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The Mechanism of Aromatization on Platinum Black Catalyst; Dehydrocyclization of Hexadienes and Hexatrienes

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The aromatization of hexadiene isomers as well as *trans*- and *cis*-1,3,5-hexatriene on Pt-black catalyst has been studied in the presence of helium and hydrogen–helium mixtures. The extent of benzene formation from all of the hydrocarbons was of the same order of magnitude, and the activity of the catalyst rapidly decreased when subsequent pulses of hydrocarbons were introduced without regeneration. The only exception was *cis*-triene where the benzene yield was much higher and deactivation slower. The presence of hydrogen even at small partial pressure considerably slowed down the deactivation. The role of hexatrienes as intermediates of aromatization has been evaluated in the case of different hexadiene isomers. A stepwise scheme of aromatization involving steps of dehydrogenation and *cis–trans* isomerization has been proposed. The importance of these two processes is considered to be about the same in the overall reaction rate, whereas the ring closure step is regarded as very fast. The precursors of coke formation on the catalyst surface are supposedly *trans*-polyenes. The relative importance of benzene and coke formation are determined by the presence of hydrogen in the gas phase.

INTRODUCTION

The "classical" concepts of the mechanism of catalytic aromatization of open chain hydrocarbons in the presence of metal and oxide catalysts were different. The aromatization in the presence of oxides was explained by the Twigg mechanism (*1*) according to which the first step of the reaction was a paraffin → olefin transformation. The olefin assumedly isomerized into cyclohexanic hydrocarbon followed by the dehydrogenation of the latter into aromatics. On the other hand, aromatization in the presence of platinum-on-charcoal supposedly involved a direct paraffin → cycloparaffin reaction (*2*).

These classical theories have recently had to be reconsidered. It was found that during aromatization of *n*-heptene on chromia no methyl cyclohexane was formed. Instead, heptadiene and heptatriene intermediates were found (*3, 4*).

Moreover, it has been shown recently (*5, 6*) that cyclohexane dehydrogenation on metals does not exclusively follow the classical sextet mechanism. On this basis, subsequent experiments have shown that *n*-hexenes are the primary products of the dehydrocyclization of *n*-hexane in the presence of Pt and Ni catalysts (*7*). These, in turn, aromatize via hexadiene (*8*) and hexatriene (*9*) intermediates. Similar unsaturated intermediates of the aromatization have since been observed also in the presence of palladium catalyst (*10, 11*). At the same time, it was proved by radiotracer experiments that neither cyclohexane nor cyclohexene was formed during the ring closure step (*12*). These experiments indicated an analogous mechanism of aromatization in the presence of oxide and metal catalysts, involving stepwise hydrogen elimination.

Recently, Dautzenberg and Platteeuw (*13*) proposed, on a mainly speculative basis, a *n*-hexane → *n*-hexatriene reaction in the course of aromatization on Pt followed by the thermal cyclization of the latter; at the same time, however, they assumed another, unspecified "platinum-catalyzed direct way of aromatization." Their results indicated that the partial pressure of hydrogen present had a considerable effect on the ratio of the two reaction paths.

It can be seen that the exact nature of the closing steps of stepwise aromatization leading ultimately to the formation of the benzene ring has not yet been elucidated in every detail. In the present work we considered it reasonable to investigate these steps using hexadiene and hexatriene as the starting materials (in most possible cases individual isomers) to obtain a deeper insight into the problems mentioned. No experiments have been carried out so far with separate *cis*- and *trans*-1,3,5-hexatriene isomers in spite of the well-known fact (*20*) that their reactivities are very different.

It is well known that the presence of hydrogen is necessary for reactions of aromatization, mainly to maintain the catalyst activity (*14*). Recent investigations have shown that whereas the presence of hydrogen has an enhancing effect on the extent of aromatization, it can also affect the direction of the reactions; in addition to aromatization, C_5-cyclization and isomerization can take place on Pt-black in hydrogen-rich atmosphere (*15*). The former process is sometimes supposed to play an important role in benzene formation (*10*).

We have therefore investigated both the effect of hydrogen on the reactivities of the hydrocarbons and the reaction possibilities. This has been carried out by reacting the hexadiene and hexatriene isomers on a platinum black catalyst in helium and in the presence of helium-hydrogen mixtures containing different amounts of hydrogen.

EXPERIMENTAL METHODS

Apparatus and Catalyst

The experiments were carried out in a pulse type microreactor described in detail earlier (*7*). The carrier-free platinum black catalyst was prepared from H_2PtCl_6 by reducing it with HCHO in KOH according to (*16*). The catalyst activity was adjusted before experiments by pulse-like injections of air and (subsequently) hydrogen. In some experiments, however, no treatment was done before introducing the hydrocarbon pulses. The amount of the latter was 3–5 μl. The carrier gases were pure (99.9%) He, H_2 and their mixtures made up in advance in steel cylinders. The hydrogen content of the mixtures was 5.25 or 20.4%; these mixtures will later be quoted as ones containing 5 and 20% of hydrogen, respectively.

The analyses were carried out by using two gas–liquid chromatographic columns alternatively: the stationary phases of these were 17% of triethylene glycol dibutyrate and 14% of squalane, respectively, both on Chromosorb P. The length of the columns was 160 cm. A thermal conductivity cell served as the detector; its sensitivity was better than 0.1 μg which corresponded to about 0.05% of the usual pulse size.

Hydrocarbons

n-Hexane: Merck "Reference for gas chromatography," better than 99.9%.

1-Hexene: EGA-Chemie, purity of 99.95%.

1,5-Hexadiene: was synthesized from allyl bromide (*17*) and was purified by repeated fractional distillation.

1,4- 1,3- and 2,4-Hexadienes: were synthesized by pyrolysis of 3-acetoxy- and 4-acetoxy-1-hexene, respectively (*18*). In all cases a mixture of hexadiene isomers was produced which was subsequently separated by preparative gas chromatography. The starting hydrocarbons always contained some of the other isomers; their composition is shown in Table 1.

1,4-Hexadiene and 1,3-hexadiene consisted predominantly of *trans*-isomer, as their ir spectra have shown. In some experiments the mixture of the three geometrical isomers of 2,4-hexadiene was used, but experiments were carried out also with pure *cis*–*trans*- and *trans*–*trans*-2,4-hexadienes supplied by Fluka.

1,3,5-Hexatriene was prepared according to the method described in (*19*). The re-

TABLE 1
CONVERSION OF DIFFERENT HEXADIENE ISOMERS[a]

Starting hydrocarbon	Composition (mass %)											
				Hexadienes								
	$<C_6$	Hexane	Hexenes	1,5-	1,4-	1,3-	*t*-*t*-2,4-	*c*-*t*-2,4-	*c*-*c*-2,4-	1-Methyl-cyclopentene	*trans*-1,3,5-Hexatriene	Benzene
A. Analysis of starting hydrocarbons												
1,5-Hexadiene	0.2	—	—	99.8	—	—	—	—	—	—	—	—
1,4-Hexadiene	1.0	0.95	1.9	—	96.0	0.15	—	—	—	—	—	—
1,3-Hexadiene	—	—	—	—	1.7	96.4	0.9	1.0	—	—	—	—
2,4-Hexadiene	—	0.15	—	—	—	2.2	8.9	75.6	12.8	0.35	—	—
B. Reaction without catalyst, t = 360°C												
1,5-Hexadiene	0.3	—	—	99.6	—	0.1	—	—	—	—	—	—
1,4-Hexadiene	1.1	1.1	2.0	—	95.6	0.2	—	—	—	—	—	—
1,3-Hexadiene	—	—	—	—	1.7	96.0	0.1	2.2	—	—	—	—
2,4-Hexadiene	—	—	—	—	—	8.1	8.4	70.0	13.3	0.6	—	—
C. Catalyst 0.76 g Pt, t = 360°C												
1,5-Hexadiene	—	1.4	18.8	34.4	8.3	5.9	12.9	11.3	2.7	0.2	0.4	4.0
1,4-Hexadiene	1.0	1.4	16.7	3.9	23.8	8.8	19.2	17.0	3.4	0.3	0.9	3.5
1,3-Hexadiene	0.7	0.3	19.1	3.9	1.8	26.2	20.0	19.7	4.7	—	0.6	3.0
2,4-Hexadiene	0.2	0.1	20.0	—	1.5	9.4	22.6	34.9	7.2	0.1	0.2	3.7

[a] Carrier gas: 60 ml/min helium, 3 μl hydrocarbon pulses each.

sulting geometrical isomers were separated using preparative gas chromatography. Experiments were carried out within 24 hr after separation to prevent the spontaneous degradation of the triene isomers.

RESULTS

Aromatization of Hexadienes

It has been shown earlier that a mixture of hexadienes can be converted into benzene with a rate in the range of that of the hexenes (*8*). The rates of aromatization of individual hexadiene isomers were close to each other (Table 1). It can be seen that the aromatization was accompanied by other reactions: hydrogenation (to hexenes and to a minor extent to hexane) and a considerable double bond isomerization. The latter reaction resulted in isomers with mainly conjugated double bonds. It should be noted that 2,4-hexadiene can transform into 1,3-hexadiene even without catalyst, when introduced to a heated empty reactor (Table 1). At the same time other hexadienes showed hardly any reaction under these circumstances.

As a result of the rapid double bond isomerization we observed the reaction products of a mixture of hexadiene isomers in the case of catalysts of higher activity, that is after regeneration. If, however, we allow an appropriately small catalyst sample to lose its activity gradually by introducing hydrocarbon pulses without regeneration, the isomerization activity may be suppressed to a large extent and at the same time its aromatizing activity is still observable. Under these conditions we are able to follow the aromatization of individual isomers on a catalyst gradually losing its activity.

In the course of the catalyst deactivation 1,3,5-hexatriene appears among the products (Table 2). Its amount has a maximum as a function of the catalyst activity, whereas the amount of benzene decreases monotonically with decreasing activity. This behavior is characteristic of the production of an intermediate and end product in a multistage reaction.

In Fig. 1 the percentages of 1,3,5-hexatriene (%triene) and benzene (%bz) formed from different hexadienes have been shown as a function of the "overall dehydrogenating activity" Y_{DH} of a catalyst in the process of its deactivation. Y_{DH} was defined the following way:

$$Y_{DH} = 2.(\%\text{bz}) + (\%\text{triene}) \qquad (1)$$

The scaling of the abscissa is exponential, corresponding to the exponential relationship between the length of a tubular reactor (i.e., "amount" of catalyst in it) and the degree of conversion (in the case of a supposed first order reaction).

The curves are different for different hexadienes; for 1,3- 1,4- and 1,5-hexadienes

TABLE 2

CONVERSION OF HEXADIENE-1,4 ON A CATALYST OF DECREASING ACTIVITY[a]

No. of pulse	Composition (mass %)							
	$<C_6$	Hexane	Hexenes	1,5-Hexadiene[b]	1,4-Hexadiene	1,3- + 2,4-Hexadienes	*trans*-1,3,5-Hexatriene	Benzene
1	2.9	0.7	3.4	2.7	82.5	2.0	0.03	5.7
2	0.3	—	0.5	0.6	92.7	4.8	0.25	0.9
3	0.2	—	0.65	0.7	90.4	6.75	0.55	0.75
4	0.1	—	0.6	0.5	92.3	5.6	0.6	0.3
5	0.1	—	0.65	0.65	92.7	5.15	0.5	0.2
6	0.05	—	0.55	0.5	93.1	5.05	0.5	0.2
7	0.05	—	0.7	0.65	93.1	4.8	0.5	0.15
8	—	—	0.6	0.5	94.0	4.4	0.4	0.1

[a] Catalyst, 0.4 g Pt; t = 360°C; carrier gas: 60 ml/min He, 5 μl hydrocarbon pulses each.

[b] Not separated from *cis*-hexene-2 the amount of which may be considerable only in the product of the first pulse.

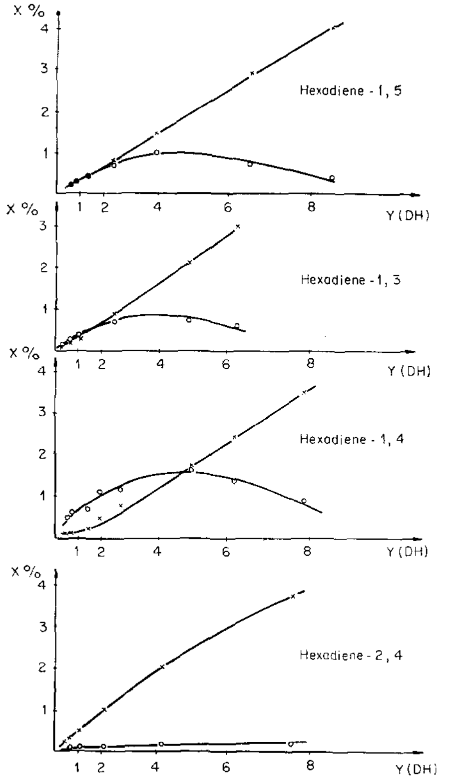


FIG. 1. The amounts of benzene (×) and *trans*-1,3,5-hexatriene (○) formed from individual hexadiene isomers as a function of catalytic activity, i.e., apparent contact time. Catalyst: 0.76 g Pt, $t = 360°C$.

there are maxima on the hexatriene curves (although the relative positions of the benzene and triene curves are not identical) while in the case of 2,4-hexadiene no maximum could be observed.

Aromatization of Hexatrienes

The behavior of the individual geometric isomers of hexatriene was different under analogous conditions. The extent of benzene formation from *trans*-triene was not much higher than that from hexadienes, whereas the reaction of *cis*-triene was almost quantitative. The catalyst was deactivated by both isomers although to a very different extent; during this process the amount of benzene formed decreased and an increasing quantity of cyclohexadiene appeared (Table 3).

In order to study the possible role of thermal cyclization of hexatriene isomers in aromatization [assumed in (*4*, *13*)], the behavior of an equilibrium mixture of *cis*- and *trans*-1,3,5-hexatriene was studied in the presence and absence of catalyst (Table 4), as a function of the temperature. A very rapid thermal cyclization of the *cis*-isomer could be observed (*20*), whereas that of the *trans*-isomer took place only above about 360°C. At higher temperatures where

TABLE 3

CATALYTIC REACTIONS OF *cis*- AND *trans*-1,3,5-HEXATRIENE[a]

	Composition (mass %)											
				Hexadienes						1,3,5-Hexatriene		
No. of pulse	<C$_6$	Hexane	Hexenes[b]	1,4-	1,3-	*t*-*t*-2,4-	Cyclohexane	Cyclohexene	1,3-Cyclohexadiene[c]	*trans*	*cis*	Benzene
A. Starting hydrocarbon: *trans*-1,3,5-hexatriene												
1	2.2	0.1	1.7	0.4	0.3	0.6	—	—	18.8	62.6	—	13.4
2	—	—	—	0.3	0.2	0.1	—	—	30.6	65.9	—	3.0
5	—	—	—	0.1	0.2	0.1	—	—	29.5	69.2	—	0.8
B. Starting hydrocarbon: *cis*-1,3,5-hexatriene												
1	6.2	0.7	0.4	—	—	—	—	—	—	—	—	92.7
2	2.5	—	1.2	—	0.4	1.9	0.4	2.5	12.1	1.0	—	78.3
5	0.2	—	0.1	—	1.2	2.3	1.8	2.6	55.8	3.7	0.4	32.0
8	—	—	—	—	0.6	1.3	1.1	0.9	71.8	7.7	1.3	15.4

[a] Catalyst, 0.4 g Pt; $t = 360°C$; carrier gas: 60 ml/min He, 5 μl hydrocarbon pulses each.

[b] With 1,5-hexadiene.

[c] With *cis*–*trans*- and *cis*–*cis*-2,4-hexadiene.

TABLE 4

Catalytic and Thermal Transformations of 1,3,5-Hexatriene Mixture of Isomers[a]

	Products (mass %)							
	In empty reactor			In the presence of 0.16 g of Pt				
Temp (°C)	*cis*-Triene	*trans*-Triene	CHD[b]	Hydr. and cracked prod.	*cis*-Triene	*trans*-Triene	CHD[b]	Benzene
20	29.7	70.3	0	—	—	—	—	—
240	17.0	68.0	15.0	—	—	—	—	—
270	1.3	69.7	29.0	2.1	7.1	66.4	23.6	0.9
300	0	69.1	30.9	3.6	0	64.2	29.5	2.7
330	0	69.5	30.5	1.9	0	66.0	28.8	3.3
360	0	67.2	32.8	1.2	0	62.9	33.0	2.9
390	0	59.7	40.3	1.5	0	57.5	36.5	4.5
405	0	56.6	43.4	—	—	—	—	—
420	0	38.6	61.4	1.2	0	42.5	48.4	7.8
450	0	9.0	91.0	3.4	0	6.6	40.0	50.0
480	0	1.5	98.5	1.5	0	0	0.5	98.0

[a] Carrier gas: 60 ml/min helium, 2 μl of hydrocarbon pulses each.

[b] CHD = 1,3-cyclohexadiene.

the thermal *trans* → *cis* reaction is rapid, the rate of catalytic benzene formation increased to a very large extent. The lower yields in Table 4 compared with Table 3 are due to the deactivated character of the catalyst.

Effect of Hydrogen on the Reactions of Hexadienes and Hexatrienes

In the presence of small partial pressures of hydrogen an enhanced benzene formation from hexadienes and hexatrienes was

TABLE 5

Deactivation of Aromatizing Activity of Pt-Black in the Presence of Carrier Gases of Different Composition[a]

	Benzene (mass %) in the product of the first hydrocarbon pulse if the carrier gas is			Remaining activity of the catalyst (%)[b] after passing 30 μl of hydrocarbon if the carrier gas is		
Starting hydrocarbon	He	5% H_2 + 95% He	20% H_2 + 80% He	He	5% H_2 + 95% He	20% H_2 + 80% He
n-Hexane	8.1	10.0	16.0	9.4	26.5	56.5
1,5-Hexadiene	7.1	8.3	8.7	—	36.4	83.0
1,4-Hexadiene	5.7	10.3	10.5	3.6	40.7	—
1,3-Hexadiene	4.3	7.9	8.4	1.4	45.0	69.0
2,4-Hexadiene						
trans–trans	4.5	9.5	12.8	2.2	33.0	55.5
cis–trans	4.7	10.0	11.6	2.1	31.0	62.0
1,3,5-Hexatriene						
trans	13.4	19.4	17.7	5.6	23.5	90.5
cis	92.7	90.1	87.7	25.7	99.2	97.5

[a] Catalyst: 0.4 g Pt; t = 360°C; carrier gas: 60 ml/min.

[b] Expressed as [benzene (%) from final pulse/benzene (%) from first pulse] × 100.

TABLE 6

CONVERSION OF HEXADIENES AND HEXATRIENES IN THE PRESENCE OF HYDROGEN[a]

Starting hydrocarbon	Composition (mass %)												
				Hexadienes									
	$<C_6$	Hexane	Hexenes	1,5-	1,4-	1,3-	*t-t*-2,4-	*c-t*-2,4-	*c-c*-2,4-	1,3-Cyclohexadiene	1-Methylcyclopentene	*trans*-1,3,5-Hexatriene	Benzene
1,5-Hexadiene	4.0	8.1	21.5	37.4	5.3	3.2	5.8	6.3		—	0.3	0.06	8.3
1,4-Hexadiene	5.2	10.0	58.6		3.7	1.1	4.2	4.6	1.7	—	0.45	—	10.3
1,3-Hexadiene	7.35	11.35	57.0	2.0	—	4.0	4.7	5.2	0.65	—	0.1	—	7.9
t-t-2,4-Hexadiene	7.8	8.6	43.1	2.0	—	1.9	19.4	6.2	1.1	—	0.3	—	9.5
c-t-2,4-Hexadiene	6.5	11.3	54.5	—	—	2.1	5.3	8.4	0.7	—	0.35	—	10.0
t-1,3,5-Hexatriene													
Pulse 1	3.7	3.7	24.8		5.4	4.4	11.0	17.5			—	9.9	19.4
Pulse 5	—	0.2	4.2		3.9	4.7	7.7	23.4			—	51.1	5.0
c-1,3,5-Hexatriene													
Pulse 1[b]	5.9	3.4	0.4		—	—	—	—	—	—	—	—	90.1
Pulse 5[c]	2.5	6.6	2.5		—	—	—	—	—	0.3	—	—	87.6

[a] Catalyst: 0.4 g Pt; t = 360°C, carrier gas: 60 ml/min 5% H_2 + 95% He, 5 μl hydrocarbon pulses each.

[b] +0.1% cyclohexene.

[c] +0.2% cyclohexane + 0.2% cyclohexene.

TABLE 7

Product Composition of Different Hydrocarbons Transformed in the Presence of Hydrogen[a]

Starting hydrocarbon	Composition (mass %)							
	$<C_6$	Isohexanes	*n*-Hexane	Hexenes[b]	Hexadienes	Hexatriene	Benzene	C_5-cyclic
n-Hexane	25.0	4.4	57.9	—	—	—	16.0	1.1[c]
1-Hexene	22.7	5.0	59.6	1.7	—	—	11.0	0.1[d]
1,3-Hexadiene	19.3	1.8	65.7	4.3	0.1	—	8.4	0.4[d]
1,4-Hexadiene	19.9	0.6	63.0	5.8	0.1	—	10.5	0.2[d]
trans-1,3,5-Hexatriene	16.6	0.5	54.9	9.4	0.1	—	17.7	0.7[d]
cis-1,3,5-Hexatriene	7.5	—	4.3	0.4	—	—	87.8	—

[a] Catalyst: 0.4 g Pt, $t = 360°C$, 5 μl of hydrocarbon pulses each; carrier gas: 60 ml/min 20% H_2 + 80% He.

[b] With methylcyclopentane.

[c] Methylcyclopentane.

[d] 1-Methylcyclopentene.

observed, similarly to previous experiments when n-hexane was used as the starting material (*15*). An even more marked effect could be observed with respect to the deactivation of the catalyst: in the presence of hydrogen this was much slower than in helium (Table 5).

Table 5 shows that in this case, too, a very considerable difference can be observed between the *trans*- and *cis*-triene.

At the same time that hydrogen enhanced aromatization, the reverse reaction of unsaturated hydrocarbons, i.e., hydrogenation, took place to a considerable extent. Even 5% hydrogen in the carrier gas led to the hydrogenation of most of the hexadienes into hexenes (Table 6). The contact time in our experiments was long enough for the hydrogenation of most of the unsaturated hydrocarbons, except for *cis*-triene, into hexane in 20% H_2 (Table 7).

The decrease of dehydrogenating activity in the presence of hydrogen was too slow and did not permit us to follow the variation of the concentration of intermediates as a function of catalyst activity. The hydrogenating activity, however, showed a more marked decrease during subsequent pulses. This phenomenon was observed in the case of each hydrocarbon, *trans*-hexatriene producing the most dramatic effect (Table 6).

In the presence of hydrogen, n-hexane transformed to some extent into isohexanes and methyl cyclopentane (*15*). These products appeared only when using a mixture containing 20% hydrogen (Table 7) and their amount was not considerable.

DISCUSSION

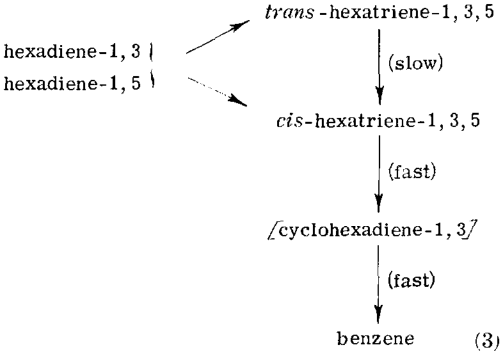
In the course of the stepwise dehydrogenation of normal chain and cyclic hydrocarbons it was supposed that hydrogen elimination takes place from a carbon atom adjacent to an existing double bond (*12*); presumably, a π-allyl interaction (*21*) will occur involving a double bond and the newly formed dehydrogenated carbon atom. Hexadienes, however, have only two carbon atoms in the sp^3 hybrid state and the process and products of their dehydrogenation depend on their actual position in the chain. Three different cases are illustrated in Fig. 1.

1. In the case of hexadiene-1,3 and hexadiene-1,5 the stepwise dehydrogenation can go on without disturbing the remaining part of the molecule:

$$\left.\begin{array}{l} CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH_3 \\ \\ CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \end{array}\right\} \xrightarrow{-H_2} CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 \qquad (2)$$

We assume that the probability of formation of the two hexatriene isomers is nearly equal. The *cis*-isomer reacts further very rapidly, forming benzene. The dehydrogenation of the *trans*-triene, however, especially at lower catalytic activities as demonstrated by direct experiments, is much slower. Thus, as it can be seen in Fig. 1 the curves of benzene (formed from *cis*-triene) and *trans*-triene tend to the origin very close to each other.

Thus, the scheme of aromatization in Case 1 is as follows:



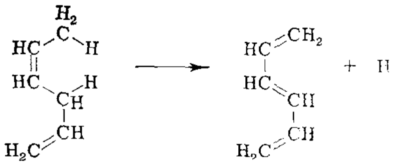
(3)

the curves in Fig. 1 corresponding to the triangular scheme involved in Eq. 3.

2. In the case of hexadiene-1,4, Fig. 1 indicates that the primary product of dehydrogenation is *trans*-1,3,5-hexatriene, the amount of which surpasses that of the ben-

zene at smaller activities. The curve of benzene tends tangentially towards zero. Stepwise dehydrogenation can, of course, occur in the case of 1,4-hexadiene, too. Considering the models of *cis*- and *trans*-1,4-hexadiene, it can be seen that *cis* dehydrogenates exclusively, whereas *trans* predominantly into *trans*-1,3,5-hexatriene.

Furthermore, in this case, conjugated elimination of hydrogen atoms from carbons in position 3 and 6 can be assumed. This is the reverse reaction of the 1,4 hydrogen addition to conjugated dienes which can also take place in the presence of metal catalysts (*22*, *23*). The process requires the adsorption of 1,4-hexadiene in the following configuration:


(4)

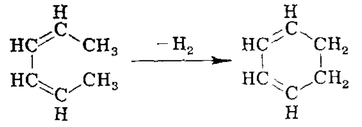
Hence, the conjugated elimination of two hydrogen atoms can result in exclusively *trans*-hexatriene.

Thus, the mechanism of benzene formation in this case is:

$$\text{hexadiene-1,4} \longrightarrow trans\text{-hexatriene-1,3,5} \xrightarrow{\text{slow}} cis\text{-hexatriene-1,3,5} \qquad (5)$$

$$\xrightarrow{\text{fast}} [\text{cyclohexadiene-1,3}] \longrightarrow \text{benzene}$$

3. In the case of hexadiene-2,4 the formation of hexatriene was negligible (Fig. 1); thus we may regard it as a by-product or a secondary product formed from other hexadienes (produced via catalytic or thermal isomerization). This suggests that the 1,6 hydrogen elimination necessary for hexatriene formation results, in fact, in a cyclic product, viz., cyclohexadiene.


(6)

Cyclohexadiene, however, could not be observed directly, due to its difficult gas chromatographic separation from *cis*–*cis*-2,4-hexadiene.

The formation of some short-lived adsorbed *cis*-triene species is not probable, but in principle cannot be excluded from the mechanism. This reaction needs some further investigation as does the reason why we cannot observe more hexatriene formation from 2,4-hexadienes with *trans*-configuration.

The behavior of hexatriene isomers verifies all the individual steps written in the schemes above.

It may be noted that no reservations were made concerning the type of adsorption of the diolefin: the supposed mechanisms may be valid in the case of either associative or π-type adsorption.

In our earlier publication (*12*) two steps, viz., dehydrogenation and ring closure, were suggested as being significant in the stepwise dehydrocyclization. Hydrocarbon molecules arriving at the catalyst surface will dehydrogenate, regardless of their actual configuration and/or conformation. The probability that the result of this process will be a structure ready to form a six-membered ring is fairly limited in all cases, except for *cis*-hexatriene. As a consequence, geometrical isomerization must be included as a third elementary step of the aromatization process. Its rate may be of the same order of magnitude as that of the dehydrogenating steps, considering the differences between the rates of aromatization of hexadienes and *trans*-triene on the one hand, and *cis*- and *trans*-triene on the other. Ring closure itself, in fact, may be one of the fastest steps of the whole sequence, requiring, in principle, no catalyst at all (*cis*-hexatriene → cyclohexadiene). The assumption of an *exclusively* thermal cyclization, however, seems illogical because it would then require the desorption of *all* hexatriene molecules, and their readsorption after cyclization (cyclohexadiene does not form benzene without a catalyst, see Table 4). In fact, we hardly believe that such a process has any importance in aromatization as supposed in (*13*). A possible 2,4-hexadiene → cyclohexadiene ring closure step is basically not different from other hydrogen elimination steps except for the fact that it results in the formation of a σ C–C bond instead of a π-bond.

Molecules which do not have a configuration required for aromatization are not less reactive than their opposite numbers: the formation of intermolecular C–C bonds between them are theoretically not less probable than ring closure. Deactivation of our catalyst indicates that these polyenes with *trans*-configuration are the parent compounds of unreactive carbonaceous deposits, i.e., coke. The presence of *trans*-triene can slow down benzene formation even from highly reactive cyclohexadiene (Table 4). At temperatures where *trans*-triene suffered thermal cyclization, this poisoning effect ceases to exist and benzene yield increases abruptly. The effect of hydrocarbon structure on coke formation has been shown in other experiments, too (*25*).

Trans–cis isomerization takes place through a half-hydrogenated state, and therefore needs hydrogen (*26*). In helium carrier gas the hydrogen retained by the metal during regeneration (*27*) together with the amount liberated during aromatization are the main and rapidly exhausted sources of hydrogen. The application of even small amounts of hydrogen in the carrier gas, however, facilitates geometrical isomerization and enhances aromatization. In addition, hydrogen can considerably slow down the deactivation of the catalyst by facilitating the desorption of hydrocarbons blocking the active sites (*28*).

This dual effect of hydrogen can be seen in Table 5, in the sequence hexene—hexadiene—*trans*-hexatriene; at the same time the results with *cis*-triene have been affected only to a minor extent.

Larger amounts of hydrogen favor further hydrogenation of half-hydrogenated species to olefins and paraffins (Tables 6 and 7). Table 6 contains good evidence of stepwise hydrogenation (as the reverse reaction of stepwise dehydrogenation). It should be noted that the attachment of the first two hydrogens can occur by either 1,2 or 1,4 or 1,6 addition to the triene resulting in 1,3 1,4 and 2,4-hexadienes, respectively. This may serve as additional indirect evidence for the reverse reactions, i.e., "conjugated" 1,4 and 1,6 hydrogen elimination suggested above. At the same time hydrogenation of readily cyclizable *cis*-triene results in both open chain and six-membered cyclic hydrocarbons.

Hydrogenation is unfavorable for aromatization since it decreases the concentration of its unsaturated intermediates. In the process of reforming, this difficulty has been overcome by applying much higher temperatures, thus increasing the equilibrium concentration of unsaturated species even at higher hydrogen pressures. The minor amount of C_5 rings in products formed in the presence of hydrogen (Table 7) indicates that C_5-cyclization was not important in our case. Thus, our experiments indicate a uniform mechanism of aromatization in the presence and absence of hydrogen. It includes a sequence of reversible dehydrogenation-hydrogenation isomerization reactions which may ultimately lead irreversibly to either aromatization or coke formation. It has been pointed out in (*29*) that, in the case of C_4-hydrocarbons, the actual hydrogen concentration determines which of the individual reactions of the *reversible* sequence will prevail. This has been fully confirmed by our experiments. In addition, hydrogen concentration will also determine which of the *irreversible* processes will be predominant.

In the presence of helium carrier gas the rapid blocking of active sites facilitates the "freezing" of the multistage process in a state far from equilibrium, thus making it possible to study its individual steps. In hydrogen, the overall reaction becomes so rapid that, especially at higher temperatures, the reaction of surface intermediates becomes far more rapid than the rate of their desorption; thus the aromatization of the hexane may appear as a single-step reaction. The "Pt-catalyzed direct aromatization" suggested by Dautzenberg and

Platteeuw (*13*) may be attributed to such a process.

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