



Investigation of the aromatization of C₆₊ hydrocarbons on chromia/lanthana–zirconia catalyst. Part II Theoretical investigations of stabilities of reactant and intermediate structures

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Received 23 July 2003; received in revised form 23 July 2003; accepted 1 October 2003

Abstract

The force field technique and semiempirical calculations with AM1 have been used to calculate stabilities of various linear and branched reactant and product molecules of the aromatization. The most stable conformer is the 2,5-dimethylhexane (25DMHx), which corresponds to experimental findings, that 25DMHx shows the highest conversion within aromatization on chromia/lanthana–zirconia catalysts. Additionally, calculated stabilities of intermediate and product structures support the idea of a triene-like mechanism with late ring closure.
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Keywords: Molecular mechanics; Conformer analysis; Aromatization

1. Introduction

Aromatization is one of the desired reaction pathways during conversion of conventional petroleum light naphtha feeds (C₆₊). Recently the chromia/lanthana–zirconia system was shown to be a selective catalyst towards aromatization [1–6].

Two main reaction pathways are generally discussed which differ in their final product distributions (PD) (see Part I). One of them, the monofunctional mechanism, should be essentially determined by the structure of the substrates. The only pathway in this mechanism is dehydrogenation and ring closure from linear saturated to aromatic structures without side reactions. The reactant structure is assumed to comprise the ability of directing the reaction and thus the product distribution in contrast to a pd which arises from rearrangements and isomerization during a reaction via bifunctional mechanism.

Therefore, our theoretical investigations aim to compare stabilities of reactant conformations to find a correlation

between structure and experimentally observed product distributions. Additionally, all intermediate structures were calculated. As rearrangement towards an aromatic structure necessary, the conformational energies of possible intermediates should give an information whether an early or late ring closure is more or less favorable.

As reactants, C₈H₁₈ isomeric model structures, with variations of chain length (C₆ and C₇) and branching of the chain (methyl groups at different chain positions), were used. To investigate the conformational behavior, we employed a molecular mechanics force field which is able to reproduce conformational energies and barriers to rotation. To consider the influence of resonance effects from double bonds on minimum structures, we additionally used semiempirical methods for the intermediate structures, which are possibly formed by conversion from saturated to unsaturated linear or cyclic structures. All calculations only describe the conformational properties of the systems in gas phase and thus neglect the role of the catalyst [7]. Nevertheless, the information of inherent conformational energy of a system may give reasonable hints whether one pathway of reaction is more or less favored.

The recognition of molecular flexibility may also play a role for the reactant adsorption process on the catalyst sur-

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face. For other cases, it has been experimentally verified that even small molecules like H₂ or CO adsorb in more than one configuration on a surface [8]. Thus, for larger and more complicated molecules, the role of configuration and conformation regarding surface sorption is much more important and may also play a role here. Also the diffusion in pores [9] was shown to depend on the rigidity and conformation of linear and branched pentanes and hexanes. Both sorption and diffusion are processes connected with the catalyst and can not be discussed fully here.

2. Theory

Force field calculations were performed within the consistent valence force field (CVFF) implemented in CERIUS2 [10]. Force fields generally enable fast handling of larger molecules with sufficient accuracy for the calculated internal energies. The internal energy of a molecule is of special interest because equilibria are dependent upon relative internal energies (among other things) [11]. Nowadays, there are lot of commercial force field methods available. With respect to molecular structure and energy, the results are substantially the same for all force fields even though the details of the single force field may be different. Force fields generally have been parameterized to reproduce different properties as for instance heats of formation. Herein, hydrocarbons were the first substance class which were used to parameterize force fields [11]. Thus, the available parameter sets are fully tested for this substance class and no side affects from insufficient parameter sets are to be expected. Total energies are calculated being the sum of stretching, bending, van der Waals and torsional contributions which give ground state molecular structures as well as molecular heats of formation with good accuracy compared to experimental values [12].

Beyond the conformational energy contributions from the electron system, e.g. conjugation, are of interest, which may play an important role in the process of aromatization. Force fields do not give a picture of the electron system at all. For that reason, semiempirical methods have been used here, too. For large molecules, the usage of semiempirical methods as PM3 [13] or AM1 [14] is established. In general, semiempirical methods predict barriers to rotation which are smaller than found in experiment. Conformational energies of hydrocarbons are reasonably well reproduced by AM1 and with one exception also, PM3 [15]. The conformational energy of this substance class is generally determined by the *gauche* interaction which starts from chains greater than four and is thus a basic fragment in our reactant molecules. The energy difference for *gauche* and *anti* conformation is well reproduced by AM1 [15]. This also holds for all cyclic derivatives and aromatic ring systems derived. Therefore, we preferably used AM1 to calculate reactant, intermediate and product structures giving us a good combination of a prediction of conformational and conjugational effects. The calculations were performed within the MOPAC package of

CERIUS [10]. All geometries are fully optimized with respect to their geometry.

All energies are given in kJ/mol and will be marked as relative or absolute values. Relative energy values are preferably given for the force field results while for the semiempirical results, the absolute values for the heat of formation are listed, thus enabling a comparison of different molecules.

3. Results and discussion

All C₈H₁₈ and C₈H₁₂ linear structures were optimized with high convergence criteria resulting in minimum geometry conformations.

First, we were interested in the conformational behavior of all isomeric C₈H₁₈ structures which differ in chain length and branching. Tables 1 and 2 summarize all minimum structures, for a better survey divided into hexane-derived, heptane-derived and octane structures and as chemical drawing.

The most stable structure of the saturated C₈H₁₈ group is 25DMHx (abbreviations see part I). Ten and 11 kJ/mol

Table 1
Minimum structures of hexane-derived saturated isomeric C₈H₁₈ calculated with the force field CVFF

No.	Structure	E (kJ/mol)
1		0
2		11
3		28
4		41
5		45

The energy is given as relative to the most stable conformer in kJ/mol.

Table 2
Minimum structures of heptane-derived saturated isomeric C₈H₁₈ calculated with the force field CVFF

No.	Structure	E (kJ/mol)
1		10
2		22
3		24

The energy is given as relative to the most stable conformer in kJ/mol.

Table 3
Minimum structures of unsaturated hexane-derived isomeric hydrocarbons with C₈H₁₂ calculated with the force field CVFF

No.	Structure	E (kJ/mol)
1		0
2		57
3		62
4		81
5		89
6		91
7		111
8		145
9		154

The energy is given as relative to the most stable conformer in kJ/mol.

higher energies are found for the 2MHP and 24DMHx. The next four isomers *n*-Oc (20 kJ/mol), 4MHP, 3MHP, and 23DMHx lie in a small range of 20–28 kJ/mol above the 25DMHx, whereas 34DMHx and 3-ethylhexane are destabilized more clearly with 41 and 45 kJ/mol, respectively. The sequence of these conformational energies reflects the stability of the ground state of the substrates. Destabilization for molecules 3, 4, 5 (see Table 1) arises from sterical hindrances of methyl groups on adjacent positions.

The next step was the calculation of all associated unsaturated C₈H₁₂ structures, which have three double bonds in the chain, thus reflecting one selected status of dehydrogenation. For all structures, more than one isomer has to be considered. This increases the number of intermediate structures. Tables 3 and 4 give a summary for the unsaturated structures up to energy differences of 150 kJ.

The most stable isomeric structure is the triene, derived from 25DMHx. Within 20 kJ/mol, the triene of 2MHP follows. With more than 48 kJ/mol destabilized are the trienes of *n*-octane (no terminal double bond), one 2MHP and 3MHP, followed by 24DMHx- and 23DMHx-derived isomers. In principle, the order of stable structures is nearly the same as for the saturated compounds.

The analysis of all stable minimum structures shows some common features which determine the stability of those structures. First, it is obvious that symmetric structures regarding the position of the double bond and the branching are favored. Second, stable structures do not have a double bond within the branching. Third, for the linear *n*-oct-3-en double bonds are not favored if they are in terminal positions. Fourth, terminal positions of double bonds

Table 4
Minimum structures of unsaturated heptane-derived isomeric hydrocarbons with C₈H₁₂ calculated with the force field CVFF

No.	Structure	E (kJ/mol)
1		19
2		48
3		54
4		66
5		68
6		88
7		102
8		109

The energy is given as relative to the most stable conformer in Table 1.

are more stabilized in combination with branching of the chain.

As there is a reaction pathway from alkane to aromatics via triene structures, under discussion, we estimated analogue to a correlation analysis a value for the formation reaction of C₈H₁₂ from C₈H₁₈ (see Eq. (1)). Table 5 shows the conversion from saturated to the associated unsaturated one.



The formation to linear unsaturated 25DMHx is minimal, compared to octane and 24DMHx due to the stabilization of reactant and product molecule. As the order for the stable linear saturated and linear unsaturated structures do not change in principal, the order of the barriers here do also have the same trend.

Additionally, to the force field calculations, a semiempirical method (AM1) was employed to investigate the influence of conjugation on the stability of intermediate and product molecules. A combination of the advantages

Table 5
Energy differences for conversion of C₈H₁₈ to C₈H₁₂ for selected stable isomers; ΔE (kJ/mol) calculated from heats of formation of minimum structures, CVFF

	105
	115
	144
	134
	152

	-223
	-212

Scheme 1. Comparison of linear saturated dimethylhexanes with variable branching; E refers to as the heat of formation in kJ/mol calculated with AM1.

of force field method (conformer analysis) and semiempirical method (electron effects) is thought to enhance the interpretation of the overall stability of the molecules.

In principle, all structures were calculated within AM1 and also PM3. In agreement with literature, PM3 gives lower differences between the conformers (only 0–8 kJ/mol, not shown here). With AM1, the differences between conformers are generally larger and the order of stability is nearly the same as for the force field calculations (not all structures are shown here). Thus, AM1 is also able to reproduce the conformational stress of these molecules in a sufficient way.

The following examples will compare selected structural features which may have influence in the formation procedure of intermediates and products during aromatization.

Scheme 1 compares the absolute heats of formation from fully geometry optimized structures for the most stable 25DMHx with the less stable 34DMHx to show that the principal order of stability is also reproduced by AM1. Those absolute values are easily comparable to experimentally-derived heats of formation which are listed in [17].

Following a “linear” route, the first step to form an aromatic system is dehydrogenation of the saturated structure to give single unsaturated linear molecules. **Scheme 2** compares the stability of the four possible octen double bond isomers.

It is obvious that the evolution of a terminal double bond is not favored. All other double bond isomers exhibit the same heat of formation.

In comparison to octen, **Scheme 3** compares single unsaturated structures derived from 25DMHx and 34DMHx regarding the position of the double bond. For the 34DMHx the *trans*-like position of the methyl groups is mostly favored and is only recognized here.

	-126
	-125
	-125
	-103

Scheme 2. Comparison of octen linear structures with variable position of double bond. Heat of formation (kJ/mol) calculated with AM1.

	-104
	-101
	-108
	-82

Scheme 3. Comparison of single unsaturated 25DMHx and 34DMHx with variable position of double bond. E (kJ/mol) with AM1.

In accordance with the force field results, the terminal position is only stabilized through simultaneous branching at this position. This effect is especially evident for the 34DMHx-derived structure which shows an energy difference of 26 kJ/mol.

Going further to aromatization via linear route, the evolution of another double bond in the molecule may be stabilized if it is situated close to the first one. **Scheme 4** clearly shows this effect of conjugation. Again, terminal double bonds are destabilized.

All above mentioned effects are also found for the double unsaturated branched structures derived from 25DMHx and 34DMHx as can be seen in **Scheme 5** for comparison.

The conjugation again slightly stabilizes the intermediate structures 1 and 3 over 2 and 4 (**Scheme 5**). Structures with double bonds in terminal position and without opportunity to conjugation are destabilized.

The last step on the linear route before ring closure would be dehydrogenation to linear triene-like structures. **Schemes 6 and 7** compare the heats of formation for oct-3-en and the trienes of 25DMHx and 34DMHx.

The oct-3-en is again more stable if no terminal double bond exists. Both conjugated hexane-derived structures only differ in their chain branching, thus showing the steric effect of the adjacent methyl groups which destabilizes those structures with steric hindrance.

In general, the calculation of the linear reactant and intermediate structures with force field and semiempirical meth-

	-15
	-8
	-1
	+6

Scheme 4. Comparison of double unsaturated, linear octen structures. E (kJ/mol) with AM1.

	+14
	+16
	+30
	+48

Scheme 5. Comparison of double unsaturated 25DMHx and 34DMHx with variable position of double bond. E (kJ/mol) with AM1.

$C-C=C-C=C-C=C-C$	+95
$C=C-C=C-C=C-C-C$	+115

Scheme 6. Comparison of two possible octen structures with three double bonds. E (kJ/mol) with AM1.

ods enabled us to describe structure–reactivity relations for the aromatization, which are consistent with experimental results.

Fig. 1 shows, for a better survey, the comparison between experimental catalytic data and selected results of the calculations. It is obvious, that a decreasing aromatic yield is always correlated with a strong increase of the relative energy of the corresponding alkane minimum structure. Additionally, the decrease of aromatic yield is accompanied by an increasing energy difference for the reaction of alkane to triene. However, this increase is not so pronounced as that found for the energy of alkane minimum structures.

To differentiate between an early or late ring closure, two points have to be considered. First, the ability to form a ring from the alkane as a criterion for an early ring closure mechanism has to be evaluated. We found, that steric effects caused by adjacent methyl groups in the chain determine the stability of the isomers for all saturated as well as

	+126
	+140

Scheme 7. Trienes for 25DMHx- and 34DMHx-derived structures. E (kJ/mol) with AM1.

all unsaturated linear structures. This has clearly an influence on the flexibility of the chain itself. Rotational barriers for saturated and unsaturated structures were calculated [16] and showed, that octane (not shown here) and 25DMHx (see Fig. 2) have the highest flexibility in the chain. Flexible molecules are able to adopt many conformations with low energy. Molecules like 34DMHx have only a limited number of flexible chain arrangements (see Fig. 3). These conformations have a higher energy content compared to 25DMHx. Thus, the opportunity to make a ring closure would decrease drastically for structures with adjacent methyl groups due to inflexibility of the chain itself and should decrease the PD towards aromatic structures for this compounds. Figs. 2 and 3 clearly show the difference of the ability of both molecules to adopt low energy conformations. The flexibility to rotate around both the single bonds in the structure decreases from 25DMHx to 34DMHx.

Despite this, the triene structure itself has, in principle, enough flexibility left to rotate and is able to form ring structures subsequently. Again this structural effect would correlate with the experimental PD (see Fig. 1), that 25DMHx has the highest conversion rate to aromatics but all other molecules are also converted with lower rates. However, the steric effects of adjacent methyl groups determine the stability of the isomers for all saturated as well as all unsaturated linear structures in the same way. Thus, from this point of view, there is no possibility to distinguish between an early or late ring closure mechanism. Both of them are consistent with our experimental results as well as calculation.

Second, we have to consider the ability to form a triene and its ring closure, which determines the mechanism of the late ring closure. The tendency to triene formation can be expressed by the energy differences for the reaction of alkane to triene (Scheme 5 and Fig. 1). We found that saturated and unsaturated linear structures have the same stability order of conformers. Thus, intermediate structures show a comparable conformational behavior as their parent compound. 25DMHx is the most stable conformer either as saturated or as unsaturated structure. This ability of forming stable triene structures, based on the parent compound should be therefore recognized as important structural feature which directs to a structure dependent product distribution according to a triene mechanism with late ring closure.

Additionally, the comparison of the stability of two possible octatriene structures (Scheme 6) points to the preferable formation of the intermediate, that leads to *o*-xylene. This is in accordance to our catalytic experiments (see part I). For *n*-octane conversion, significantly more *o*-xylene was formed than ethylbenzene. This PD cannot be explained by thermodynamics because the yield of the thermodynamically favored *p*-/*m*-xylene was very low (see also part I). This correlation between the stability of trienes and the product distribution support the triene mechanism with late ring closure, too.

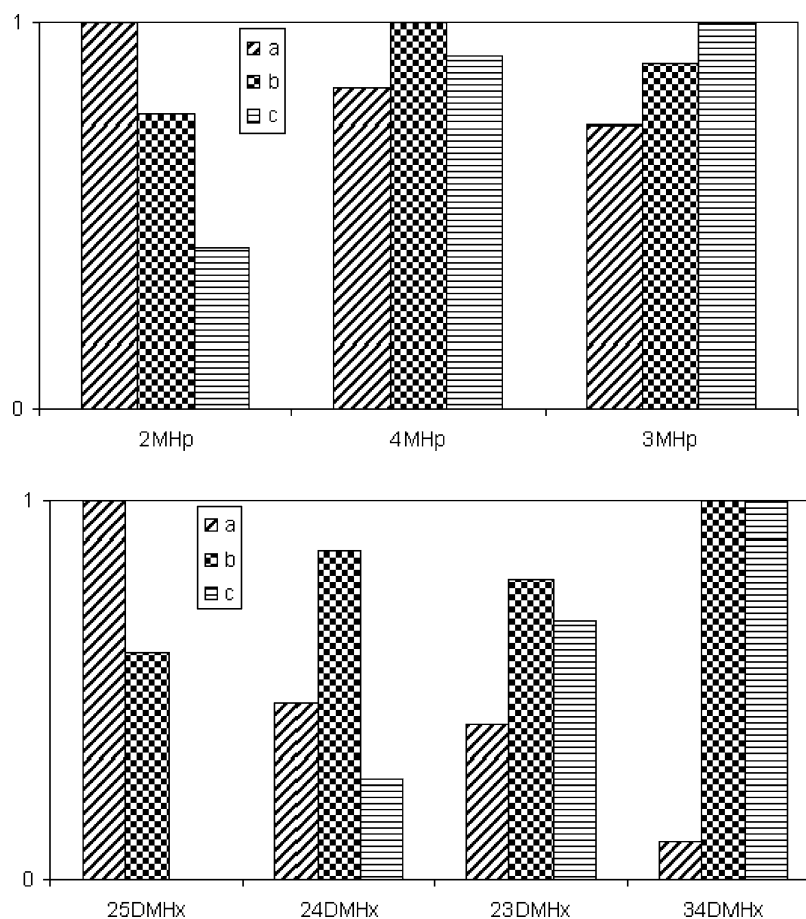


Fig. 1. Normalized experimental aromatic yields (a), normalized energy differences for reaction of alkane to triene (b), normalized relative energy of alkane minimum structures (c). 25DMHX is the most stable structure ($c = 0$).

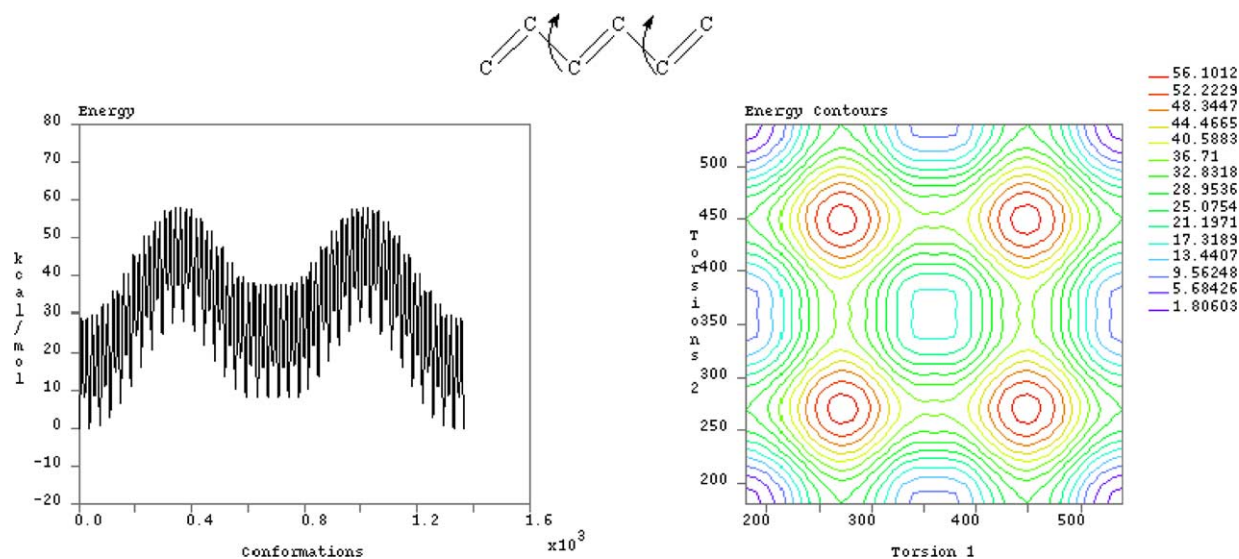


Fig. 2. Energy contour diagram for simultaneous rotation of two bonds in the hexatriene 25DMHX (energy in kcal/mol; CERius output). The left diagram shows the number of possible structures with associated energies.

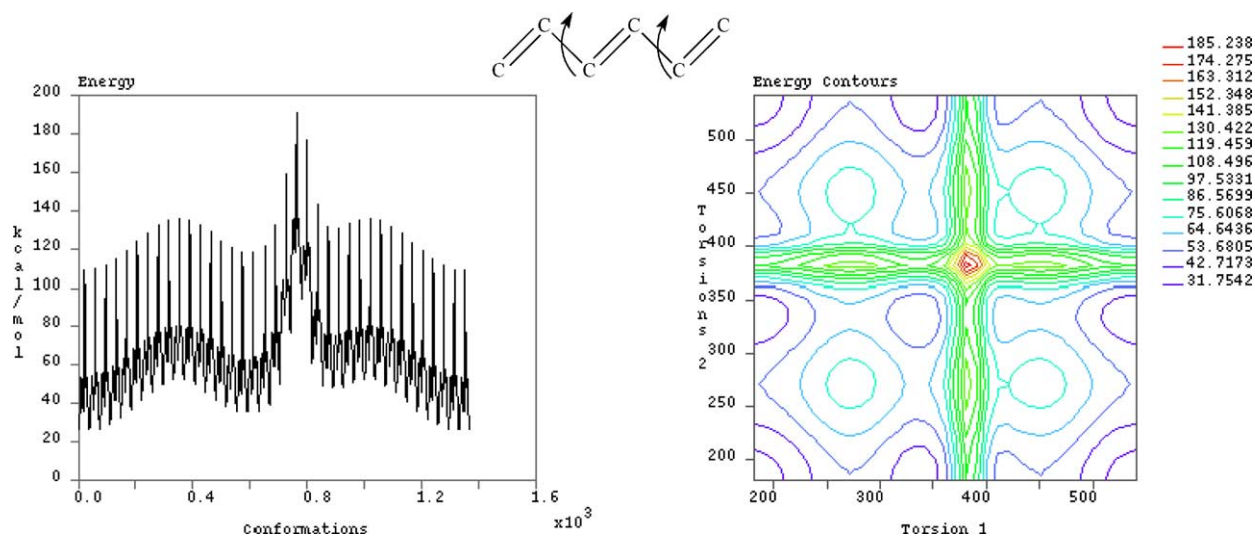


Fig. 3. Energy contour diagram for simultaneous rotation of two bonds in the hexatriene 34DMHx (energy in kcal/mol; CERIUS output). The left diagram shows the number of possible structures with associated energies.

4. Conclusions

Theoretical methods have been used to calculate stabilities of various linear and branched reactant and product molecules of the aromatization reaction. The most stable conformers of the calculations correspond to the conversion order within the aromatization on chromia/lanthana–zirconia catalysts.

Differences in conformer structures and their stabilities support the idea of structure directing conversion, which proceeds via a monofunctional mechanism.

Acknowledgements

Thanks to Mr. A. Borowski for calculating some structures with AM1 and a lot of cyclic structures (not shown here).

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