

# Investigation of the aromatization of C<sub>6+</sub> hydrocarbons on chromia/lanthana-zirconia catalyst

## Part I. Catalytic experiments

Olaf Klepel\*, Cornelia Breitkopf, Mirko Standke

*Institute for Technical Chemistry, University of Leipzig, Linnestr. 3, D-04103 Leipzig, Germany*

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### Abstract

The aromatization pathway on a chromia/lanthana-zirconia catalyst has been investigated by the conversion of 13 linear and branched hydrocarbons. The product distribution is determined by the educt structure and points to a mechanism without side reactions like isomerization or cracking. The differences in aromatization reactivities could be explained by a mechanism via a stepwise dehydrogenation to a conjugated triene structure. First calculations show that methyl or methylene groups close to terminal double bonds can stabilize these trienes. Such substrates show higher aromatic yields than those without stabilizing groups.

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**Keywords:** Aromatization; Catalysis; Chromia/lanthana-zirconia; Reaction mechanism

### 1. Introduction

Aromatization of C<sub>6+</sub> hydrocarbons is an important source for aromatics as a raw material in petrochemical industry and chemical synthesis as well. Especially for the latter case, it is an attractive task to make catalysts available, which are able to convert appropriate paraffins selectively into alkyl aromatics, without undesirable side reactions as cracking or different kinds of isomerization.

Recently, it was shown that chromia/lanthana-zirconia is an interesting catalyst system for *n*-octane aromatization with high selectivities to *o*-xylene and ethylbenzene. The characterization of this catalyst system has been subject of several studies [1–7]. Chromia clusters as well as isolated Cr<sup>3+</sup> ions seem to be active centers. Since TPD experiments revealed only low acidity, acid centers can be excluded as active sites [2]. The deactivation of the catalyst during *n*-octane conversion is caused by coke deposition leading to loss or modification of active sites [7].

Concerning the mechanism of aromatization different versions on different types of catalysts are under discussion.

Bifunctional catalysts contain both dehydrogenation and acid active centres [8,9]. On such catalysts, skeletal isomerizations and alkyl group shifts are possible, and product distributions near the thermodynamic equilibrium can be expected. On non-acid monofunctional catalysts, such acid catalyzed reactions hardly occur, and the product distribution should essentially be determined by the substrate structure. Monofunctional mechanisms can be divided into the so called “triene mechanism” and the mechanism of the “early ring closure”. The triene mechanism includes a stepwise dehydrogenation resulting in a conjugated triene, followed by ring closure [10–20]. Another possibility would be a ring closure already in an early stage of the reaction, then followed by a dehydrogenation to the aromatic product [21–27].

The product distribution of *n*-octane conversion on our investigated catalyst points to a monofunctional mechanism. That could be caused by the low acidity, as shown by TPD experiments [2]. The aim of this work was to obtain further detailed information about the mechanism of aromatization on chromia/lanthana-zirconia catalysts by investigation of the reaction behavior of *n*-hexane, *n*-heptane and nine different C<sub>8</sub>-isomers because “the catalytic reaction itself—using appropriate probe molecules—may be one of the best methods for catalyst characterization” [28]. For that, we investigated the dependence of product distribution

\* Corresponding author. Tel.: +49-341-9736321; fax: +49-341-9736349.

E-mail address: [klepel@chemie.uni-leipzig.de](mailto:klepel@chemie.uni-leipzig.de) (O. Klepel).

and reactivity of the different substrates on their molecular structure.

## 2. Experimental

### 2.1. Catalyst

The catalyst was prepared by impregnating amorphous zirconium hydroxide doped with 7.0 wt.%  $\text{La}_2\text{O}_3$  (MEL, UK) with an aqueous solution of  $(\text{NH}_4)_2\text{CrO}_4$  to yield a catalyst “4CLZ” loaded with 4.0 wt.% Cr. By ammonia addition, the solution pH was kept at 10. Under stirring, the excess water was slowly evaporated at 50–60 °C. The products obtained were calcined in air at 600 °C for 4 h.

### 2.2. Substrates

The following hydrocarbons were used: *n*-hexane (*n*-Hx); *n*-heptane (*n*-Hp); *n*-octane (*n*-Oc); 2-methylheptane (2M-Hp); 3-methylheptane (3MHP); 4-methylheptane (4MHP); 2,3-dimethylhexane (23DMHx); 2,4-dimethylhexane (24DMHx); 2,5-dimethylhexane (25DMHx); 3,4-dimethylhexane (34DMHx); 3-ethylhexane; 1-hexene; 1-octene. The abbreviations in the brackets are used in the text, too. The substrates were supplied by Fluka and Laborchemie Apolda.

### 2.3. Test reaction

Aromatization was carried out by using of two home-made flow apparatus, in the following named 1 and 2. Both apparatus consist a fixed-bed quartz reactor, the reaction was carried out under normal pressure at 550 °C. As carrier gas hydrogen (flow rate 4.5 l/h) was used. The catalyst weight was 250 mg and the educt stream 13.8 mmol/h (according to  $W/F = 18 \text{ g h/mol}$ ). In apparatus 1, the feed was supplied by a syringe pump followed by an evaporator. The reaction products of this apparatus were analyzed by an on-line gas chromatograph HP5860 Series II, equipped with a 50 m PONA capillary column.

In apparatus 2, the supply of the liquid educt was done by using a pressure vessel connected with liquid flow measure and evaporator. The reaction products of this apparatus were analyzed by an on-line gas chromatograph Shimadzu, equipped with a 50 m  $\text{Al}_2\text{O}_3$  plot capillary column.

### 2.4. Computational method

Molecular mechanics force field calculations were performed using the consistent valence force field implemented in CERIUS [29]. Force field methods are able to reproduce conformational energies and barriers to rotation [30] and have been successfully used for describing hydrocarbons [31]. As we were interested in stabilities of the hydrocarbons at first we neglected the role of the catalyst surface and described the conformational behavior of our systems in a comparative way, only. The calculations were performed on a INDIGO<sup>2</sup> work station. All energies are given as relative values, referred to as the most stable structure.

## 3. Results and discussion

The product distribution for the conversion of *n*-hexane, *n*-heptane and nine different  $\text{C}_8$ -isomeres (on apparatus 1) is shown in Fig. 1.

For all substrates the overall conversion is from about 30 up to 50%. For *n*-Oc, 2MHP, 4MHP, 25DMHx, 3MHP and *n*-Hp the main products are aromatics. However, cracking products and  $\text{C}_{5+}$ -compounds are the dominant products in the case of 24DMHx, 23DMHx, 3EHx, *n*-Hx and 34DMHx. As opposed to the educts with higher aromatic yields, the latter mentioned substrates have only six atoms in their longest carbon atom chain. The only exception is 2,5-dimethylhexane. The aromatic yields have a wide range from about 40% (*n*-octane) to 4% (3,4-dimethylhexane). The distribution of the aromatic products, as shown in Table 1, differs depending on the substrate molecular structure. For example, 3-ethylhexane reacts selectively to ethylbenzene and *n*-octane was converted selectively to

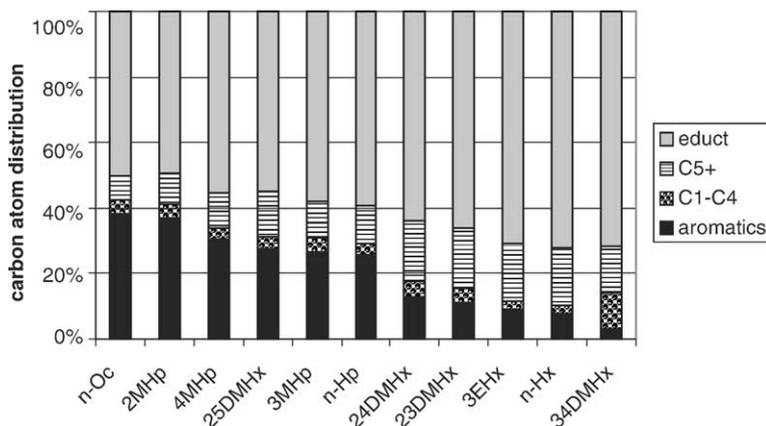
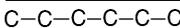
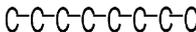
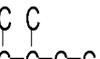
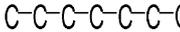
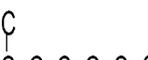
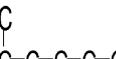
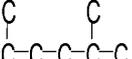
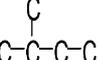


Fig. 1. Product distribution for the conversion of saturated  $\text{C}_{6+}$  isomers after 5 min time on stream.

Table 1  
Distribution of aromatic products (5 min time on stream; carbon atom based;  $\Sigma = 100\%$ )

	Benzene	Toluene	Ethylbenzene	<i>p/m</i> -Xylene	<i>o</i> -Xylene
	<b>100</b>	0	0	0	0
	2	3	<b>85</b>	7	3
	2	8	<b>30</b>	10	<b>50</b>
	0	5	2	15	<b>78</b>
	0	0	8	13	<b>79</b>
	7	<b>93</b>	0	0	0
	0	14	2	<b>77</b>	7
	0	3	<b>17</b>	<b>43</b>	<b>37</b>
	0	18	2	<b>76</b>	4
	0	3	7	<b>90</b>	0
	0	4	0	<b>94</b>	2

The bold letters show the products expected from educt structure by 1,6-ring closure performed on equipment 1.

*o*-xylene and ethylbenzene, too. In the latter case, *o*-xylene was the dominating product as expressed in the ratio *o*-xylene/ethylbenzene = 1, 6.

Table 2 reports the results of the comparative conversion of the linear molecules *n*-octane, 1-octene, *n*-hexane and 1-hexene (apparatus 2). To compare the reaction behavior the ratio of aromatic products to products of hydrogenation or dehydrogenation (in the following: Aro/H;DH) was estimated. For *n*-octane and *n*-hexane, the dependence on time on stream (from 5 up to 40 min) is shown.

Table 2  
Conversion of the linear molecules *n*-octane, 1-octene, *n*-hexane and 1-hexene by using equipment 2 (yields: % carbon atom based)

Educt	Yields H; DH <sup>a</sup>		Yields aromatics		Yield ratio aromatics/H; DH	
	5 min	40 min	5 min	40 min	5 min	40 min
<i>n</i> -Octane	4 ( <i>n</i> -C <sub>8</sub> <sup>≡</sup> )	7.5	60	15	15	2
1-Octene	5 ( <i>n</i> -C <sub>8</sub> )		60		12	
<i>n</i> -Hexane	14 ( <i>n</i> -C <sub>6</sub> <sup>≡</sup> )	8	10	3	0.7	0.4
1-Hexene	22 ( <i>n</i> -C <sub>6</sub> )		15		0.7	
<i>n</i> -Hexane <sup>b</sup>	13 ( <i>n</i> -C <sub>6</sub> <sup>≡</sup> )		3.3		0.25	

<sup>a</sup> DH: dehydrogenation products (monoolefines); H: hydrogenation products (alkanes).

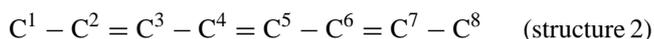
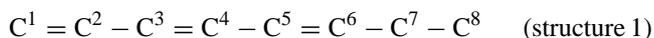
<sup>b</sup> W/F=7.2 g h/mol.

It is obvious, that for molecules with the same number of carbon atoms and at the same contact time there is no significant change of the ratio Aro/H; DH. However, with an increasing carbon atom number from six to eight the value of that ratio increases drastically. There is a slight increase in aromatization activity for C<sub>6</sub>-compounds by using the olefin instead of the paraffin as an educt. The aromatic yields for the linear C<sub>8</sub>-hydrocarbons are nearly independent from the kind of educt but, the overall conversion increases from 80% (paraffin) up to 95% (olefin) due to a increasing yield of cracking products. For *n*-hexane a decrease in Aro/H; DH with decreasing contact time W/F was found. The same trend is obvious for *n*-octane as shown by the comparison of our investigation with results from the literature [7]: there is no olefin formation at a W/F of 225 g h/mol [7] (consequently, Aro/H; DH = infinity) in comparison to Aro/H; DH = 15 at lower W/F of 18 g h/mol.

Both investigated alkanes show a decreasing yield of aromatics with time on stream (see Table 2). However, since the ratio aromatics/octenes decreases drastically in the case of *n*-octane, there is only a moderate decrease obvious for *n*-hexane. In other words, for *n*-octane conversion the formation of olefins is getting more favored with time on stream in comparison to that of aromatic products. For *n*-hexane this effect is less pronounced. Due to the less defined formation

of cracking products we prefer the use of the ratio aromatics/octenes instead of the selectivities. The deactivation of this catalyst system for *n*-octane dehydrocyclization was investigated by Ehwald et al. [7] in more detail.

Thus it was of interest to estimate the stabilities of possible intermediates of the *n*-octane cyclization. As example structures we calculated the following two triene structures which differ only in the positioning of their double bonds:



Structure 2 is the most stable conformer while structure 1 is destabilized by 4.89 kcal/mol compared to structure 2.

As mentioned above, different mechanisms for aromatization have been suggested. The bifunctional mechanism, described by the so-called “two-dimensional” reaction scheme [8,9], occurs on catalysts containing both dehydrogenation and acid active centres. On such catalysts, skeletal isomerizations and alkyl group shifts are possible, and product distributions near the thermodynamic equilibrium can be expected. On non-acid monofunctional catalysts, such acid catalyzed reactions hardly occur, and the product distribution should essentially be determined by the substrate structure.

To decide between monofunctional and bifunctional mechanism we investigated the aromatic product distribution in dependence on the educt structure. This approach for investigation cyclization steps has been widely used for metal or bifunctional catalysts [32]. For all investigated substrates, products of acid catalyzed reactions according to the bifunctional mechanism are essentially missing in the product mixture obtained on our investigated catalyst. This agrees with the low acidity of the catalyst as shown by TPD-experiments [2]. As shown by our experiments with *n*-octane, *n*-heptane, *n*-hexane, 3-ethylhexane, 2,3-dimethylhexane and 3,4-dimethylhexane the distribution of aromatic products points clearly to a mechanism that includes the direct formation of a six-carbon ring. Unfortunately, due to analytical difficulties it was impossible to elucidate that fact exactly for substrates with *p*-xylene and *m*-xylene as the main product. But in these cases those products, which are unexpected for direct C<sub>6</sub>-ring closure, are absent. So, that kind of ring closure should be suitable for the cyclization of 2-, 3- and 4-methylheptane as well as for 2,5- and 2,4-dimethylhexane, too.

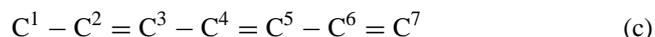
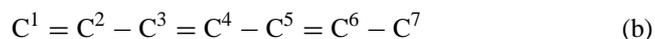
For the direct C<sub>6</sub>-ring closure as the cyclization step, two alternative ways to the aromatic final product are conceivable. First, the ring closure step can occur at the beginning of the reaction, resulting in a cyclohexane structure and followed by further dehydrogenation to the aromatic [21–26]. On the other side, a mechanism according to a stepwise dehydrogenation of the paraffin to a conjugated surface all-*cis*-trienes followed by cyclization and dehydrogenation to the corresponding aromatic is under discussion, too [10–15]. This mechanism is the so called “triene mechanism”.

Assuming the triene mechanism, one has to consider the possibility of formation of conjugated trienes. Trienes are general not very stable species. If their formation is hindered, then an aromatization mechanism through such intermediates should be excluded.

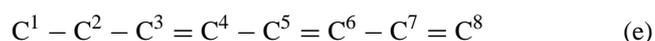
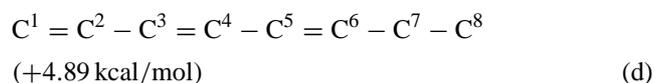
Interestingly those investigated substrates exhibit the lowest aromatization reactivity, which can form only trienes, that do not have terminal double bonds surrounded by methyl or methylene groups. For example, the aromatization reactivity for *n*-octane, *n*-heptane and *n*-hexane follows the order *n*-oc > *n*-hep > *n*-hex. *n*-Hexane has only one possible triene without any by methyl or methylene group surrounded terminal double bond:



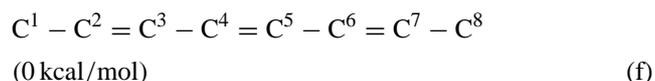
For *n*-heptane there are two structures with one end standing double bond surrounded by a methyl group:



whereas, for *n*-octane there are two structures with one double bond surrounded by a methylene group:



and one structure with two end standing double bonds surrounded by methyl groups:



The relative energies are given in the brackets. It is evident from the calculated energy differences that structures with terminal methyl groups are more stabilized, while structures with terminal methylene groups are destabilized by a few kcal/mol. If the surrounding groups have a stabilizing effect on the double bonds, one can assume, that the triene formation for such structures should be favored and aromatics, which can be derived from those structures, should be the preferred and dominating products. This seems to be the case for the above mentioned examples. The favored formation of *o*-xylene over ethylbenzene for *n*-octane conversion supports this assumption. *o*-Xylene can be derived from structure (f) which is more stabilized in comparison to structure (d) and (e) which should lead to ethylbenzene. Additional, *p/m*-xylene, which should be favored thermodynamically cannot be formed by a direct ring closure. We found them only to a very low degree, far from the thermodynamic equilibrium.

For the other branched C<sub>8</sub>-isomers, the situation could be similar. For example, the aromatization reactivity for 2,5-dimethylhexane is much higher (about 10 times) than that for 3,4-dimethylhexane. That could be explained by the

same way as shown above. As 25DMHx has four different structures of methyl groups surrounded by terminal double bonds, there is no possibility to stabilize terminal double bonds by methyl (or methylene) groups in the case of 34DMHx. However, if the stabilization of triene intermediates would be the only criterion, then 25DMHx should show the highest aromatization reactivity among all investigated isomers. As shown in Fig. 1, the aromatic yield of 25DMHx is surpassed by those of the less branched 2MHP, 4MHP and *n*-octane. It is obvious, that other criterions like sterical hindrance or rotation ability, which can influence the ring closure, have also to be considered. To elucidate these problems in more detail, further calculations regarding the stability of substrates and intermediate as well as their ability to a ring closure by using the molecular mechanics calculation method were done. The results of these investigations are published in the second part.

If the reaction proceeds according to a stepwise dehydrogenation of the substrates, the use of one possible intermediate as an educt should give valuable information about the mechanism. We investigated the conversions of the olefins 1-hexene and 1-octene and compared them with the results obtained from the corresponding paraffins (Table 2). It has been shown for metal catalysts, that the irreversible adsorption of the reactant should be the rate determining step of the dehydrocyclization mechanism [33,34]. So, it seems likely, that the olefin should produce much higher aromatic yields, because the C=C double bond can be involved in the adsorption of the reactant. Competitive conversion of a mixture of C<sub>8</sub>D<sub>18</sub> and 1-heptene on a metal catalyst (Pt-SiO<sub>2</sub>) showed that the conversion of the olefin was much higher than that of the paraffin [35]. However, on our oxide catalyst, there was only a slight increase in aromatization reactivity by using the olefin instead the paraffin for C<sub>6</sub> and no increase in the case of C<sub>8</sub>. That could be caused by a single low barrier at the beginning of the reaction, probably the adsorption on the catalyst. Furthermore, the almost unchanged values of the ratio Aro/H; DH by using the olefin in comparison to the paraffin conversion for both, C<sub>6</sub> and C<sub>8</sub>, could be explained by the absence of an activation barrier between paraffin and monoolefine.

A drastical increase in the aromatization reactivity at the expense of the olefins is obvious by change from C<sub>6</sub> to C<sub>8</sub>. Since the stabilization of C<sub>6</sub>-trienes is hindered as shown above, the reaction will stop at the stage of the monoolefines. With increasing hindrance of the triene stabilization the further dehydrogenation of the monoolefines will be suppressed and the ratio Aro/H; DH decreases. That points to a barrier at the end of the reaction coordinate. In addition, the almost identical aromatic product distribution for the conversion of both C<sub>8</sub>-substrates emphasizes that the aromatic product distribution is not determined by initial steps of the reaction. This is in accordance to results found by Shi et al. [36] for *n*-octane conversion on Pt/SiO<sub>2</sub>.

If the aromatization is a consecutive reaction of paraffin dehydrogenation and the observed effects were not deter-

mined by the thermodynamics, then a shorter contact time should result in decreasing ratio aromatics to olefins. As shown in Table 2 and by comparison with results from the literature [7] this was confirmed by *n*-hexane and *n*-octane conversion. With decreasing contact time the amount of olefins increases at the expense of the aromatics.

The assumption of a consecutive reaction is confirmed by the dependence of the reaction behavior on time on stream, too. With time on stream (i.e. with catalyst deactivation) the ratio aromatics/olefins decreases drastically in the case of *n*-octane. This points to a limitation of later steps of the aromatization reaction chain. Since for *n*-hexane the reaction will stop at an early stage as shown above, there is only a slight change of the ratio aromatics/olefins in dependence on time on stream.

#### 4. Conclusions

The aromatic product distribution is determined by the educt structure and thus points to a monofunctional mechanism. The differences of aromatization reactivity between the hydrocarbons are consistent with the idea of a sequential dehydrogenation mechanism. The criterion could be a difference in the stabilization of the triene-intermediates. If the terminal double bonds of the triene are not stabilized by surrounding groups, the formation of that triene is not favored and the formation of aromatics should be hindered. There could be a barrier at the end of the reaction coordinate. Steps at the beginning of the reaction obviously do not influence the aromatic product distribution as shown by the comparative conversion of *n*-octane and 1-octene. However, as mentioned above, the stabilization of triene-intermediates cannot be the only criterion, as shown by the reactivity of the 25DMHx. Other facts, such as ability to ring closure have to be considered, too. So, for more clear distinction between triene mechanism and a mechanism according to an early ring closure further theoretical calculations regarding the stability as well as the ability to ring closure of possible intermediates for both mechanisms were done. The results will be shown in second part. The dependence of the reaction behavior on time on stream and contact time points to a consecutive dehydrogenation reaction.

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