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Theoretical Study of the Heptamethylbenzenium Ion. Intramolecular Isomerizations and C_2, C_3, C_4 Alkene Elimination

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Recent experimental work on the methanol-to-hydrocarbons (MTH) reaction in zeolite H−Beta suggests that the heptamethylbenzenium (heptaMB$^+$) cation is an important intermediate. We have carried out quantum chemical calculations to investigate intramolecular isomerization reactions and eliminations of small alkenes such as ethene, propene, and isobutene from heptaMB$^+$ isomers. Two types of reaction paths have been investigated for the alkene formation: One starting with an initial ring contraction, and one starting with an initial ring expansion of the heptaMB$^+$ ion. The reaction starting with an initial ring contraction leads to a bicyclic species that may split off propene or, after further isomerizations, isobutene. Expansion to a seven-membered ring may, via further isomerizations, lead to formation of ethyl and isopropyl groups that may in turn be split off as ethene and propene. The calculations have been carried out at the B3LYP/cc-pVTZ//B3LYP/6-311G(d,p) level of theory with zero point energy corrections. Comparisons with experimental data are made where possible.

Introduction

Methanol-to-hydrocarbons (MTH) conversion over acidic zeolites and related materials is an important step in the synthesis of olefins from methane and has for a long time been a highly investigated catalytic process.[1−4] Recent research has revealed much of the nature of the MTH reaction. The mounting experimental evidence is in strong support of the indirect mechanism termed the "hydrocarbon pool mechanism".[5−21] The main feature of this mechanism is that it involves a hydrocarbon species that is methylated by methanol/dimethyl ether and subsequently splits off small alkenes such as ethene, propene and butenes. Figure 1 shows the initially proposed scheme for this reaction. The mechanism may operate in different ways depending on the zeolite/zeotype materials and reaction conditions, but the most important hydrocarbon pool constituents are methylbenzenes.[8,9,14,16] Recently, the heptamethylbenzenium (heptaMB$^+$) ion has become of particular interest.[10,11,17,22,23] Species such as methylcyclopentenyl cations[12] and methylnaphthalenes[15] have also been shown to function as reaction centers for alkene formation. These compounds are, however, not investigated here.

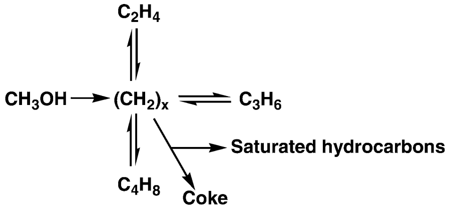

Figure 1. Schematic description of the hydrocarbon pool mechanism.[5]

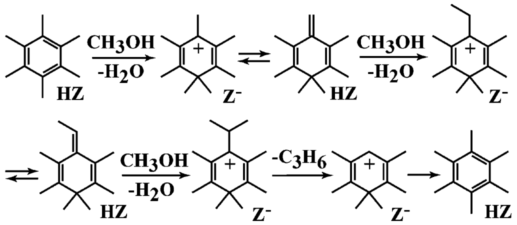

Figure 2. Side-chain methylation mechanism for propene formation. The zeolite is abbreviated by HZ.[17]

Two mechanisms have been considered to explain the alkene formation from methylbenzenes: The side-chain methylation mechanism and the "paring reaction". The side-chain methylation mechanism, which was first suggested by Mole et al.,[24] was further elaborated by Sassi et al.[17] and theoretically modeled by Arstad et al.[25] This mechanism involves deprotonation of an alkyl group on an alkylbenzenium species and formation of an exocyclic double bond. In the presence of methanol, this exocyclic double bond is later methylated, re-forming a benzenium ion with a higher alkyl chain, up to *tert*-butyl. In Figure 2, the scheme presented by Sassi et al. is shown. The higher alkyl chains are subsequently eliminated as alkenes.

The so-called "paring reaction" was originally introduced to explain isobutane formation when hexamethylbenzene was reacted over a bifunctional catalyst.[26] It involves ring contractions/expansions to extend an alkyl group on the cationic species. Bjørgen et al.[11] studied methylation of [^{12}C]benzene with [^{13}C]methanol, where hexamethylbenzene with ^{12}C-atoms in the benzene ring and ^{13}C-atoms in the methyl groups is formed. At slightly higher temperatures propene and isobutane were formed with a ^{12}C/^{13}C distribution that agreed with the contraction/expansion schemes of the paring mechanism.

Several experimental studies of heptaMB$^+$ are reported in the literature.[27−29] Irradiation of heptaMB$^+$ with light (λ_{max} 400

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nm) in acidic media produced the heptamethylbicyclo[3.1.0]-hexenyl cation that is slowly re-forming heptaMB$^+$ when the irradiation is stopped.[27] 1,2-Methyl group shifts along the benzenium ring was studied by Borodkin et al.[29]

Even if there are few reported studies of the heptaMB$^+$ ion, there is a large amount of literature on variously substituted benzenium ion chemistry. A substantial part of this work has been carried out in the mass spectrometer and relates to monomolecular reactions in isolated molecules, i.e., reaction systems related to the reactions we study in this paper. Comprehensive reviews of these mass spectrometric studies have been published.[30−32]

Recently, Mormann and Kuck[33] reported mass-spectrometric data that showed methane and ethene loss from long-lived gaseous protonated xylenes. They suggested that the reaction preceding the losses was expansion of the xylenium ions to protonated methylcycloheptatriene, isomerization, and finally contraction. In conjunction with this work, Kuck and co-workers also carried out experimental studies of (protonated) 1,3,5-cycloheptatriene and alkylated derivatives.[34,35]

We later carried out a theoretical study[36] of unimolecular reactions in protonated xylenes that agree well with, and explain, the experimental results obtained by Mormann and Kuck.

In the present study we report computational results based on density functional theory (DFT) of various intramolecular reactions of the heptaMB$^+$ ion. Ring contraction and subsequent rearrangements that finally may lead to propene and isobutene formation have been considered, as well as ring expansions and further isomerizations leading to ethene and propene formation. Barriers for methyl shifts in heptaMB$^+$ and cyclopropyl group migration in the heptamethylbicyclo[3.1.0]hexenyl cation are also calculated and compared with the experimental results.[27,29]

Computational Details

All computations where carried out using the Gaussian98 program package.[37] The structures where first optimized at the B3LYP/6-31G(d) level of theory, and then re-optimized at the B3LYP/6-311G(d,p) level of theory to investigate the basis set effects. The geometry changes with the larger basis set were marginal and the energies were also very similar. Analytical frequencies were calculated at the B3LYP/6-311G(d,p) level of theory using the geometries found at the same level of theory. It was ensured that the transition states had one, and only one, imaginary frequency and that the minima had none. Zero point energy corrections were obtained from the frequency calculations. Single point energies were finally calculated at the B3LYP/cc-pVTZ level. All reported energy values are thus calculated at the B3LYP/cc-pVTZ//B3LYP/6-311G(d,p) + ZPE level and reported in kJ mol^{-1}. Furthermore, intrinsic reaction coordinate (IRC) calculations as implemented in Gaussian98, were performed to ensure that the transition states connected the desired minima. To minimize numerical noise, which may impair convergence in the geometry optimizations, the "ultrafine" grid was chosen for the numerical integration scheme in all calculations.

Results

All species except the alkenes are numbered sequentially, as shown in the schemes. The addition of "TS" to the numbers shows transition states. The heptaMB$^+$ ion is numbered **1** and it is taken as the reference species; thus, all given energies are relative to that of **1**. Figure 3 gives a schematic representation of the heptaMB$^+$ ion. Important atom distances and the dihedral angle describing the nonplanarity of the benzene ring are given in Table 1.

1

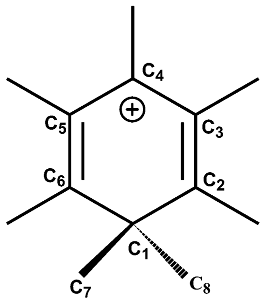


Figure 3. Atomic labeling in the heptamethylbenzenium ion.

TABLE 1: Bond Lengths and Dihedral Angle in heptaMB$^+$ [a]

	1
C_1C_2	1.501
C_2C_3	1.378
C_3C_4	1.427
C_2C_6	2.538
C_1C_7	1.570
C_1C_8	1.575
C_2C_{methyl}	1.502
C_3C_{methyl}	1.514
C_4C_{methyl}	1.497
$C_1C_2C_6C_4$	175

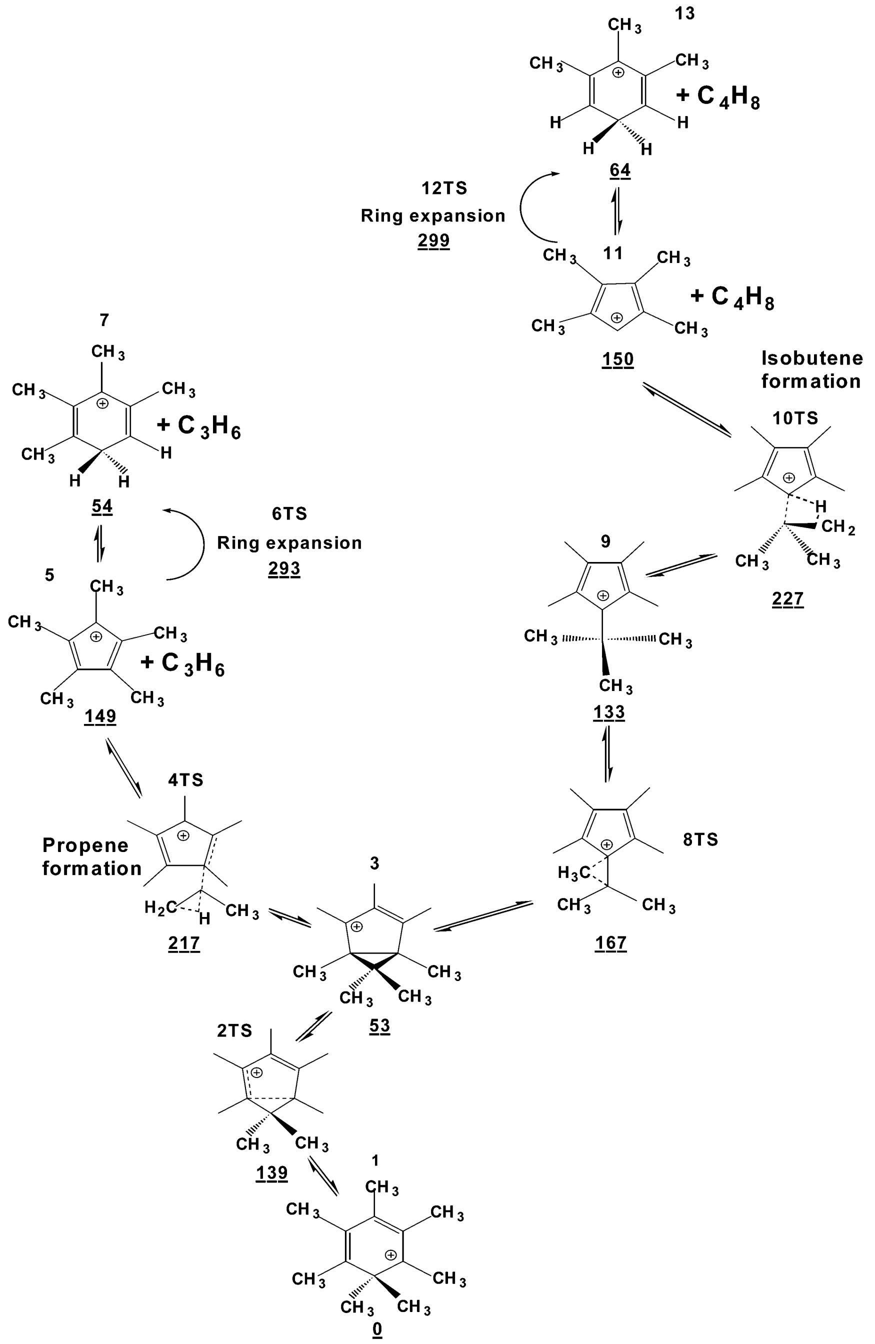
[a] Atomic numbering as in Figure 3.

Heptamethylbenzenium Ring Contraction: Propene and Isobutene Formation. This series of reactions is shown in Scheme 1. A contraction of the benzenium ring forms a bicyclic species, **3** (heptamethylbicyclo[3.1.0]hexenyl cation). The heptaMB$^+$, **1**, the ring contraction transition state, **2TS**, and the resulting bicyclic structure, **3**, are shown in Figure 4. The drawings are based on the calculated molecular structures. A ring contraction of the heptamethylbenzenium ion may according to common views be expected to proceed as indicated in Figure 5. Our computations indicate, however, that the tertiary alkyl cation that would be formed is not stable; all attempts to find a stable structure failed. The optimization calculations consistently resulted in the bicyclic structure, **3** (see also below). The contraction of **1** is similar to those ring contractions we reported for protonated xylenes.[36] Figure 6 and Table 2 show schematic drawings and some of the most important geometric parameters for four species (**2TS**, **3**, **4TS** and **8TS**) in Scheme 1.

1 and **3**, both have a mirror plane, but the transition state, **2TS**, leading to **3** is asymmetric, as can be seen from Table 2. In the transition state, **2TS**, a formal charge on C_2 is attacked by an electron pair from C_6 and a new C−C bond starts to form between C_2 and C_6. In the transition state, the C_2C_6 distance is 2.21 Å. The transition state energy is 139 kJ mol^{-1} and the bicyclic structure, **3**, is 53 kJ mol^{-1} uphill compared to the heptaMB$^+$ cation. In **3**, the C_2C_6 bond length is 1.50 Å and it is the longest bond in the five-membered ring. The dihedral angle $C_1C_2C_6C_4$ changes from 175.1° in **1**, via 128.6° in **TS2** to 109.2° in **3**. The dashed line in **2TS** in Figure 4 shows the C−C bond that is formed in the reaction. Bouchoux et al. carried out a theoretical study of ring contraction of protonated benzene in the gas phase. Also in this case a bicyclo[3.1.0] isomer resulted.[38]

The back-reaction of **3** to re-form **1** has been studied experimentally with NMR techniques. Childs and Winstein[28] reported photochemical reactions of the heptaMB$^+$ cation. Irradiation of the heptaMB$^+$ ion with light (λ_{max} 400 nm) at

SCHEME 1: Reaction Paths for Propene and Isobutene Formation Starting with a Ring Contraction in HeptaMB$^+$ (1)[a]



[a] Energies (below each structure, in kJ mol^{-1}) are relative to that of **1**. Transition states are shown by adding "TS" to the label.

−78 °C in $HFSO_3$ resulted in formation of **3** in relatively high yield. After formation of **3**, the authors raised the temperature to −9 °C (without irradiation) to investigate the thermal regeneration of **1** and found an activation energy of 83 kJ mol^{-1} for this reaction. This value is in excellent agreement with the present work's calculated barrier, (139 − 53 =) 86 kJ mol^{-1}, for forming **1** from **3**.

Childs and Winstein also observed another reaction taking place in species **3**, a discrete stepping of the cyclopropyl ring around the five-membered ring. This kind of reaction, and similar ones, are often termed as circumambulatory rearrangements and a review of such reactions is given by Childs.[39] We have found a transition state for a circumambulatory rearrangement in **3**, which is shown in Scheme 2 and Figure 7. Further, in Figure 8 and Table 3 some geometric parameters of this transition state are given. The transition state was found without imposing any symmetry restrictions, but not surprisingly it has C_s symmetry. In the transition state, the former bridging fragment is singly bonded along the C_2C_1 bond. This bond length is 1.49 Å. The C_6C_1 bond distance is 2.36 Å, and the C_3C_1 bond distance is 2.37 Å. The transition state's normal mode corresponds mainly to a "turning" movement of the $(CH_3)_2C-$ part around the C_2C_1 axis. The barrier for this reaction relative to **3** is 29 kJ mol^{-1}. The experimentally obtained rates for this stepping reaction gave 42 kJ mol^{-1} as the free energy of activation, so the agreement between the calculated and experimental activation barriers is fairly good. The NMR data showed that the methyl groups on C_1 retained their identity during the stepping, i.e., the axial methyl group remains axial after the stepping, and our computational result is in accordance

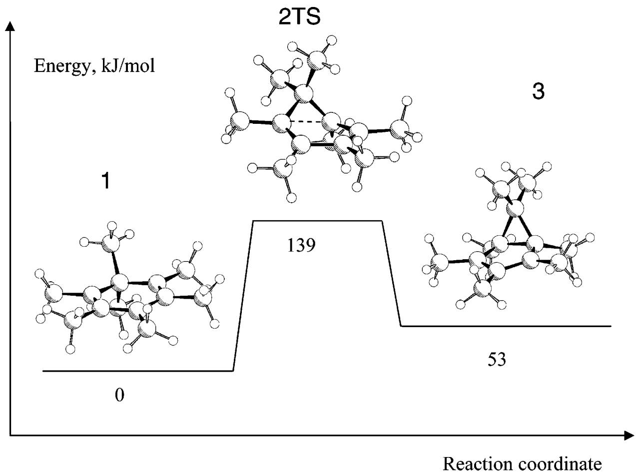


Figure 4. Ring contraction reaction from **1** to **3**.

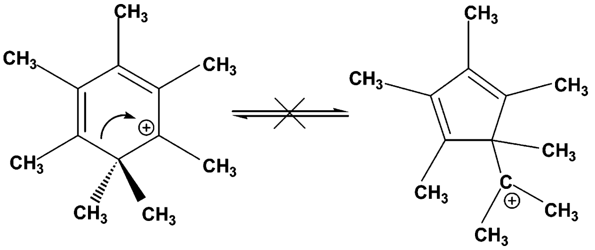


Figure 5. Usually proposed reaction for ring contraction.

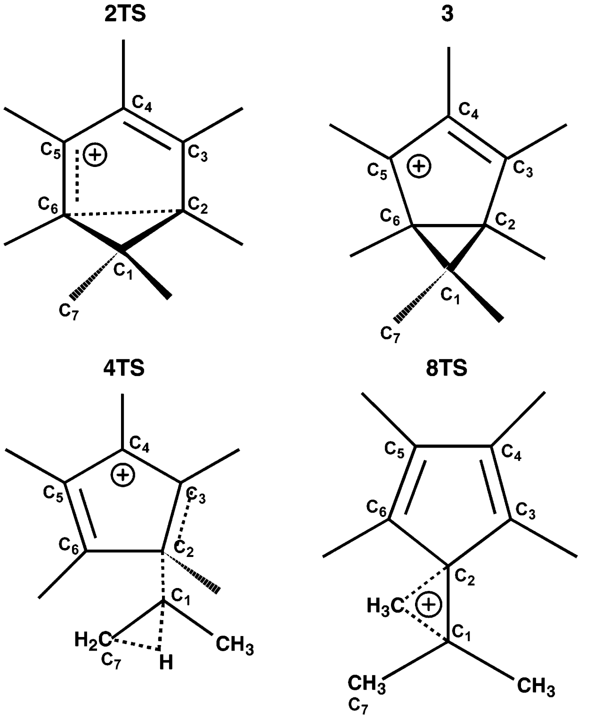


Figure 6. Atomic labels in **2TS**, **3**, **4TS** and **8TS**.

with this finding. Circumambulatory rearrangements have recently been the subject of experimental and theoretical work.[40,41]

TABLE 2: Bond Lengths in Species 2TS, 3, 4TS, and 8TS, and Dihedral Angle in 2TS and 3[a]

	2TS	3	4TS	8TS
C_1C_2	1.643	1.589	1.765	1.420
C_2C_3	1.350	1.472	1.542	1.516
C_3C_4	1.507	1.401	1.347	1.351
C_4C_5	1.348	1.402	1.493	1.495
C_5C_6	1.470	1.471	1.368	1.349
C_6C_1	1.448	1.589	2.559	
C_2C_6	2.212	1.499	1.476	1.520
C_1C_3			2.655	
$C_1C_2C_6C_4$	128.6	109.2		

[a] Atomic numbering as in Figure 6.

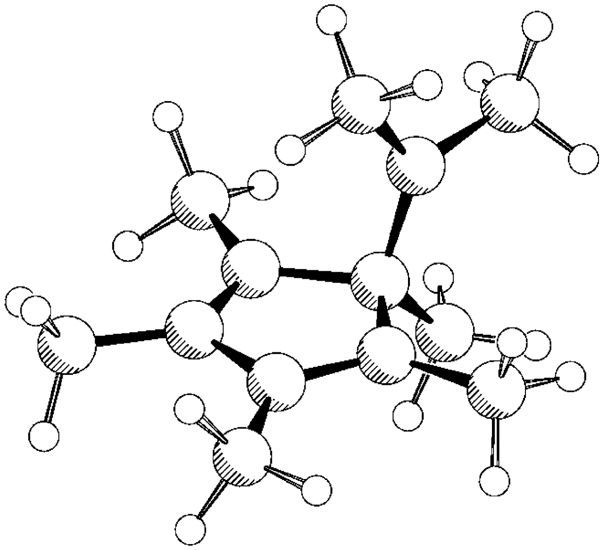


Figure 7. Transition state structure for the cyclopropyl migration on **3**.

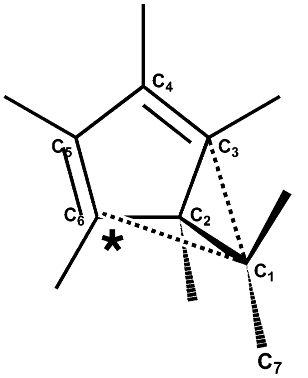
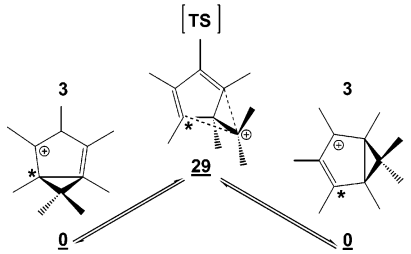


Figure 8. Cyclopropyl migration transition state, atomic labels.

SCHEME 2: Cyclopropyl Migration in 3, Barrier in kJ mol^{-1}



Two routes may lead to alkene formation from **3**. Propene and isobutene are the possible products. Propene formation will be described first. **3** may split off propene in one concerted reaction step with transition state **4TS**, as shown in the left branch of Scheme 1 (see also Figure 6). The propene elimination can be illustrated formally with a sequence of electron pair movements that all take place simultaneously, but which are described as if it were a series of sequential events. There are no local energy minima involved. Starting with the electron pair in the C_1C_6 bond attacking the formal positive charge on C_5, a transient tertiary cation with the positive charge on C_1 is formed.

TABLE 3: Cyclopropyl Walk in HeptaMB$^+$ ^{a}

C_1C_2	1.488
C_2C_3	1.526
C_3C_4	1.375
C_4C_5	1.454
C_5C_6	1.375
C_6C_2	1.526
C_6C_1	2.363
C_1C_3	2.369

[a] Interatomic distances in the transition state. Atomic numbering as in Figure 8.

If a hydrogen atom migrates from C_7 to C_1, and the electron pair in the C_1C_2 bond simultaneously switches over to form a bond between C_1 and C_7, a propene molecule is split off. The C_1C_2 bond length in **4TS** is 1.77 Å. After having passed the transition state, a pentamethylcyclopentadienyl cation, **5**, is formed together with a propene molecule. The energy of **4TS** is 217 kJ mol^{-1} relative to **1**. The cation **5** may expand, via **6TS**, to 1,2,3,4-tetramethyl-5*H*-benzenium, **7**. The energy of **6TS** plus propene is 293 kJ mol^{-1}. The ring expansion of **5** takes place via a 1,2-hydrogen shift from a methyl group onto the partial charge on the ring. This transition state has primary carbocation character and thus has to overcome a high energy barrier. See our earlier paper[36] for further details on hydrogen shifts.

Another rearrangement that may take place in **3** is illustrated in the right branch in Scheme 1 (see also Figure 6). A methyl group may move from C_2 to C_1, as shown in **8TS**, whereby a cyclopentadienyl cation with a *tert*-butyl group is formed, **9**. This reaction starts out similarly to the reaction above: the electron pair in the C_1C_6 bond switches over to the formal charge at C_5. If there is a simultaneous methyl shift from C_2 to C_1, rather than a hydrogen shift from C_7 to C_1, a *tert*-butyl group is formed, **9**. The transition state energy for this reaction step is 167 kJ mol^{-1}. Subsequently, an isobutene molecule may be split off from **9** by a 1,3-hydrogen shift from one of the methyl groups in the *tert*-butyl group to the formally positive charge on the ring (C_2). The transition state energy for the isobutene elimination, **10TS**, is 227 kJ mol^{-1}. A ring expansion to a benzenium ring might also take place before the isobutene is split off. From earlier studies on ring expansion reactions,[36] we expected this reaction to have a very high transition state energy, and indeed, we found a transition state with energy 283 kJ mol^{-1} for a direct expansion of **9** to give a *tert*-butylbenzenium ion (not shown). The high energy can be rationalized by the fact that the ring expansion must proceed via a 1,2-hydrogen shift from a methyl group, a step known to require a high energy.[36]

After isobutene is split off from **9**, the resulting tetramethylcyclopentadienyl cation, **11**, may expand, via **12TS**, to 1,2,3-trimethyl-5*H*-benzenium, **13**. The energy of **12TS** plus isobutene is 299 kJ mol^{-1}.

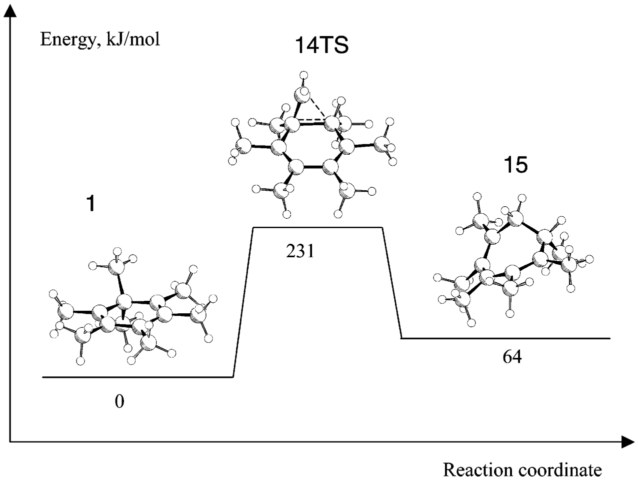


Figure 9. Ring expansion of **1** leading to **15**.

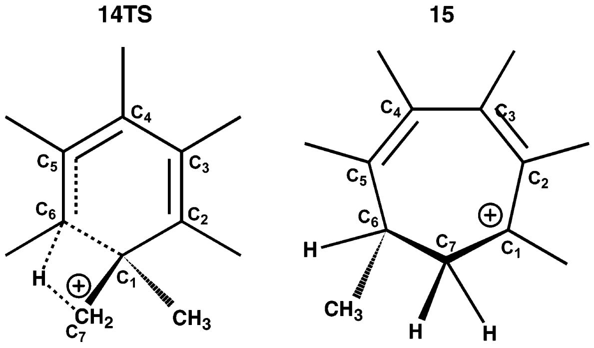


Figure 10. Atomic labels in **14TS** and **15**.

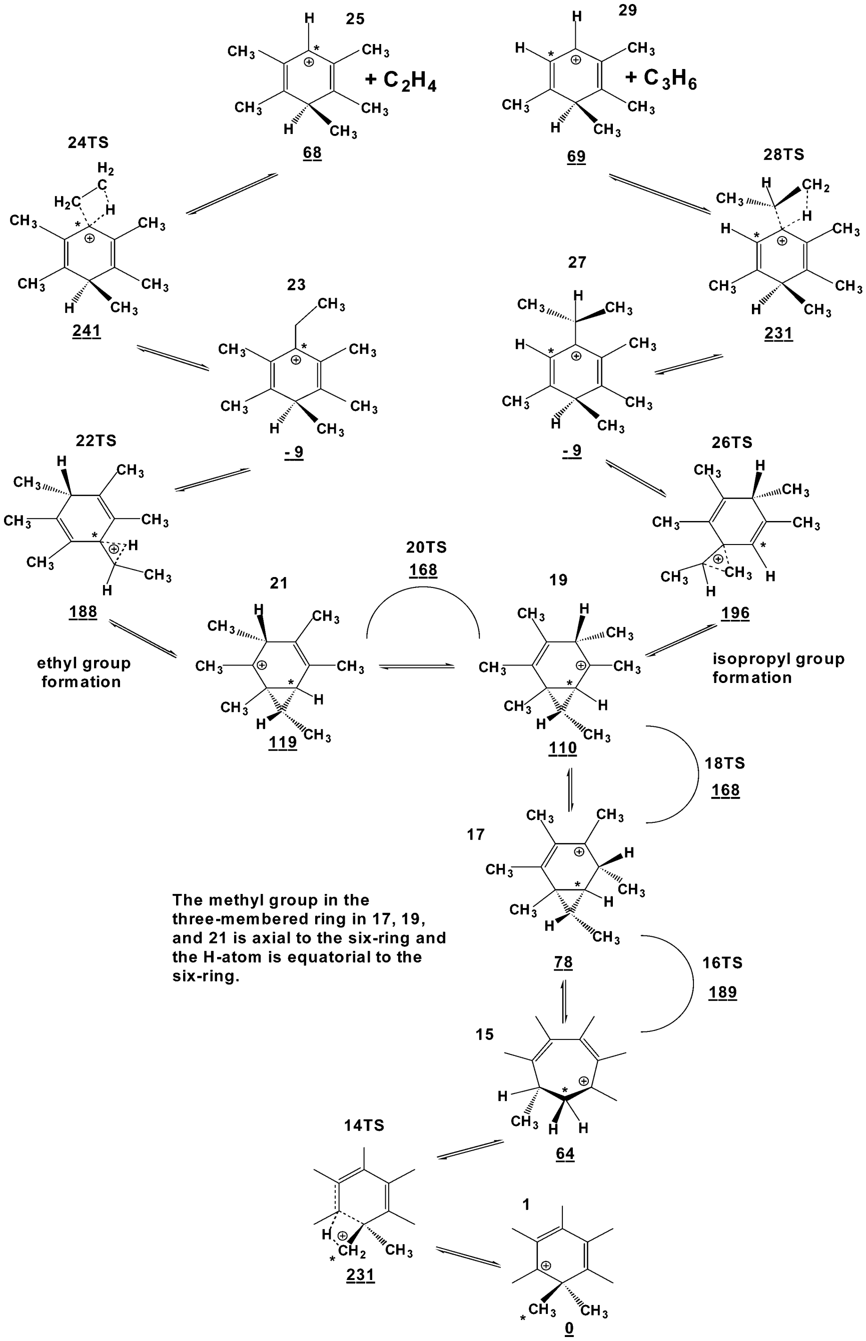
TABLE 4: Bond Lengths in 14TS and 15^a

	14TS	15
C_1C_2	1.506	1.377
C_2C_3	1.349	1.442
C_3C_4	1.484	1.439
C_4C_5	1.349	1.389
C_5C_6	1.511	1.501
C_6C_1	1.721	-
C_7C_6	1.842	1.531
C_7C_1	-	1.496

[a] Atomic numbering as in Figure 10.

Heptamethylbenzenium Ring Expansion: Ethyl and Isopropyl Group Formation. Instead of undergoing a ring contraction, **1** may expand to a seven-membered ring in one elementary step. This expansion is initiated by a hydrogen atom migration from a methyl group. The CH_2 group that is left is inserted into one of the adjoining ring C−C bonds. As described in the preceding work on protonated xylenes,[36] there are two similar ring expansion mechanisms that lead to a seven-membered ring from a methylbenzenium cation. These are either a 1,2-hydrogen atom shift or a 1,3-hydrogen atom shift from a methyl group onto the benzenium ring. In the case of a 1,3-hydrogen shift, there must be another atom or alkyl group on the same ring carbon atom as the alkyl group from which the migrating hydrogen atom originates. In the case of protonated xylenes, ring expansion in conjunction with a 1,3-hydrogen shift was clearly more facile than the corresponding expansion where there is a 1,2 hydrogen shift. The two ring expansion steps have been investigated for cation **1**. From the seven methyl groups on **1**, a 1,3-hydrogen shift may take place from one of the two methyl groups on C_1 (Figure 3), and a 1,2-hydrogen shift may take place from the methyl groups on C_2, C_4, and C_6. Our results indicate that the 1,3-hydrogen shift mechanism is clearly the more facile. The barrier for a 1,3-hydrogen atom shift and ring expansion is 231 kJ mol^{-1}, and the barrier for the 1,2-hydrogen shift from the methyl group in para-position relative to the two *gem*-dimethyl groups is 65 kJ mol^{-1} higher. Reactions starting with a 1,2-hydrogen atom shift will therefore not be further explored. Figure 9 shows the transition state for the reaction associated with a 1,3-hydrogen shift, **14TS**, and the resulting seven-membered ring, **15**. Figure 10 and Table 4 show geometric parameters of **14TS** and **15**. Scheme 3 shows possible reaction paths for formation of ethyl or isopropyl groups on a polymethylbenzenium ion. In the transition state, **14TS**, the C−C bond length (C_1C_6) that widens to admit the CH_2 group

SCHEME 3: Minima and Transition States for Ethyl and Isopropyl Formation after a Ring Expansion of 1[a]



The methyl group in the three-membered ring in 17, 19, and 21 is axial to the six-ring and the H-atom is equatorial to the six-ring.

[a] Energies (in kJ mol^{-1}) are relative to that of **1** and given below each species. Transition states are shown by adding "TS" to the label.

into the ring is 1.72 Å and the C−C bond that is being formed (C_6C_7) is 1.84 Å. The resulting species, **15**, can be viewed as a protonated hexamethylcycloheptatriene. The C−C bonds that are broken and formed during the transition state are shown with dashed lines in Figures 9 and 10.

Species **15** may react in several ways, but only a few H- or CH_3-group migrations will be explored. The transition state energies for ring hydrogen atom migrations are shown in Scheme 3, but the actual transition state structures are omitted.

Carbon C_7 in **15** has bonds to two hydrogen atoms. As is conveyed by Figures 9 and 10, one of the CH bonds is essentially normal to a plane roughly defined by the ring atoms C_2−C_5 (atomic coordinates are given in Supporting Information) and may be termed axial; the other is essentially parallel to that plane and may be termed equatorial. C_7 is lifted well above the plane, and C_6 is slightly beneath it. If the axial hydrogen migrates to C_1, a bicyclic structure, **17**, is formed. Formation of such a bicyclic species was observed also when rearrangements in protonated xylenes were studied, and also when protonated 1,3,5-cycloheptatriene was studied by Salpin et al.[34,36] **17** can react further through more hydrogen atom migrations as shown in Scheme 3, and eventually an ethyl or an isopropyl group may be formed. The last transition states in the series of reactions forming alkyl groups are given as **22TS** and **26TS** respectively. They are similar to the *tert*-butyl-group-forming step, **8TS**, in Scheme 1. The two resulting species, **23** and **27**, are 1-ethyl-2,3,4,5,6-pentamethyl-4*H*-benzenium and 1-isopropyl-2,3,4,5-tetramethyl-4*H*-benzenium, respectively. Structures **23** and **27** are both 9 kJ mol^{-1} more stable than **1**, and they can both eliminate the alkyl group as an alkene in conjunction with a 1,3-hydrogen shift of a β-hydrogen on the alkyl group onto the ring carbon that binds the alkyl group. The transition state

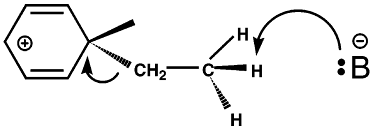


Figure 11. Ethene elimination from protonated ethylbenzene in zeolite catalyst.

energies for the two alkene eliminations, **24TS** and **28TS**, are 241 and 231 kJ mol^{-1}, respectively. The two transition states for intramolecular alkene elimination reactions have approximately the same energy as the initial ring expansion step, **14TS**. However, on a real zeolite catalyst, **23** and **27** may eliminate ethene and propene via the reaction mechanism we have previously described,[42] a concerted antiperiplanar elimination of the alkyl chain, aided by a basic oxygen atom in the zeolite that snatches a proton from the alkyl group (see Figure 11).

Elimination of an alkene might also take place via formation of an ion−neutral complex, as described by Berthiomieu et al.[43] In this case a hydrogen migration to the ipso position of the isopropyl group in **27** would be a preliminary first step. By a (heterolytic) breaking of the bond between the benzene ring and the isopropyl group an ion−neutral pair is formed. The pair supposedly forms a rather stable complex. The complex may split up and form benzene and an isopropyl cation. Alternatively, a proton may be transferred from the isopropyl cation moiety to benzene, resulting in propene and a benzenium ion complex that may subsequently split up.

We have not investigated this type of reaction. DFT methods such as B3LYP are not able to give a good description of the long distance interactions that are decisive for complex stabilities,[44,45] and according to our experience with related problems, it is very difficult to find stationary points for transition states; re-formation of the bond usually takes place. Berthiomieu et al. avoided this problem by not allowing structural changes in the two moieties and thus not formation of new bonds. Such a procedure may, however, make the outcome of the computations somewhat unrealistic.

The bond breaking mechanism issue is, however, interesting and might well deserve a treatment at higher levels of theory, but this would require computations on a ion species smaller than **19**, like isopropylbenzenium or ethylbenzenium, the smallest ions where such reactions may be studied.

It should be noted that several of the species shown in Scheme 3 might undergo other reactions in addition to those shown. As an example, our previous study of protonated xylenes showed that if a seven-membered ring species contains a $-CH(CH_3)-CH_2-$ group, a ring contraction may take place, forming an ethyl group in the process. Species **15** has this atomic arrangement and might be expected to form an ethyl group with such a ring contraction. However, **15** does not have the correct spatial geometry for a direct contraction to form an ethyl group. By a direct re-contraction **1** is re-formed. If, however, a conformational change takes place whereby C_7 is taken below the “ring plane” (as described above) and C_6 is lifted above the same plane, the reaction is possible. After a conformer change of **15** into **15′** (not shown), in which the axial methyl group on C_6 is turned into an equatorial one, **15′** may contract and form the 1-ethyl-2,3,4,5,6-pentamethyl-1*H*-benzenium ion. When the ring expansion takes place, the C_1-C_6 bond is broken and a C_6-C_7 bond was formed. In the contraction step where an ethyl group is formed, the C_6-C_7 bond is broken and a C_5-C_7 bond is formed in the process.

Alternatively, because the methyl group bonded to C_6 in **15′** is axial to the ring plane, it might migrate along the ring and finally become bonded to C_1. This species may then contract and form an isopropyltetramethylbenzenium species, in analogy to the ethyl group formation described above.

At first looks also **17** appears to be a potential species for reactions leading directly to ethyl or isopropyl group formation. **17** may, however, not directly form an ethyl or an isopropyl group. To transform the cyclopropyl ring into an alkyl chain, an electron pair must switch over from the three-membered ring to the formally positively charged C-atom on the six-membered ring. If this kind of electron pair leap is thought to take place in **17**, formation of an ethyl group might be expected to follow, but a closer scrutiny of the geometry showed that this reaction is for steric reasons not possible. **17** must therefore isomerize into **19** or **21** before a higher alkyl chain attached to the benzenium skeleton can be formed via these pathways.

In analogy to **4TS**, an ethene molecule might be eliminated from **17** in a single concerted reaction. Ethene eliminations directly from such bicyclic species have fairly high transition state energies (∼290 kJ mol^{-1} for species similar to **17** and **19**). As these reactions have been studied earlier for protonated xylenes[36] (energies around 295 kJ mol^{-1}), they will not be further considered here.

Methyl Group Ring Migration on the Heptamethylbenzenium Cation. One of the methyl groups in the *gem*-dimethyl group in **1** may shift to an adjacent ring carbon atom in a 1,2-methyl group shift. The resulting species is still a heptaMB$^+$ cation. Borodkin et al.[29] measured the Arrhenius activation barrier for the 1,2-methyl shift both in the solid state and in solution using NMR spectroscopy. In a crystalline sample of the tetrachloroaluminate salt of **1**, NMR data gave an activation energy of 44 kJ mol^{-1} for the methyl shift. When the salt was dissolved in CH_2Cl_2, the activation energy was found to be 69 kJ mol^{-1}. Borodkin et al. found the ring migration rates in solution and in solid state to be equal at −77 °C. This indicates a preexponential factor that is 4×10^6 larger in solution than in the solid, and a different mechanism in the two cases. Our calculated value (which is based on a gas-phase model) for the 1,2-methyl shift activation energy is 87 kJ mol^{-1}, which is in fair agreement with the experimental results in solution. Methyl group shifts in gaseous xylenium ions were studied by Büker et al.[46]

Discussion

The present work describes several intramolecular reaction paths for alkene formation from the heptaMB$^+$ cation. In a study of the MTH reaction over H−Beta zeolite, indications were found that intramolecular reactions leading to alkene formation took place in heptaMB$^+$ that was formed inside the catalyst pores.[11] The study of gas-phase intramolecular reactions studied here is likely to be relevant also for the reactions taking place in zeolite pores.

Experimental observations when the MTH reaction over zeolite type catalysts is studied have shown that the rate of alkene formation and the selectivity for propene, rather than ethene, both increase with the number of methyl groups on the methylbenzenes.[16] The barrier for the described 1,3-hydrogen shift leading to ring expansion of heptaMB$^+$ is about 30 kJ mol^{-1} higher compared to similar 1,3-hydrogen shift barriers for protonated xylenes. In contrast, the ring contraction step of the heptaMB$^+$ cation has a lower barrier compared to the similar contraction steps found for protonated xylenes (139 kJ mol^{-1} vs 189 and 196 kJ mol^{-1}). The resulting bicyclic species is also 80−100 kJ mol^{-1} more stable than the corresponding bicyclic species resulting from a contraction of a protonated xylene. If methylbenzenium ions undergo intramolecular reactions to form alkenes, the initial ring contraction is the only reaction step found so far that becomes more facile with an increasing number of methyl groups. There are, however, no obvious reaction paths for ethene formation from **3**, and ethene formation from the heptaMB$^+$ ion therefore probably proceeds either via the ring expansion mechanism (Scheme 3) or, e.g., by side-chain methylation and subsequent ethene elimination.

Turning to alkene elimination issues, we note that if alkene eliminations from **1** take place in the gas phase, the transition state energies for the different reactions are fairly similar, between 217 and 241 kJ mol^{-1}. Propene elimination from **3** (via **4TS**) has the lowest transition state energy, and ethene elimination from **23** (via **24TS)** has the highest. However, if **1** is inside a zeolite pore, another possibility for alkene elimination arises. We have previously described a concerted dealkylation reaction that takes place on a zeolite acidic site.[42] It is important to note that the zeolite-assisted alkene elimination reactions become much more facile with an increasing number of methyl groups on the ring. If the heptaMB$^+$ cation undergoes a ring contraction as the initial step, the resulting species, **3** or **9**, is not able to eliminate alkenes with the aid of the zeolite catalyst. In contrast, the paths shown in Scheme 3 lead to a benzenium ring with an ethyl or isopropyl group. These alkyl chains may be eliminated as alkenes via the catalyst-assisted pathway. The calculated barrier for ethene elimination from ethylpentamethylbenzene using a cluster model as the acidic site, was found to be 165 kJ mol^{-1} at the B3LYP/cc-pVTZ//B3LYP/6-31G(d) + ZPE level of theory.[42] The cluster model is known to give too high activation energies. Hence, on a zeolite catalyst, the highest transition state energies will probably be the alkene elimination step if the reaction proceeds by a ring contraction that forms **3** from **1**, and it will be the initial ring expansion if **1** expands to the seven-membered ring, **15**.

Conclusions

We have computationally investigated various intramolecular reaction paths for the heptaMB$^+$ cation. Some of these reactions may lead to ethene, propene, and isobutene formation. Intramolecular rearrangements that may lead to C_2-C_4 alkyl groups may proceed through a ring contraction or a ring expansion. An initial ring contraction of heptaMB$^+$ leads to formation of the bicyclic heptamethylbicyclo[3.1.0]hexenyl cation (**3**). The barriers for re-forming heptaMB$^+$ from **3**, and for cyclopropyl ring migration on **3**, have been calculated and found to agree well with the experimental values. After further rearrangements **3** may split off propene or form *tert*-butylmethylcyclopentadienyl cations that may split off isobutene, leaving a methylcyclopentadienyl cation. Ring expansion in heptaMB$^+$ gives a seven-membered ring that may rearrange via hydrogen and methyl shifts and recontract to a benzenium ring with an ethyl or isopropyl group. In the presence of a zeolite catalyst, the barrier for splitting off an alkyl group is much lower from an alkylbenzenium ion than from an alkylcyclopentadienyl cation because the latter cannot transfer a proton back to the zeolite.

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Supporting Information Available: Cartesian coordinates, absolute energies given in Hartrees, zero point energy corrections, and the transition states' imaginary frequencies are given for the stationary points that were investigated. This material is available free of charge via the Internet at http://pubs.acs.org

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