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Catalytic C_6-Dehydrocyclisation of Aliphatic Hydrocarbons on Oxide Catalysts

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The results obtained during the past two decades on the dehydrocyclisation of aliphatic hydrocarbons in the presence of oxide catalysts are reviewed. New work on catalysts (composition, properties, promotion, regeneration, "development") is surveyed. Recent results are given on the dehydrocyclisation of alkanes, alkenes, dienes, and alkynes, with information on the accompanying side-reactions. A possible multistage mechanism for the dehydrocyclisation of alkanes on alumina-chrome catalysts is examined. A list of 257 references is included.

CONTENTS

I. Introduction	715
II. Catalysts for the dehydrocyclisation of hydrocarbons	716
III. Reactions involved in the dehydrocylisation of hydrocarbons on oxide catalysts	720

I. INTRODUCTION

The catalytic conversion of alkanes into aromatic hydrocarbons, discovered by Soviet chemists in 1936,[1-3] allowed for the first time these two types of hydrocarbon, apparently so different in chemical properties, to be interconverted by a simple transition, without recourse to intermediate compounds containing functional groups.

This reaction was of interest to the rapidly developing petroleum industry as a potential process for the production of aromatic hydrocarbons, and came to be studied intensively in the USSR and abroad. Numerous patents appeared on procedures and catalysts for accomplishing the reaction, and from 1939 also research papers by American[4], English[5], Dutch[6], and German[7] chemists, i.e. scientists in countries having an established industry for processing petroleum or for the manufacture of liquid fuel from coal. During recent years scientists of many countries have studied this reaction, not only in connection with its practical application but also with the aim of elucidating its mechanism and kinetics. Interest has not yet died away, and during 1967–1970 new patents and papers have been published on the aromatisation of alkanes. A detailed summary of all the work up to 1947 was given in Plate's exhaustive monograph[8]. (The later reviews by Hansh[9] and by Steiner[10] were somewhat incomplete and one-sided.) The aim of the present Review is to survey work published mainly during the past twenty years.

The aromatisation of alkanes has been termed "C_6-dehydrocyclisation"[11], in contrast to the "C_5-dehydrocyclisation" of alkanes discovered by Kazanskii, Liberman, et al.[12], which occurs on platinum catalysts and yields cyclopentane and its homologues. (Henceforward we shall use the term "dehydrocyclisation" instead of "C_6-dehydrocyclisation".)

In the case of n-hexane this reaction can be represented by the overall equation

$$C_6H_{14} \rightarrow C_6H_6 + 4H_2$$

It takes place on oxide catalysts (chromic oxide without a carrier; chromic, molybdenum, tungsten, and vanadium oxides deposited on aluminium oxide) and on metallic catalysts (platinum, palladium, nickel, and other Group VIII metals on various carriers or without a carrier). The present Review covers the dehydrocyclisation of aliphatic hydrocarbons on oxide catalysts.

II. CATALYSTS FOR THE DEHYDROCYCLISATION OF HYDROCARBONS

1. Composition and Properties of the Catalysts

Almost all the catalysts for the reaction known hitherto were found during the first decade after the discovery of the dehydrocyclisation of alkanes[8]. The most active was chromic oxide deposited specially on aluminium oxide, and molybdenum oxide on alumina was rather less active. This assessment has been confirmed by recent investigations. Thus McGrath[13] compared three types of catalysts used in the petroleum-chemical industry—alumina–platinum, alumina–molybdenum, and alumina–chrome—and found the last to be the most effective for the preparation of benzene from n-hexane, while the first was the least effective; in the preparation of benzene from cyclohexane the alumina–platinum and alumina–molybdenum catalysts were similar in activity and more active than the alumina–chrome catalyst. The highest yield of benzene from methylcyclopentane was given by the alumina–platinum catalyst, and the lowest by the alumina–chrome catalyst[14]. It is not fortuitous, therefore, that most work on the dehydrocyclisation of aliphatic hydrocarbons has been done with an alumina–chrome catalyst.

Investigations during the 1950s and 1960s added little that was fundamentally new to the list of oxide catalysts for dehydrocyclisation. It was found that alkanes can undergo dehydrocyclisation on aluminium oxide containing ferric oxide[15]. Neodymium and samarium oxides also showed dehydrocyclising activity[16,17]. Minachev et al. investigated[18–22] the dehydrocyclisation of n-heptane on the oxides of neodymium, samarium, gallium, holmium, erbium, and yttrium at 530–560°C. The content of aromatic hydrocarbons in the products (at 545°C) was 9–28% depending on the oxide taken. Gadolinium oxide possessed the highest specific activity, and yttrium oxide the lowest. The activities of the rare-earth oxides were somewhat improved by depositing them on activated carbon.

Finally, oxide catalysts were used in "oxidative dehydrocyclisation" processes. Thus the dehydrocyclisation of alkanes on an alumina–chrome catalyst in the presence of sulphur dioxide has been described[23,24]. The only C_8 aromatic hydrocarbons formed by the dehydrocyclisation of n-octane on magnesium oxide in the presence of sulphur dioxide are ethylbenzene and *o*-xylene[25]: i.e. under these conditions the dehydrocyclisation of octane is not accompanied by isomerisation, as is observed in other cases.

The industrial use of alumina–chrome catalysts for the dehydrogenation of alkanes and alkenes and of alumina–molybdenum catalysts for the reforming of gasolines has promoted the study during the past 10–12 years of many properties of these catalysts, especially those based on chromic oxide. The properties of the oxides of chromium themselves have been described in some detail in the monographs of Rode[26] and Udy[27] (see also Ref. 28). Pool and McIver[29] have recently published a very interesting review of the physicochemical properties of alumina–chrome catalysts. Burwell et al.[30] published a survey (based mainly on his own work) of the chemisorption and certain catalytic properties of pure chromic oxide. Information on the oxides of molybdenum can be found in monographs by Killeffer and Linz[31] and by Perel'man and Zvorykina[32], and also in papers by Rode and Lysanova[33,34].

Several workers[35–38] studied the relation between the dehydrocyclising activity of alumina–chrome catalysts and their content of chromic oxide. Special interest attaches to comparison of dehydrocyclising activity with certain other properties of alumina–chrome catalysts. Thus Eischens and Selwood[37] studied the dehydrocyclising activity and magnetic properties of alumina–chrome catalysts containing different contents (1.5–58 wt. %) of chromic oxide. They found that the specific activity of the chromic oxide dropped sharply with increase in its content from 2.9% to 9%, after which it diminished only slightly. The magnetic properties of the specimens indicated that the chromic oxide formed individual groups of microcrystals on the surface of the aluminium oxide, and that variation in catalytic activity was associated with variation in the degree of dispersion of these microcrystals, which depended on several factors, including the concentration of chromic oxide in the catalyst.

Griffith et al.[38–41] studied the dehydrocyclising activity of pure aluminium and chromic oxides and of the mixed catalysts with different contents of the latter, as well as their adsorption properties, specific surface, electrical conductivity, and crystalline structure. In agreement with Visser[35] they found that the yield of toluene from n-heptane passes through two maxima corresponding to 30% and 70–75% of chromic oxide in the catalyst. Griffith and his coworkers established a correlation between the activation energy for the dehydrocyclisation of n-heptane and the activation energy of electrical conduction for samples having different contents of chromic oxide, and explained it on the assumption that the rate-determining stage of the overall reaction was the transfer of electrons from active centres, on which heptane is chemisorbed, to the conduction band. In their opinion the activity of the catalyst was due to the presence of a superficial highly disperse solid solution of alumina in chromic oxide, which differed from the α-phase in crystalline structure. According to Davis et al.[41] and Visser[35] the function of the alumina was to produce a developed surface on the chromic oxide (the specific surface of the catalyst increased from 45 to 306 $m^2 g^{-1}$ from pure chromic oxide to aluminium oxide[39]) and to stabilise the chromic oxide in the solid solution as a cubic phase instead of the hexagonal α-phase characteristic of pure chromic oxide.

All oxide catalysts gradually become covered with carbon deposits ("coke") during use for the high-temperature transformation of hydrocarbons. This diminishes the activity of the catalyst, which can be restored by regenerating the latter, i.e. by heating it in a current of gas containing oxygen. As a consequence of the need for the periodic regeneration of oxide catalysts for dehydrocyclisation, they are located alternately in an oxidising atmosphere (during regeneration) and in a reducing medium (during the reaction). A characteristic feature of oxide catalysts for dehydrocyclisation, which distinguishes them from aluminosilicate catalysts and pure alumina, is the periodic oxidation or reduction of metals of variable valency. For example, chromium(III) oxides are partly converted into chromium(VI) oxides and back again depending on the conditions. Study of the oxidation and reduction of the catalysts could be important for an understanding of

their catalytic activity and necessary in the practical conduct of industrial processes using alumina–chrome and alumina–molybdenum catalysts.

These aspects have been most fully studied for alumina–chrome catalysts, whose oxidation and reduction have interested many investigators[42-59]. Since detailed information on the valency states of chrome and alumina–chrome catalysts has been given in a review[29] and for pure chromic oxide in a monograph[26], we note here merely that the chromium(VI) content of the oxidised catalysts increases with rise in temperature[47] and with increase in the concentration of oxygen in the gas used for regenerating the catalyst[51]. Increase in the content of chromic oxide in the catalyst results in a decrease in the proportion which is oxidised to chromium(VI).[47] This may be due to a weakening of the effect of the carrier (alumina) and to coarser crystals of chromic oxide as its content increases[37], for according to Matsunaga[47] the coarser the microcrystals of chromic oxide the more difficult are they to oxidise.

Different oxides are formed depending on the conditions under which catalysts containing chromium(VI) are reduced. The usual product is the sesquioxide containing chemisorbed water in the form of hydroxy-groups. But the reduction of chromium trioxide deposited on silica gel at not very high temperatures yields chromium(V) oxide, to which is attributed the polymerising activity of chrome–silica gel and chrome–aluminosilicate catalysts[29,56]. Balandin et al.[49] found that the reduction of an alumina–chrome catalyst with atomic hydrogen forms chromium dioxide. Many workers consider that a small quantity of chromium(II) oxide is formed on the surface, together with chromic oxide, in the reduction of alumina–chrome and chrome–silica gel catalysts. This possibility was first pointed out by Weller and Voltz[44]. Van Reijen et al.[52] reached the same conclusion from a study of the magnetic properties and the electron spin resonance spectra of the catalysts, and Steiner[53] and Slovetskaya et al.[54,55] from the formation of hydrogen when the reduced catalyst is treated with water at high temperatures. Whether this hydrogen is evolved as a result of the reaction $2CrO + H_2O = Cr_2O_3 + H_2$ or as a consequence of the displacement by water of hydrogen adsorbed on the reduced catalyst is a matter of debate[57,60,61]. On the basis of the optical spectra of chrome–silica gel catalysts Przheval'skaya et al.[58] consider that chromium(VI) contents below 1% are reduced by hydrogen or carbon monoxide almost completely to chromium(II), a situation somewhat resembling the effect of the quantity of chromic oxide in an alumina–chrome catalyst on the extent of its oxidation.

2. Effect of the Addition of Various Oxides on the Dehydrocyclising Activity of the Catalysts

Greensfelder et al.[62] reported the promoting action of the oxides of several alkali and alkaline-earth metals on an alumina–chrome catalyst in the dehydrocyclisation of n-heptane. Kazanskii et al.[63,64] studied the effects of additions of all alkali metals and most Group II elements to an alumina–chrome catalyst on the yields of aromatic compounds in the dehydrocyclisation of n-heptane and the dehydrogenation of cyclohexane. Except in the case of lithium, the introduction of oxides of the alkali and alkaline-earth metals diminished the cracking of the hydrocarbons and had a promoting effect on the catalyst, especially noticeable in the dehydrocyclisation of n-heptane (Fig. 1). Later Timofeeva et al.[65] observed that these oxides had a similar effect in the same reactions on an alumina–chrome catalyst prepared in a different way. The promotion of an alumina–chrome catalyst by potassium oxide diminishes the formation of carbon[66] (see also Fig. 2), by increasing the activation energy of the reaction limiting carbonisation[67]. Nowak and Vieweg[68-70] have also studied the action of lithium and potassium oxides on the dehydrocyclisation of n-heptane on alumina–chrome catalysts. Nicolescu et al.[71] showed that the particular alkali-metal ion added influenced not only the activity but also the selectivity of an alumina–chrome catalyst in the dehydrocyclisation of n-octane, i.e. the relative quantities of ethylbenzene and *o*-xylene formed. The dehydrocyclising activity of alumina–chrome catalysts promoted by alkali-metal oxides was found to increase from lithium to rubidium[63,65,68]. A parallel increase occurs in the chromium(VI) content of the oxidised catalysts[68-72].

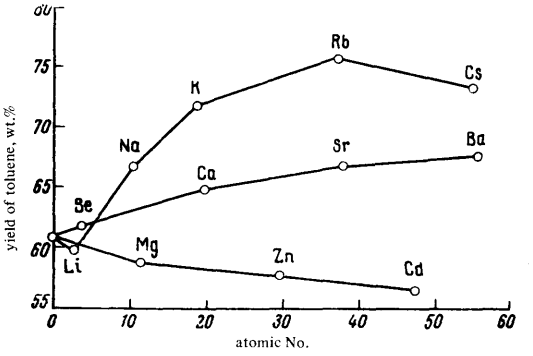


Figure 1. Yield of toluene from n-heptane on alumina–chrome catalysts to which have been added equivalent quantities of the oxides of various metals[63,64] (flow apparatus at 535°C).

It is noteworthy that the addition of potassium oxide to an alumina–chrome catalyst affects also its physicochemical properties[73-75], e.g. texture and electrical properties. Rubinshtein et al.[74] consider that addition of the potassium ion stabilises the lattice of γ-alumina.

In contrast to the promoting action of potassium oxide on an alumina–chrome catalyst, Kazanskii et al.[76] showed that it poisons pure chromic oxide for the aromatisation of n-heptane and cyclohexane at 450°C. Bridges et al.[77] later reached the same conclusion regarding the aromatisation of cyclohexane. Barium oxide has no effect on the activity of pure chromic oxide in the dehydrocyclisation of n-heptane, and somewhat increased its activity for the dehydrogenation of cyclohexane[78]. Addition of a small quantity of phosphoric acid, however, deactivated pure chromic oxide in both reactions[76].

Potassium oxide promotes also alumina–molybdenum catalysts for the dehydrocyclisation of hydrocarbons, as was shown by Bitepazh et al.[79] and independently by Rozengart and Kuznetsova[80]. Adzhieva[81] investigated the action of various quantities of magnesium oxide on an alumina–molybdenum catalyst in the dehydrocyclisation of heptane, and demonstrated a promoting effect with a small content[81]. Belen'kii and Skorupko[82] found that the yield of toluene from n-heptane on an alumina–molybdenum catalyst promoted with strontium oxide passed through a

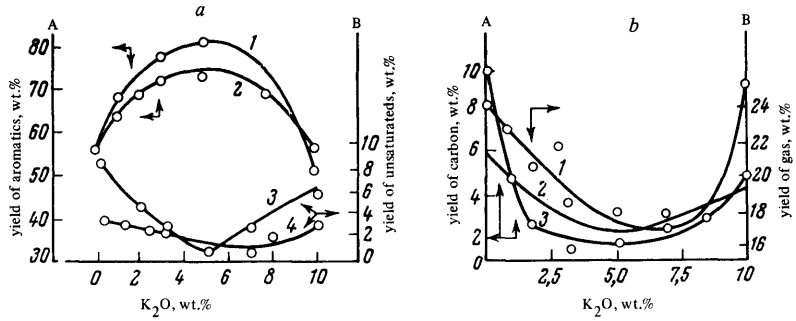


Figure 2. Effect of content of potassium oxide in alumina–chrome catalysts on yields of main products in the dehydrocyclisation of n-heptane[66] (in a flow apparatus):
(*a*): 1) aromatic hydrocarbons on catalysts of type KA-237 at 535°C; 2) aromatic hydrocarbons on catalysts of type A-30 at 550°C; 3) unsaturated hydrocarbons on KA-237; 4) unsaturated hydrocarbons on A-30.
(*b*): 1) gas on A-30; 2) carbon on KA-237; 3) carbon on A-30.

maximum (at 0.3 mole % SrO), but the yield of benzene obtained in the dehydrogenation of cyclohexane increased monotonically with increase in the strontia concentration in the catalyst.

The effect of an alkali-metal oxide depends on the quantity added to the catalyst. According to Visser[35] the maximum yield of toluene from n-heptane was obtained with the proportions $Cr_2O_3 : K_2O = 100 : 12$ with each series of catalysts containing the same total quantity of chromic oxide but different amounts of potassium oxide, independently of the proportion of the former oxide in the catalyst (over the range 40–70 mole %).

The work of Kazanskii[66], Dorogochinskii[83], and their coworkers shows that small amounts (up to 5–8 wt. %) of potassium oxide in an alumina–chrome catalyst act as a promoter, and the yield of toluene from heptane passes through a maximum as a function of this content (Fig. 2). However, comparison of the results suggests that the maximum shifts to higher contents with rise in the reaction temperature. With further increase in the content of potassium oxide (10% and above) the catalyst begins to be poisoned.

Clark[84] attributed the promoting action of alkaline additives to a diminution in the cracking and carbonising power of catalysts based on aluminium oxide. The same effect was noted by Kazanskii et al.[63], who ascribed it to a decrease in the acidity of the catalysts, and later by other workers[68] in a study of the dehydrocyclisation of hydrocarbons. Voltz et al.[85] showed that the introduction of potassium oxide into an alumina–chrome catalyst did in fact diminish its acidity. However, the role of the potassium oxide was subsequently found to be far more complicated than had been thought initially. Thus cracking and carbonisation are intensified at relatively high contents (8–10%) in the catalyst (Fig. 2*b*), which may be associated with a change in the mechanism of side reactions (see Section III, 3).[66]

It is noteworthy that the promotion of alumina–chrome catalysts produces a greater increase in the yield of toluene from heptane than in the yield of catalytic products[63,64]. Hence the promoting action of alkaline additions is not due solely to a change in the acidity of the catalyst. Starting with Voltz and Weller[45] several workers observed an increase in the content of chromium(VI) in the oxidised catalysts with increase in the quantity of potassium oxide. Results obtained by a number of workers[68,69,72,86–88,107] show that the activity of alumina–chrome catalysts increases to a limit in parallel with the increase in the chromium(VI) content in oxidised specimens, independently of whether this increase is due to the introduction of the same quantity of different alkaline additives or to different quantities of the same alkali-metal oxide. A similar parallelism between activity and chromium(VI) content is observed with samples of an alumina–chrome catalyst containing different quantities of chromic oxide[68] and with specimens which have undergone different heat-treatments[87]. All these results suggest that the activity of alumina–chrome catalysts is usually determined by the quantity of a finely dispersed microcrystalline chromic oxide phase formed on the reduction of oxygen compounds of chromium[73,107] as a carrier of active centres.

Rubinshtein et al.[73] showed that, when chromates present in an oxidised alumina–chrome–potash catalyst are reduced, the potassium ion migrates to the aluminium oxide to form surface aluminates. This was confirmed by determining the content of chromium and aluminium ions in aqueous extracts of oxidised and reduced catalysts[73,107].

Kim and Krieger[89] studied the effect of additions of silica on the dehydrocyclising activity and certain other properties of pure chromic oxide. Maximum activity for the dehydrocyclisation of n-heptane was found in a specimen containing 4.7 wt. % SiO_2. This effect was due to inhibition of the crystallisation of chromic oxide and of its dehydration during the experiments, so that deactivation of the catalyst was diminished.

3. Regeneration of Alumina–Chrome Catalysts

During the dehydrocyclisation of alkanes the activity of the catalyst varies with time (Fig. 3). If the reaction starts with an oxidised catalyst, the yield of the aromatic product increases initially, remains constant for some time, and then falls gradually, owing to the deposition of carbon on the surface of the catalyst[90]. The activity of oxide catalysts is usually restored when they are regenerated with oxygen-containing gases[91,92] or mixtures of steam and air[35,93]. No difficulties are usually involved in the regeneration of a catalyst in laboratory reaction

vessels of diameter up to 20 mm. With vessels of diameter 30 mm and larger up to industrial sizes, however, the considerable quantity of heat evolved by the combustion of carbon and the poor thermal conductivity of the layer of granulated catalyst[94] produce considerable temperature rises in the reaction vessel during regeneration of the catalyst.

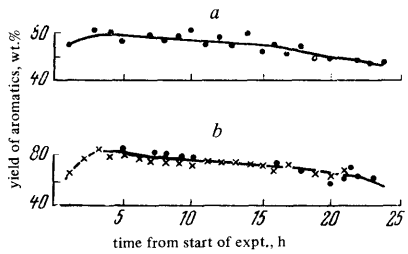


Figure 3. Variation in yield of aromatics during experiment[91] (flow apparatus, alumina–chrome catalyst, space velocity 0.35 h^{-1}) with: *a*) n-hexane at 550°C; *b*) n-heptane at 535°C.

When a stationary bed of an alumina–chrome catalyst, which has undergone carbonisation in the dehydrocyclisation of n-heptane, is regenerated with air, the carbon is burnt out layer by layer, as was established simultaneously by Modavskii and Kamusher[95] and also by ourselves[96,97]. The extent of the zone of intense combustion along the axis of the reaction vessel, the maximum temperature in this zone, and its rate of advance along the bed depend on the rate of supply of air and the distance from the start of the bed[96-98]. Oxidation of carbon in portions of the bed through which the temperature maximum has already passed takes place at a lower temperature, approximating to the temperature of the bed before regeneration began: i.e. two periods of combustion of the carbon are observed.

Comparison of the variation in the temperature of the layer of catalyst with the composition of the waste gases from the regeneration enabled Rozengart and Kazanskii to put forward in 1948 the hypothesis that the burning of carbon on an alumina–chrome catalyst occurs in the diffusion range or is subject to diffusion retardation. The presence of two periods of regeneration—the first at high temperatures and the second occurring more smoothly—is due to the different dimensions of the channels between the catalyst grains and of the pores in the grains. During the first period combustion of the carbon takes place mainly on the surface of the grains, and in the second period mainly in the pores of the catalyst.

Many workers have since arrived at similar conclusions on the presence of two periods in the regeneration of a catalyst under the influence of macrokinetic factors[86,99-101]. Rode and Balandin[102] found, in a thermographic study of alumina–chrome catalysts, including one which had become carbonised in the dehydrocyclisation of heptane, that the non-uniform composition of the carbon could also contribute to the appearance of these two periods of regeneration of the catalyst: the light components of the deposit burn out initially, and later the heavier components. The same view is held by Tyuryaev and Gusakova[103].

When regeneration is effected by a gas with a low (0.2–2%) oxygen content flowing at a high speed, the carbon burns uniformly throughout the length of the catalyst bed at a rate exceeding regeneration by air and also at a lower temperature, since part of the heat is removed by the inert gas. This method of regeneration is used in pilot plants and in industry[104]. The dynamics of combustion of the carbon is greatly influenced by its distribution and by the variation in its chemical composition along the catalyst bed. In a fluidised bed, which has good thermal conductivity and a quite uniform temperature distribution throughout the reaction vessel, carbon formed in the dehydrocyclisation of n-heptane has been shown by Novikova et al.[105] to burn uniformly throughout the bed even in a current of air in a vessel of diameter 40 mm. However, regeneration took longer in the fluidised bed than in a stationary bed.

The chemical composition of the catalyst, in particular its content of potassium oxide, has a substantial influence on regeneration[106]. The rate of combustion of the carbon was increased by the addition of 2–5% K_2O to the catalyst.

The regeneration of alumina–chrome catalysts is not confined to burning out the carbon. Restoration of their activity requires that part of the chromium(III) should be oxidised to chromium(VI).[42] This is explained by the role of oxygen compounds of chromium(VI) in producing a highly disperse chromic oxide phase, which acts as a carrier for the active centres (Section II, 2). The oxidation of chromic oxide is considerably slower than that of the carbon, and completes the regeneration of the catalyst[51].

4. "Development" and Thermal Deactivation of Catalysts

The yields of aromatic hydrocarbons obtained on regenerated oxide catalysts are extremely low initially, and gradually increase to a more or less constant level (Figs. 3 and 4).[62,90,108] This phenomenon, which has been termed "development" ("activation", "formation"[69]) of the catalyst, has considerable significance in the technology of processes using moving alumina–chrome catalysts, where they remain in the reaction zone for only 15–30 min. If a developing catalyst enters the reaction vessel, this period is so short that it functions with diminished activity, and a lower yield of aromatic hydrocarbons is obtained than on a catalyst operating with its maximum possible activity[109]. The development of alumina–chrome catalysts in the dehydrocyclisation of n-hexane and n-heptane has been studied in detail by Kazanskii, Rozengart, Dorogochinskii, and their coworkers[80,88,107-111] using a stationary bed and by Novikova et al.[112] using a fluidised bed.

When hydrocarbons are in contact with an oxidised catalyst (e.g. a regenerated catalyst) containing oxygen compounds of chromium(VI), these are reduced, while part of the hydrocarbon is oxidised to carbon monoxide, carbon dioxide, and water. This is accompanied by a rise in temperature of the layer of stationary catalyst[43,78] by 20–100 deg depending on the diameter of the reaction vessel, the initial temperature, and the chromium(VI) content of the regenerated catalyst.

Reduction of the catalyst with the formation of lower oxides of chromium is complete within a few minutes[107], but development lasts 30–40 min at 530°C. The duration of development is determined[88] by the rate of desorption of the water formed (Fig. 4), which poisons chrome catalysts for dehydrocyclisation (Ref. 8, p. 51). When the

temperature is lowered, and the rate of desorption diminishes, therefore, the development time increases, and at 470°C it is 12 h.[78] If the catalyst is first reduced with hydrogen or hydrocarbon gases, and water vapour is then desorbed by a stream of an inert gas, hardly any development of the catalyst is observed, and the latter functions with its maximum possible activity almost from the start of the reaction[88]. In industrial processes with a moving bed, therefore, the regeneration of alumina–chrome catalysts is followed by their reduction in special equipment, and only after this are they moved into the reaction vessel[113-115]. Addition to an alumina–chrome–potash catalyst of zinc oxide, boron oxide, or more aluminium oxide shortens the period of development[116]. Such rapidly developed catalysts may be of interest for processes with a fluidised bed of an alumina–chrome catalyst.

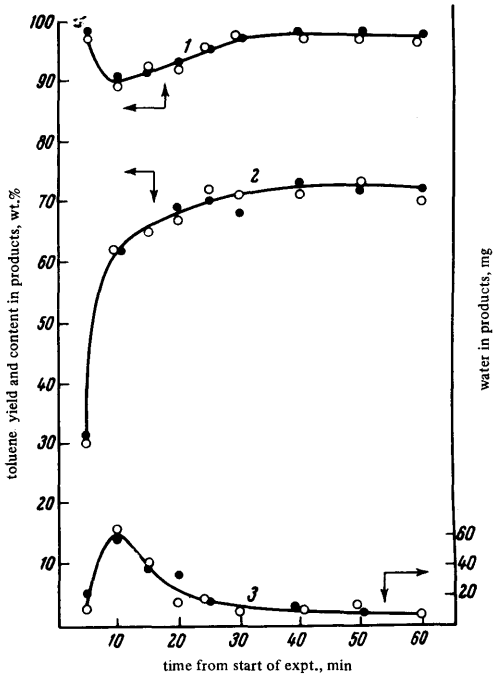


Figure 4. Variation during experiment[88] (flow apparatus at 535°C, space velocity 0.35 h^{-1}, regenerated alumina–chrome–potash catalyst) of: 1) content of aromatic hydrocarbons in products of catalysis; 2) yield of aromatic hydrocarbons; 3) content of water in products.

The development time of a stationary bed of regenerated alumina–chrome–potash catalyst in the dehydrocyclisation of alkanes corresponds to a very unusual variation in the content of aromatic hydrocarbons among the products during the experiment, represented by a characteristic "ladlelike" curve (Fig. 4, curve *1*). The left-hand, descending portion of the curve is due to increased oxidation and degradation of the less stable aliphatic hydrocarbons caused by the temperature rise at the start of the experiment. During the first 10–15 min the degradation diminishes rapidly, and the yield of catalytic products increases more rapidly than does the yield of aromatics, so that the content of the latter in the products falls. The continuing increase in the yield of aromatics, while the total yield of products remains stable, results in the content of aromatics rising to a maximum value. In a fluidised bed no rise in temperature occurs owing to its good thermal conductivity, so that the left-hand portion of curve *1* is absent[112]. The content of aromatics is lowest at the beginning of the experiment. Curves intermediate between these two extreme cases may be observed depending on the experimental conditions and the diameter of the reaction vessel, which govern the rise in temperature.

The promotion of alumina–chrome catalysts by oxides of alkali metals[107] and alkaline-earth metals[78] lowers the initial yield of aromatics and increases the development time. The principal reason is the increase in the quantity of oxygen combined with chromium(VI) on the introduction of an alkaline promoter into the catalyst, and the consequent increase in the quantity of water formed when hydrocarbons are in contact with the catalyst. Another reason is that the presence of potassium ions slows down the desorption of water[107]: i.e. it makes the surface more hydrophilic. Experiments on the dehydrocyclisation of n-heptane on an industrial alumina–molybdenum catalyst before and after promotion with potassium oxide[80] showed that development is characteristic of other dehydrocyclisation catalysts containing oxides of elements of variable valency.

According to Novikova and her coworkers[112,117] raising to 650–700°C the temperature of reduction of alumina–chrome catalysts by hydrogen or methane, or heating in a stream of helium at 700°C a catalyst which has been reduced at 530°C, halved the dehydrocyclising activity of an alumina–chrome–potash catalyst. It is noteworthy that deactivation of an alumina–chrome catalyst with rise in the reduction temperature had been observed earlier by Maslyanskii and Bursian[42] in the dehydrogenation of cyclohexane. Novikova's results[112], as well as investigations by Rozengart et al.[87], have shown that the thermal deactivation of reduced oxide–chrome catalysts is probably due to further dehydration, which facilitates recrystallisation of the microcrystals of chromic oxide. This decreases the surface associated with this oxide while having little effect, as experience shows, on the total specific surface of the catalyst. Heating in a current of air at 700°C usually restores both the activity of a catalyst deactivated in this way and apparently the surface area of chromic oxide in the catalyst which had been reduced at 530°C. In contrast to all other known cases of the thermal deactivation of catalysts, that of reduced alumina–chrome catalysts is reversible, provided that there is no change in the surface or the texture of the aluminium oxide.

III. REACTIONS INVOLVED IN THE DEHYDROCYCLISATION OF HYDROCARBONS ON OXIDE CATALYSTS

Dehydrocyclisation has been most fully studied on various alkanes; less is known about that of alkenes; and very little on the dehydrocyclisation of dienes, trienes, and alkynes.

1. Dehydrocyclisation of Alkanes

(*a*) Effect of molecular weight and structure of alkanes on composition of reaction products and yields of aromatic hydrocarbons

Oxide catalysts for dehydrocyclisation, even single-component catalysts like pure chromic oxide, and multifunctional, since dehydrocyclisation, dehydrogenation, and hydrogenation take place on them, as well as cracking, alkylation, dealkylation, and polymerisation; under certain conditions the disproportionation of unsaturated hydrocarbons can also occur. Therefore the composition of the products obtained on oxide catalysts from aliphatic hydrocarbons, in particular alkanes, is extremely complicated. The main products—the expected aromatic hydrocarbons and hydrogen—are accompanied by hydrocarbons containing either the same number of carbon atoms as the initial alkane or smaller or larger numbers. The quantitative proportions of the various groups of hydrocarbons and individual components in the products depend on the composition and the structure of the initial hydrocarbon, the reaction conditions, and the chemical nature of the catalyst.

The yields of aromatic hydrocarbon increase with the increase in molecular weight from n-hexane to n-nonane and n-decane. Values given in different papers vary within quite wide limits. The maximum yields obtained on alumina–chrome catalysts promoted with alkali metals are 65–80 wt. % based on the initial alkane.

Hexanes. Only n-hexane is able to undergo direct C_6-dehydrocyclisation: isohexanes form benzene on oxide catalysts after preliminary skeletal isomerisation [78]. The gaseous conversion products from n-hexane contain both straight-chain and branched-chain C_1–C_5 hydrocarbons (saturated and unsaturated). Rozengart et al. [78,90] found the product of catalysis (alumina–chrome–potash catalyst at 550°C) to contain, together with the initial hexane and the expected benzene, up to 3 wt. % of branched-chain hexanes, straight-chain hexenes (mainly hex-2-ene and hex-3-ene), and traces of branched-chain hexenes. The literature indicates that the catalytic conversion of hexanes yields also traces of hexadienes, cyclohexane, toluene, xylenes, ethylbenzene, and a higher aromatic. The detailed composition of the products of the dehydrocyclisation of hexanes on an alumina–chrome–potash catalyst is given by Shuikin et al. [118–121] and on an alumina–chrome catalyst by Pines and Csicsery [122]. The latter workers note that the xylenes formed by the dehydrocyclisation of hexanes usually have the equilibrium composition. The introduction of an alkaline promoter into an alumina–chrome catalyst almost completely suppresses the formation of toluene in the dehydrocyclisation of n-hexane [78]. Minachev et al. [123] obtained an appreciable quantity of toluene (up to 15% of the product at 520°C) by the dehydrocyclisation of n-hexane on an industrial alumina–molybdenum catalyst. The absence of heptanes and heptenes from the reaction products suggests that the formation of homologues of benzene in the dehydrocyclisation of n-hexane is most likely due to the alkylation of benzene by degradation products of the initial hexane.

Heptanes. Dehydrocyclisation of heptanes may be expected to yield toluene, but benzene is formed as well, and may reach up to 4 wt. % of the products obtained on an alumina–chrome–potash catalyst. Plate and Tarasova [124,125] showed that the unsaturated products of the dehydrocyclisation of n-heptane on an alumina–vanadium catalyst at 480°C comprised mainly hept-2-ene and hept-3-ene. Shuikin et al. [119] obtained a similar result. n-Heptane (on an alumina–chrome–potash catalyst) yields all n-heptenes, usually in proportions close to the thermodynamically equilibrium values, traces of branched-chain heptanes, mainly 2- and 3-methylhexanes, and also C_1–C_6 hydrocarbons with straight-chain and branched-chain structures [78].

Special attention was paid in the early work on dehydrocyclisation [8] to the effect of branching of the carbon skeleton in the alkane on the yield of aromatics. During recent years Pines and his coworkers have studied the dehydrocyclisation of isomeric heptanes (and also octanes). These investigations, which used ^{14}C-labelled hydrocarbons, gas–liquid chromatography, and sometimes also spectroscopic analysis, gave detailed information on the composition of the reaction products. Unfortunately, alumina–chrome catalysts were used, which were poisoned fairly rapidly (within 5–18 min) and in several cases also had a strong cracking effect. Therefore purely tentative conclusions concerning yields of aromatics can be obtained only from results with the initial samples during the first 5–9 min of an experiment.

Comparison of results obtained by Hoog et al. [6] with those of Pines and Dembinski [126] indicates that the yield of aromatics from n-heptane is very similar to that from 2-methylhexane and somewhat higher than the yield from 3-methylhexane. However, the latter workers themselves remark that the lower yields in the last case may be due to stronger poisoning of the catalyst.

Octanes. Study of the products of the dehydrocyclisation of octanes is of especial interest, since ring closure can occur in several ways. Thus n-octane should yield ethylbenzene and *o*-xylene.

In practice the catalytic products from n-octane contain every possible C_8 aromatic hydrocarbon, including styrene, together with benzene and toluene [127,128]. The latter are formed by the dealkylation of ethylbenzene and xylenes. Since ethylbenzene and *o*-xylene do not isomerise on oxide catalysts for dehydrocyclisation [127–131], the presence of *m*- and *p*-xylenes is explained by the isomerisation of n-octane into branched-chain octanes followed by cyclisation of the latter [128,132]. The expected aromatic hydrocarbons usually predominate on the cyclisation of any octane [127–141]. However, the catalytic products from n-octane have been found to contain also branched-chain octanes and octenes, octadienes (traces), and also lower hydrocarbons. n-Octane has been detected in the dehydrocyclisation of 3- and 4-methylheptanes [137]; n-octane, dimethylcyclohexanes, and other saturated and unsaturated cyclic hydrocarbons in the products from dimethylhexanes [135]; and small quantities of cycloalkanes, cycloalkenes, 3-ethyl-hexenes and -hexadienes, 3-methyl-hexenes and -hexadienes, and also 3-methylhexane from 3-ethylhexane [136]. On this basis Pines and his coworkers stated that the dehydrocyclisation of C_6–C_8 alkanes involves the intermediate formation of 5–8-membered cycloalkanes or their chemisorbed forms [130,131,133–137,141]. It must be noted that, by itself, the presence of any substance among the reaction products cannot prove that it is an intermediate in the main reaction: such proof requires additional evidence.

Several workers have studied the aromatisation of trimethylpentanes [142–149]. This probably requires preliminary isomerisation with lengthening of the main chain. The principal reactions of trimethylpentanes on oxide–chrome catalysts are degradation and dehydrogenation [147,148], accompanied by the formation of C_6–C_8 aromatic hydrocarbons. Among the products from 2,2,4-trimethylpentane Timofeeva et al. [145] found traces of 1,1,3-trimethylcyclopentane; but Lester, who also studied this reaction,

considers this to be a product of a secondary, not the main reaction[149].

Nonanes and higher alkanes. Relatively little work has been done on the dehydrocyclisation of nonanes and higher alkanes[118,119,140,150-157]. Several studies have been made of the dehydrocyclisation of n-alkanes of different molecular weights on alumina–chrome or alumina–molybdenum catalysts under comparable conditions: thus Shuikin et al.[118,119] studied the dehydrocyclisation of C_6-C_{10} n-alkanes, Perrée and Bloury[140] C_6-C_9, Suzumura and Yoshida[157] C_6-C_{12}, and Usov et al.[154,155] C_9-C_{16}. The bulk of the aromatic hydrocarbons are those containing the same number of carbon atoms as the initial alkane. Mono- and di-alkylbenzenes (mainly the *ortho*-isomers) are formed together with trialkylbenzenes, naphthalene, and its homologues; anthracene and phenanthrene could not be found.

The observation by the early investigators[1-3], that the composition and structure of the major portion of the aromatic hydrocarbons formed are determined by the modes of closure of a six-membered ring available to the initial alkane, can in general be regarded as confirmed. With increase in the number of carbon atoms in the initial alkane from 6 to 10 the yield of aromatic hydrocarbons becomes larger; further lengthening of the carbon chain in the alkane probably diminishes the yield.

(*b*) Influence of reaction conditions

Temperature and space velocity (contact time). There are numerous results of this type, since almost all investigators have studied more or less thoroughly the dependence of the yields of aromatic unsaturated hydrocarbons on the temperature and space velocity[8,78,117,120,125,128,152,155-164]. The general rules—increased yield of aromatic hydrocarbons with rise in the experimental temperature and increased contact time—apply to various hydrocarbons both in a stationary bed and in a fluidised bed of the catalyst.

At relatively low temperatures (300–450°C) and short contact times the main products are unsaturated hydrocarbons, chiefly alkenes[78,158,163]; under more severe conditions (500–600°C, longer periods of contact) aromatic hydrocarbons are mainly formed (50–80).[78,90,158] With rise in temperature over a wide range or increased contact time the yield of unsaturated hydrocarbons passes through a maximum (e.g. Fig. 5).[78,128,158,162] As a consequence of all the above generalisations, study of the effect of temperature or space velocity over not too wide ranges of variation in these parameters may reveal either parallel or opposite changes in the yields of aromatic and unsaturated hydrocarbons, as has been shown by Kazanskii et al.[160]

Levitskii showed convincingly[165] that the yield of alkenes and their content in the products of the dehydrocyclisation of alkanes are determined not only by the kinetics but also by the thermodynamics of the reactions. The concentration of alkenes during the dehydrocyclisation of alkanes is usually close or equal to the equilibrium value. In several cases, therefore, the decrease in the yield of alkenes beyond the maximum can be explained not only by the diminished rate of dehydrogenation of the alkane resulting from its diminished concentration but also by the displacement of the formation equilibrium of the alkene due to the rise in the concentration of hydrogen in the reaction mixture on formation of the aromatic.

Dilution and increased pressure. Plotnikov et al.[166] studied the effect of diluting n-hexane vapour with nitrogen or of a vacuum on the yield of benzene on an alumina–chrome–potash catalyst at 500°C. They found that the yield of benzene increased, while that of hexenes decreased, with decrease in the partial pressure of hexane, i.e. with increase in dilution by nitrogen or decrease in the total pressure. As these workers state correctly, the results can be explained on the assumption that benzene is formed via hexenes.

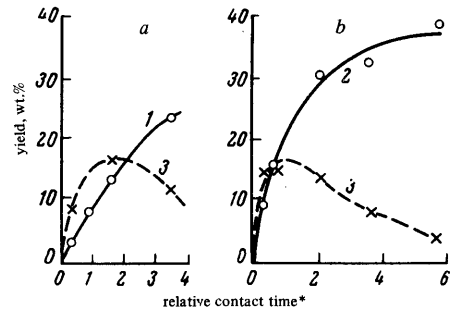


Figure 5. Effect of relative contact time* in flow apparatus[78] on yields of products from the dehydrocyclisation of: *a*) n-hexane at 550°C; *b*) n-heptane at 535°C: 1) benzene; 2) toluene; 3) unsaturated hydrocarbons.

*The relative contact time is a dimensionless quantity obtained by dividing the volume of the catalyst by the volume corresponding to the contact time adopted as unit.

Variation in the component partial pressures of the reaction mixture affects not only the total yield of aromatic hydrocarbons but also their composition. For example, Rozengart et al.[167] established that decreasing the partial pressures of all components in the dehydrocyclisation of n-octane under pulse conditions in a stream of helium produced considerable increases in the content and yield of styrene as compared with those observed in the usual flow equipment (for greater detail see Section III, 5).

Since hydrogen is a product of the dehydrocyclisation of alkanes, high pressures of the gas, as occur in the industrial process of hydroforming[14], have an especially unfavourable effect on the reaction. The influence of thermodynamic factors was examined also by Taylor and Turkevich[4] and later by Rossini et al.[168] (see also Ref. 8, p. 203) and several other authors[62,169]. It is noteworthy that the effect of the hydrogen pressure differed with alumina–chrome and alumina–molybdenum catalysts. According to Greensfelder et al.[62] the decrease in the yield of toluene from heptane with rise in the hydrogen pressure was smaller on the latter type of catalyst. This was noticed also by Maslyanskii et al.[169], who studied the hydroforming of ligroins on the two catalysts. Thus the adverse effect of hydrogen pressure on the dehydrocyclisation of alkanes is due not only to thermodynamic factors but also to the variation in the reaction velocity, which differs between the catalysts.

2. Dehydrocyclisation of Unsaturated Hydrocarbons

The catalytic dehydrocyclisation of unsaturated hydrocarbons has been studied less thoroughly than that of alkanes. However, sufficient results are known to leave no doubt that the presence of a multiple bond in a molecule facilitates its cyclisation with formation of an aromatic compound. The rate of dehydrocyclisation increases with the number of double bonds in the molecule, and hydrocarbons can be arranged in the sequence—alkanes, alkenes, dienes, trienes—with increasing rate of this reaction[170,171]. According to Kotlyarevskii et al.[172,173] alkynes are probably aromatised more rapidly than alkenes but more slowly than dienes.

(*a*) Alkenes

The structure of the aromatic hydrocarbon formed from alkenes and other unsaturated hydrocarbons is determined by that of the initial hydrocarbon, as in the dehydrocyclisation of alkanes. Therefore all that has been said concerning the composition of the aromatic products from alkanes applies also to the catalytic reactions of alkenes.

The alkene portion of the product usually comprises a mixture, in thermodynamic equilibrium, of isomers having the same carbon skeleton as the initial alkene but different positions of the double bond[78,125,140,174-177]. Arenes and alkenes in the products from alkenes are always accompanied by alkanes formed by hydrogenation of the initial hydrocarbon by hydrogen evolved in the dehydrocyclisation. Dienes[171,174,177] and traces of trienes have also been found in the products. According to Perrée and Bloury[140] the yield of aromatics rises with increase in the molecular weight of the alkene from n-hex-1- and -2-enes to the corresponding n-octenes.

Great attention has been paid to the effect of the position of the double bond in n-alkenes on the yield of aromatic hydrocarbons, since this is directly connected with the mechanism of dehydrocyclisation. According to Plate and Tarasova[124,125] the yields from hept-1-ene and hept-3-ene on an alumina–vanadium catalyst at 480°C were about the same, perhaps rather higher from the former hydrocarbon. It was observed at the same time that hept-3-ene poisoned the catalyst the more rapidly. Rozengart et al.[174] found that, on an alumina–chrome–potash catalyst at 450°C using an equimolar stream of helium in the usual flow equipment, the yield of toluene was larger from hept-2-ene than from hept-1-ene and smallest from hept-3-ene; the catalyst was poisoned most strongly by hept-3-ene, and least by hept-1-ene.

Panchenkov et al.[178,179] have recently obtained similar results to the above[174] from the dehydrocyclisation of hept-1-ene, hept-2-ene contaminated with hept-3-ene, and hept-3-ene itself on an alumina–chrome–potash catalyst in an ordinary flow apparatus. The strong effect which secondary reactions are now known to have on the main reaction, in particular the different degrees of poisoning of the catalyst in the dehydrocyclisation of individual isomers, does not always permit correct conclusions as to the reaction mechanism to be drawn from results obtained in the dehydrocyclisation of alkenes in an ordinary flow-type apparatus. This has been done by conducting the reaction under pulse conditions and analysing the reaction products by means of a capillary chromatograph.

Rozengart et al.[170,177] found that heptenes can be arranged in the sequence

cis-hept-2-ene > *cis*-hept-3-ene > *trans*-hept-3-ene > *trans*-hept-2-ene ⩾ hept-1-ene

of diminishing rate of dehydrocyclisation on an alumina–chrome–potash catalyst. Thus stereoisomerism has a greater effect than the position of the double bond on the rate of dehydrocyclisation of alkenes. The influence of branching of the carbon skeleton of alkenes on the yield of aromatics has not in fact been studied. It is interesting that 2,5-dimethylhexa-2,4-diene has been recommended as a starting material for the production of *p*-xylene[180]. Temperature and space velocity have the same effects on the yield of aromatics from alkenes as have been noted with alkanes. Cracking, the deposition of carbon, and poisoning of the catalyst are more marked in the dehydrocyclisation of alkenes[140,181].

(*b*) Dienes

Plate and Batuev[182] passed hexa-1,5-diene over an alumina–chrome catalyst at 300° and 400°C, and found 8–11% of benzene in the product. Shuikin et al.[183] studied the C_5- and C_6-dehydrocyclisation of various dienes on an alumina–chrome–potash catalyst in a vacuum, and showed that 42% of toluene is formed from hepta-1,3-diene at 600°C. When preparing *p*-xylene, Kotlyarevskii and Zanina[173] found that 2,5-dimethylhexadiene is aromatised better than is 2,5-dimethylhexene on an alumina–chrome catalyst promoted with magnesium oxide; the composition of the products from the dienes showed more individuality than those from the alkene. According to Akioshi et al.[138] the yield of aromatics obtained on a chrome–magnesia catalyst was higher from 2,5-dimethylhexa-2,4-diene than from 2,5-dimethylhexa-1,5-diene. The same yield of toluene was obtained from hepta-1,3- and -2,4-dienes on an alumina–chrome–potash catalyst at 450°C under pulse conditions[171], since the rate of migration of the double bond was higher in the dienes than in the alkenes. The heptenes (a mixture of all the n-heptenes), formed by hydrogenation of the initial diene, were accompanied in the reaction products by hepta-1,3,5-trienes, the yield of which reached 3 wt.%.[170]

(*c*) Trienes

The dehydrocyclisation of trienes on an alumina–chrome catalyst promoted with magnesium oxide has been described in a patent[184]. No other information was available on this topic before our work[170,171]. Aliphatic trienes readily undergo a peculiar thermal "cycloisomerisation" into cyclohexadienes[185-188]. According to Lewis and Steiner[188] only *cis*-hexatriene is directly cyclised, having the horseshoe configuration favourable for ring closure; other isomers first isomerise into the *cis*-form.

Rozengart et al.[170] found that hepta-1,3,5-triene is easily converted into toluene on an alumina–chrome–potash catalyst under pulse conditions in a stream of helium at 450°C. The products contained also heptadienes, formed by hydrogenation of the original triene with hydrogen resulting from the dehydrocyclisation. No cyclic hydrocarbons other than toluene and methylcyclohexadienes were detected. Komatsu has recently reported[189] that 3-methylhepta-1,4,6-triene, obtained by the dimerisation of butadiene, is converted on an alumina–chrome catalyst into a good yield of *o*- and *p*-xylenes at as low a temperature as 200°C.

(*d*) Alkynes

Information on the dehydrocyclisation of alkynes is extremely scanty. Levina et al.[190] showed that the passage of hex-1-yne and hept-1-yne over an alumina–chrome catalyst at 450°C gives yields respectively of ~25% of benzene and ~32% of toluene together with 2% of benzene.

Kotlyarevskii[191] obtained a 7% yield of aromatic hydrocarbons by passing hexadien-3-yne in a current of hydrogen over activated carbon at 500°C. On an alumina–chrome catalyst this alkenyne gave ~25% of aromatics at 450°C, and up to 85% at 500°C; in the latter experiments the products included 20% of benzene and 10% of anthracene together with naphthalene and other aromatic hydrocarbons. On the same catalyst at 400°C a yield of 24% of *p*-xylene was obtained from 2,5-dimethylhex-3-yne and up to 28% of toluene from 2-methylhexadien-3-yne.

Formation from alkynes themselves of the horseshoe configuration necessary for cyclisation may be supposed to be extremely difficult, since three or four carbon atoms lie in a straight line (in alk-1-ynes or in alk-2- and -3-ynes and hexadien-3-yne). As, however, the isomerisation of alkynes on chromic oxide yields conjugated dienes[192], it may be assumed that monocyclic aromatic hydrocarbons are formed from the dienes, not directly from the initial alkynes. Aromatic hydrocarbons having fused rings are probably formed from several molecules of the alkyne.

3. Secondary Reactions

The dehydrocyclisation of hydrocarbons on oxide catalysts is accompanied by several side reactions, which have a significant effect on the composition of the products and the yield of aromatic hydrocarbons. Amongst such reactions are cracking, the isomerisation of aliphatic hydrocarbons, the dealkylation and alkylation of aromatic hydrocarbons, carbonisation, and also the hydrogenation of unsaturated hydrocarbons. Since all these reactions other than the last are retarded when the catalysts are promoted with alkaline additions[63,66], it may be supposed that they are catalysed mainly by a carbonium mechanism involving acidic centres, and are connected with changes undergone by intermediate or initial unsaturated hydrocarbons. With a large excess of alkali-metal oxide in the alumina–chrome catalyst the mechanism of cracking and carbonisation probably changes, and these reactions begin to take place by a carbanion mechanism[66].

Cracking. This is intensified by increase in the molecular weight of the initial hydrocarbon[78,140], rise in the reaction temperature[67,140], and increase in the contact time[67,83]. Varshaver[67] has found that gas formation in the dehydrocyclisation of n-heptane on various alumina–chrome–potash catalysts is well described by a fractional linear equation.

Isomerisation. Hydrocarbons are observed to isomerise in many of their catalytic reactions, e.g. dehydrogenation of the lower alkanes[193,194]. Earlier results on the isomerisation of hydrocarbons during dehydrocyclisation were discussed in adequate detail by Obolentsev[195–197]. Isomerisation has little effect on the yield of aromatics in the dehydrocyclisation of n-hexane and n-heptane; it is responsible for the appearance of small quantities of alkanes and alkenes of branched-chain structure among the products. However, isomerisation becomes very noticeable in the dehydrocyclisation of ^{14}C-labelled heptanes and octanes. Migration of the radiocarbon atom, which has been established in these cases[122,130,141,144,198–202], is probably due to isomerisation of the carbon skeleton of intermediate unsaturated aliphatic hydrocarbons, not to peculiarities of the mechanism of dehydrocyclisation.

Hydrodealkylation. Appreciable hydrodealkylation of the aromatic hydrocarbon formed is already evident in the dehydrocyclisation of n-heptane, and leads to the formation of benzene from toluene, and to the appearance of benzene and toluene among the products of the dehydrocyclisation of octane, as stated above. On an alumina–chrome–potash catalyst the hydrodealkylation of ethylbenzene is more rapid than that of xylenes by factors of 2–10,[127] the formation of benzene from ethylbenzene probably occurring by two mechanisms—elimination of the ethyl group and initial elimination of a methyl group with subsequent detachment of a second methyl from the resulting toluene.

Alkylation. Hexane and heptane show especially appreciable alkylation of the aromatic hydrocarbons formed by dehydrocyclisation (see above discussion of the composition of the products of dehydrocyclisation). Alkylation probably occurs by a carbonium mechanism, since the introduction of potassium oxide into an alumina–chrome catalyst strongly inhibits this reaction, as has already been noted.

Carbonisation. In comparison with other side reactions carbonisation has the most adverse effect on the dehydrocyclisation of hydrocarbons, since it poisons the catalyst and makes regeneration necessary. Raising the temperature, increasing the space velocity, and extending the duration of the experimental result in increased quantities of carbon on the catalyst[67,78,203,204]. Under otherwise similar conditions the yield of carbon depends on the nature of the hydrocarbon, increasing in the sequence—cyclohexanes, alkanes, alkenes, and alkylcyclopentanes—which are converted into alkylcyclopentadienes. It follows from Section II, 2 that the yield of carbon is influenced also by the chemical composition and the properties of the catalyst, e.g. the nature of its porosity[205].

During dehydrocyclisation carbon is deposited non-uniformly along a stationary layer of catalyst[206]: the rate of deposition is highest at the beginning of the layer, and falls gradually to the end. The distribution of carbon depends also on the starting materials and the properties of the catalyst. This has been examined theoretically by Froment and Bischoff[207,208]. According to Novikova et al.[117,209] carbon is deposited uniformly throughout the mass of a fluidised bed of an alumina–chrome–potash catalyst during the dehydrocyclisation of n-heptane.

Equations for the dependence of catalyst poisoning on experiment duration in the dehydrocyclisation of alkanes have been given by Herington and Rideal[129] for an alumina–chrome catalyst, and later by Sterligov[156] for an alumina–molybdenum catalyst (see also Ref. 210 for equations describing the poisoning of a catalyst by carbon).

The carbon formed on catalysts itself catalyses the dehydrocyclisation of hydrocarbons[211], their dehydrogenation[212], and irreversible catalysis[213].

4. Kinetics of Dehydrocyclisation

Pitkethly and Steiner[5], Herington and Rideal[129], and Karzhev and Sorokin[214] assumed that the dehydrocyclisation of alkanes, in particular of n-heptane, was a first-order reaction. Griffith et al.[38] consider it to be of zero order. Tarasova and Kazanskii[158] found that dehydrocyclisation on an alumina–chrome–potash catalyst is a zero-order reaction with high rates of supply of hexane. According to Obolentsev[215] the yield of aromatic hydrocarbons and the total yield of aromatics and alkenes are exponential functions of the time of contact. Later Steiner[10] concluded that dehydrocyclisation may have a fractional order. Chinese workers[216] and later Skarchenko[217] considered that Frost's well known equation[218] gives a good description of the yield of aromatics from alkanes. According to Petrov[219] the total yield of benzene and alkenes from n-hexane can be represented by Frost's equation, but the yield of benzene requires a first-order rate equation. Panchenkov et al.[220] derived a fairly complicated kinetic equation for the dehydrocyclisation of alkanes, assuming that it involves the intermediate formation of alkenes and it accompanied by carbonisation.

Kazanskii, Rozengart, and their coworkers[206,221,222] have shown that the dehydrocyclisation of alkanes may be subject to internal diffusion retardation, which increases from hexane to heptane. The difference in the extent of diffusion retardation with different hydrocarbons depends on variations not so much in their diffusion coefficients as in their reactivities. This circumstance, and also the highly endothermic character of the reaction, leading to steep temperature gradients in the catalyst bed, together with the decrease in the activity of the catalyst during the experiments, have not always been taken into account in experiments serving as a basis for the deduction or the verification of the above kinetic equations. Therefore published kinetic parameters can be regarded only as a first approximation. Kinetic aspects of dehydrocyclisation merit special investigation in the light of modern ideas, methods, and techniques for the kinetic study of catalytic reactions[223-226].

5. Multistage Mechanism of Dehydrocyclisation

The mechanism of the dehydrocyclisation of alkanes has already been discussed for more than thirty years, but the problem has still not been finally solved. The results considered below will evidently permit a closer approach to its solution in the case of alumina–chrome–potash and alumina–molybdenum–potash catalysts, and very probably with certain other oxide catalysts.

Pitkethly and Steiner[5], Hoog[227], and later Herington and Rideal[129] assumed that the hydrocarbon molecule undergoes dissociative adsorption with formation of an alk-1-ene chemisorbed at the site of the double bond, which is converted into a chemisorbed cyclohexane and then into an aromatic hydrocarbon. Many authors have held the opinion, that an aromatic hydrocarbon is formed on chromic oxide catalysts via an alkene[219,220,228-232]. However, this has been proved for the dehydrocyclisation of alkanes only in the work of Rozengart, Kazanskii, and their coworkers with heptane on alumina–chrome–potash[174] and hexane on alumina–molybdenum–potash[233] catalysts and also with mixtures of n-hexane with labelled hex-1-ene[234].

According to the second alternative scheme of Pitkethly and Steiner[5] the alkane is present on the catalyst initially in a semi-hydrogenated state, and then forms a biradical with the chemisorbed first and sixth carbon atoms of the chain, which is subsequently converted into the aromatic hydrocarbon. The formation of alkenes is in this case a side reaction.

According to Kagan et al.[235] an alkane molecule, adsorbed on the catalyst by one carbon atom, can then be adsorbed by any other atom. If the latter is an adjacent atom, an alkene is formed; if, however, the other atom is the sixth, cyclisation occurs.

Plate and Tarasova suggested[8] that a sextet orientation of the hydrocarbon molecule is possible on an alumina–vanadium catalyst, since vanadium oxide, like chromic oxide and aluminium oxide, has the corundum type of lattice. On chemisorption on such sextets the alkane molecule forms an intermediate six-membered structure, which loses hydrogen and is converted into a benzene ring. In this case the formation of alkenes will be a side reaction, although they also are partly converted into aromatics. Plate and Tarasova do not exclude the possibility that, on a different catalyst with a distribution of active centres more favourable for the formation of alkenes, these may be the principal source of aromatic hydrocarbons. Lipovich et al.[236-238], from a study of the dehydrocyclisation on an alumina–chrome–potash catalyst of mixtures of n-heptane and n-heptenes in which one of the hydrocarbons was labelled with radiocarbon, also conclude that toluene is obtained by two routes—via alkenes desorbed into the gas phase and by a route independent of them—under the conditions of a flow experiment.

Davis[239] also supports the hypothetical sextet mechanism for the dehydrocyclisation of alkanes. He explains the fact that molybdenum oxide alone does not cause dehydrocyclisation, but is able to do so when deposited on aluminium oxide, by the absence of sextets from its crystal lattice, whereas in an alumina–molybdenum catalyst the molybdenum atoms are situated in the vacant octahedral cavities of the γ-alumina lattice, to form sextets on which the hydrocarbon molecule is chemisorbed.

Mitchell[199] explained the distribution of carbon-14 in toluene obtained from [^{14}C] heptane on the assumption that dehydrocyclisation involves the intermediate formation of a cyclopentane, which, with subsequent ring expansion or via the formation of a bicyclic hydrocarbon containing an endomethylene bridge, is converted into methylcyclohexane and then into toluene. As already mentioned, Pines and his coworkers[131,141] assume that the dehydrocyclisation of C_6–C_8 alkanes involves the formation of 5–8-membered rings, which are then converted into six-membered rings and into an aromatic hydrocarbon. However, Kazanskii, Rozengart, et al.[240-242] report that cyclohexanes or their adsorbed forms are not intermediate products on a chromic oxide catalyst, at least under pulse conditions. Hence the traces of cyclohexanes obtained in the catalytic aromatisation of alkanes are most probably products of secondary or side reactions.

Interesting information on the interaction between hydrocarbon molecule and catalyst has been obtained in a study of the adsorption and especially the chemisorption of hydrocarbons. Rubinshtein et al.[243-250] found that, contrary to the generally held view, alkanes and cyclohexane undergo chemisorption to a greater extent than alkenes or benzene on an alumina–chrome–potash catalyst, and that the chemisorption of hydrocarbons is related to their electron-accepting properties. In the opinion of Slovetskaya and Rubinshtein[250] the chemisorption of alkanes is directly connected with their subsequent dehydrogenation.

Usov et al.[252], using Balandin's method[252] to determine adsorption coefficients, also established that hexane at 490°C and heptane at 460–475°C are adsorbed on an alumina–chrome catalyst considerably better than is the corresponding aromatic hydrocarbon; at 500°C, however, the adsorption on n-heptane is almost the same as that of toluene. On an alumina–molybdenum catalyst at 480 to 490°C alkanes are adsorbed to the same extent as are aromatics.

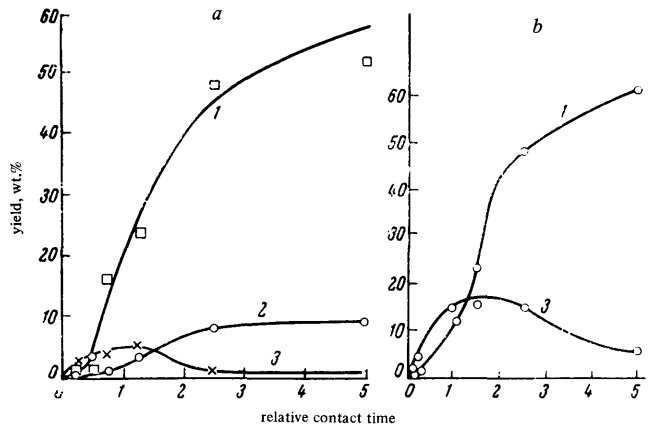


Figure 6. Dependence of yields of products of the dehydrocyclisation of hept-1-ene at 450°C on the relative contact time[172,175] (see footnote to Fig. 5) in: *a*) flow apparatus; *b*) pulse apparatus: 1) aromatic hydrocarbons; 2) n-heptane; 3) heptadienes.

A study in our laboratory of the effect of time of contact on the yield of aromatic and unsaturated hydrocarbons in the dehydrocyclisation of n-hexane, n-heptane, and n-octane on an alumina–chrome–potash catalyst in the usual flow (Fig. 5) and pulse types of apparatus has shown[78,128], in agreement with results obtained by other workers, that the yield of alkenes exceeds that of aromatics at short contact times, and passes through a maximum with increase in the contact time. The dehydrocyclisation of hept-1-ene in a stream of helium in both types of apparatus exhibits[171,174] an analogous relative arrangement of the curves for the yields of toluene and of heptadienes (Fig. 6), but in the dehydrocyclisation of hepta-1,3-diene under pulse conditions a very similar situation is observed[170,171] for the yields of aromatics and of heptatriene (Fig. 7). Indeed, it was not possible in the latter case to observe a higher yield of trienes than of toluene at short times of contact. The dehydrocyclisation of hepta-1,3,5-triene produces methylcyclohexadiene and toluene[170,171]. The yield of the latter increases with increased duration of contact with the catalyst, but the total yield of cycloalkadiene and arene remains almost constant and equal to the yield of methylcyclohexadiene in the thermal cyclisation of heptatriene under the same conditions (Fig. 8).

On the basis of the above facts Rozengart et al.[170] put forward the hypothesis that the dehydrocyclisation of alkanes is a multistage consecutive reaction:

alkane → alkenes → dienes → trienes → alkylcyclohexadienes → aromatic hydrocarbons.

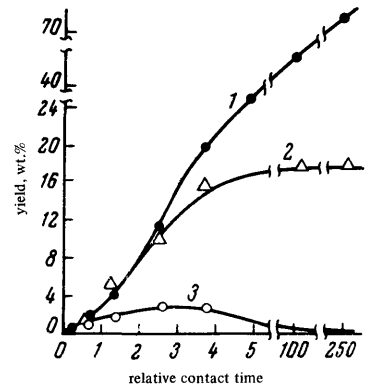


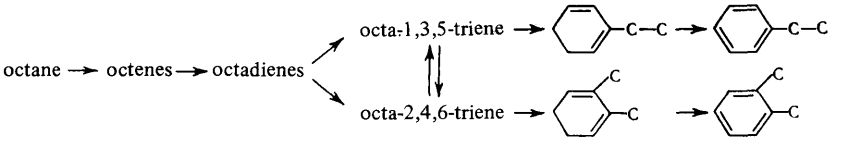
Figure 7. Dependence of product yields from the dehydrocyclisation of hepta-1,3-diene at 450°C on relative contact time (see footnote to Fig. 5) in a pulse apparatus[171,172]: 1) arenes; 2) n-heptenes; 3) heptatrienes.

All dehydrogenation stages in this scheme are catalytic, but the cyclisation stage—formation of an alkylcyclohexadiene from a triene—is thermal. Two years after publication of our results, Krause[253] suggested that heptatriene is formed in the dehydrocyclisation of heptane. In his opinion, however, toluene is formed from the intermediate heptatriene by catalytic dehydrocyclisation in a single stage, which is inconsistent with the above experimental results. The rate-determining stage of the overall process of dehydrocyclisation is probably the first stage of dehydrogenation, whatever the initial hydrocarbon—alkane, alkene, or diene.

It must be noted that our results cannot exclude the possibility of simultaneous catalytic cyclisation of part of the intermediate dienes. Since we obtained fundamentally the same results for the dehydrocyclisation of n-heptane, hept-1-ene, and n-octane in the usual flow and pulse types of equipment, the above scheme can be assumed to apply also under the conditions of the usual flow-apparatus.

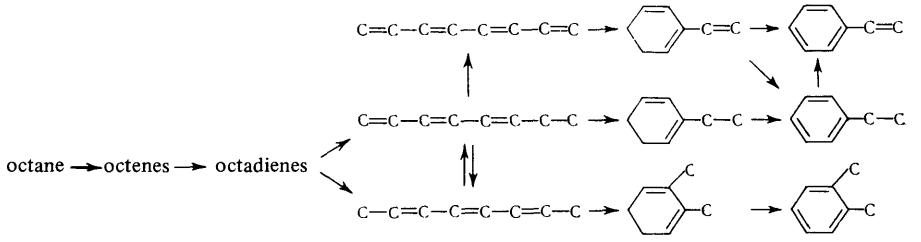
The above multistage consecutive reaction scheme has enabled us to understand certain features of the dehydrocyclisation of n-octane on an alumina–chrome–potash catalyst. Thus it has been found[167] in particular that, in experiments in pulse and flow type of apparatus, rise in temperature produces a greater increase in the yield of ethylbenzene, formed by closure of a bond between the first and sixth carbon atoms, than in that of *o*-xylene, which requires bond formation between the second and seventh carbon atoms. Variation in the relative yields of ethylbenzene and *o*-xylene cannot be a consequence of their

mutual isomerisation, because, as mentioned above, it has been established that aromatic hydrocarbons do not isomerise on chromic oxide catalysts. Since n-octane is obviously dehydrocyclised by the same scheme as has been established for heptanes, it may be supposed that in a flow apparatus ethylbenzene and *o*-xylene result from the intermediate formation of octa-1,3,5-triene and octa-2,4,6-triene respectively. The thermodynamic equilibrium of these trienes probably governs also the proportions of aromatic hydrocarbons formed in the main reaction:



From the variation in the relative yields of ethylbenzene and *o*-xylene in this series of experiments, the equilibrium shifts partly towards formation of octa-1,3,5-triene with rise in temperature.

When n-octane was diluted with helium, and especially on passing from experiments in the usual flow apparatus to pulse conditions, the yield of styrene increased[167] from 1% to 30% on an alumina–chrome–potash catalyst and to 43% on an alumina–molybdenum–potash catalyst. Analysis of the results indicated that, under pulse conditions with low partial pressures of all components of the reaction mixture (including the hydrogen formed), yields are increased in the dehydrogenation of ethylbenzene to styrene and of octa-1,3,5-triene to octa-1,3,5,7-tetraene; this last compound cyclises to vinylcyclohexadiene, which is dehydrogenated to styrene or may be partly isomerised to ethylbenzene. Therefore the scheme of conversion of hydrocarbons in the dehydrocyclisation of n-octane under pulse conditions is somewhat modified:



Under pulse conditions styrene is apparently formed in two ways, and the appearance of the second route also displaces the equilibrium between the octatrienes. As a consequence of the combined effects of dilution and rise in temperature, the products of ring closure between the first and sixth carbon atoms (with formation of ethylbenzene and styrene) come to exceed the product formed by closure between the second and seventh atoms (*o*-xylene), and the yield of styrene based on the n-octane which has reacted reaches 40% at 600°C.[167]

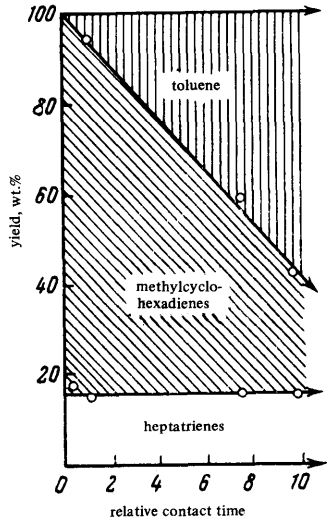


Figure 8. Dependence of product yields in the dehydrocyclisation of hepta-1,3,5-triene at 450°C in a pulse apparatus on relative contact time (see footnote to Fig. 5).[171]

If the dehydrocyclisation of aliphatic hydrocarbons is assumed to comprise a series of successive dehydrogenation stages, the interaction of the hydrocarbon with the catalyst must also be considered from this point of view. The catalyst may be supposed to detach (or draw off) a proton from the hydrocarbon molecule, and the resulting carbanion is chemisorbed; or else the hydrocarbon molecule, on losing a hydrogen atom, is chemisorbed as an alkyl radical (semi-hydrogenated state). According to Myasnikov[254] such radicals, adsorbed on semiconducting oxides, are rapidly converted into a chemisorbed carbanion†. There follows detachment of a second hydrogen atom or hydride ion from an adjacent carbon atom with formation of a double bond according to the mechanism suggested by Kazanskii[255] on the basis of the atomic characteristics of chromium as a transition metal.

If the view is held that dehydrogenation begins with the detachment of one hydrogen atom, it becomes clear why dehydrogenation and then dehydrocyclisation of an alkene are more rapid than those of an alkane: detachment of a hydrogen atom or ion should occur more rapidly in the

† No experimental results are at present available which would allow us to assess whether the chemisorption of hydrocarbons involves rupture of a carbon–hydrogen bond or its deformation-polarisation.

allyl position, since the energy of bonding of an allylic hydrogen to carbon is smaller[256].

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The information covered in this Review indicates that the dehydrocyclisation of aliphatic hydrocarbons is quite complicated and consists of a series of successive stages. Since this reaction is accompanied by several side reactions, elucidation of the fundamental laws of dehydrocyclisation presents great difficulties; as has been shown in the Review, certain aspects of the transformation of hydrocarbons on a catalyst and the mechanism of its action are still not known accurately or may not even have been revealed. However, since new methods of investigating complicated reactions have appeared during recent years, the dehydrocyclisation of aliphatic hydrocarbons may be expected to become a favourable subject for further study, which will make an important contribution to the understanding of the fundamental principles of organic catalysis. On the other hand, the appearance of publications on industrial processes based on such reactions[43,70,180,257] provides the hope that the production of individual aromatic hydrocarbons (primarily benzene) from alkanes present in petroleum will meet with practical success.

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