banner of Labour and the Order of Lenin, as well as the Stalin Prize of the First Class.

Kazanskii's profound knowledge and understanding of the most important problems in organic chemistry and his immense organisational ability and creative energy make it certain that he will, at the head of his school, make still greater contributions to Soviet science and the building of Communism.

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Zelinskii Institute of Organic Chemistry,
Academy of Sciences of the USSR