JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2004; **17:** 1023–1032
DOI: 10.1002/poc.830

Theoretical study of protonated xylenes: ethene elimination and H,C-scrambling reactions[†]

Bjørnar Arstad,[1] Stein Kolboe[1]* and Ole Swang[2]

[1]Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway
[2]SINTEF Applied Chemistry, Department of Hydrocarbon Process Chemistry, P.O. Box 124 Blindern, N-0314 Oslo, Norway

Received 5 December 2003; revised 6 February 2004; accepted 20 February 2004

epoc

ABSTRACT: Quantum chemical calculations have been carried out to investigate various unimolecular rearrangements that can take place in protonated gas-phase xylenes. Hydrogen and methyl group ring migrations were investigated. The barriers for hydrogen migrations are lower than the barriers for methyl group migrations. Mechanisms for ring expansion to seven-membered rings, and for contraction to five-membered rings were studied. Both of these mechanisms can eventually lead to ethene elimination. The most favourable ring expansion step goes through a 1,3-hydrogen shift from a methyl group onto the arenium ring, forming a protonated methylcycloheptatriene. Interconversions between various ring-expanded forms have been investigated. Re-contraction can lead to an ethylbenzenium ion that could subsequently split off ethene. Alternatively, the xylenium ion can contract to a five-membered ring. The immediate product is a bicyclic ion (bicyclo[3.1.0]hexane skeleton) that can rearrange further to give an ethylbenzenium ion, or the five-ring system can split off ethene, and be converted into a cyclopentadienyl ion that can isomerize into a benzenium ion. Stable structures and transition states are calculated both at the B3LYP/cc-pVTZ//B3LYP/6-311G(d,p) and at the MP2/cc-pVTZ//MP2/6-31G(d) levels. The energies needed for ring expansion or ring contraction are not very different, and the calculations suggest that both reaction paths are possible, but the energy needed for actually splitting off an ethene molecule is lower along the expansion path. Copyright © 2004 John Wiley & Sons, Ltd.
Additional material for this paper is available in Wiley Interscience

KEYWORDS: xylenium ions; ethene elimination; DFT study; atom scrambling; ring expansion and ring contraction; hydrogen and methyl shifts; proton affinities; protonated methylcycloheptatriene

INTRODUCTION

Recently, Mormann and Kuck published a mass spectrometric study of long-lived gaseous protonated xylenes and showed that methane and ethene are split off from these molecular ions.[1] It was found in particular that when ethene is lost, there is extensive scrambling between the methyl and ring C-atoms. They arrived at this conclusion by using ^{13}C- and ^{2}H-labeled compounds. The labeling could be either in the methyl groups or in the ring. It was concluded that the formation of ethene from protonated xylenes takes place after ring expansion of the benzenium ring to form a protonated methylcycloheptatriene (=methyldihydrotropylium ions) (PMCH), and, via several intermediates, a subsequent re-contraction to form protonated ethylbenzene.

When PMCH is studied by mass spectrometric methods ethene formation takes place but there is little methane formation.[2] This is in contrast to what happens in the case of protonated xylenes. Based on such results, Mormann and Kuck concluded that methane is formed directly from the protonated xylenes, and that ethene loss takes place after further rearrangements via seven-membered rings, whereby protonated ethylbenzene is formed. The olefin could then be expelled from this molecular ion. It was pointed out that starting from protonated xylene, repeated expansion–contraction cycles could take place before an ethyl group is formed: this series of expansions–contractions could lead to an extended scrambling between ring and methyl group atoms. Comprehensive reviews on unimolecular reactions of arenium ions are available.[3,4]

In addition to presenting further general information on the gas-phase reactions that xylenium ions can undergo, the paper by Mormann and Kuck may shed further light on the methanol to hydrocarbons reaction (MTH). This reaction takes place in protonated zeolites, which act as solid acidic catalysts, at temperatures in the range 200–450 °C. A much improved insight into the mechanistic details of this reaction has become unraveled

---

**Correspondence to:* S. Kolboe, Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway.
E-mail: steink@kjemi.uio.no

[†] Paper presented at the 9th European Symposium on Organic Reactivity, 12–17 July 2003, Oslo, Norway.

Contract/grant sponsor: Norwegian Research Council; *Contract/grant numbers:* 135867/431 and 149326/431.
Contract/grant sponsor: NOTUR Project; *Contract/grant numbers:* NN2147K and NN2878K.

recently. For a general review of this reaction see Refers 5 and 6.

According to now widely accepted views, the main reaction path of the (steady state) MTH reaction proceeds via repeated methylations of benzene to form polymethylbenzenes and eventually polymethylbenzenium ions. During, or after such methylations, alkenes are eliminated from these species. A detailed insight into the reactions leading to alkene formation is still lacking. According to one proposed scheme, the reaction proceeds by a repeated series of contractions–expansions (six- to five- to six-rings) of the protonated arenes, whereby alkyl side-chain extensions take place. It is shown below that attention should not be confined only to contraction–expansion schemes involving five-membered rings, but also to expansion–contraction schemes involving seven-membered rings. The simplest example to study such reactions is given by a xylenium ion. A detailed theoretical study of xylenium ions and rearrangement products could therefore be illuminating also for MTH studies. Reaction schemes based on side-chain methylations of the arenes also exist, but they are not relevant to this study. Very recent surveys were given by Haw and co-workers.[7,8]

The work of Mormann and Kuck represents an MS study of the smallest polymethylbenzenium ion that could be relevant in the MTH process. In order to obtain a detailed insight into the energies of the various species involved, and the barriers for interconversion between them, we have performed an extensive series of quantum chemical computations of the gas-phase species that could result if a proton is added to a xylene, or a methyl cation to toluene. We used density functional theory (DFT) and second-order perturbation theory (MP2) with extended basis sets.

COMPUTATIONAL DETAILS

The computations where carried out using the Gaussian98 program package.[9] The structures were first optimized at the B3LYP/6-31G(d) level of theory. Thereupon they were re-optimized at the B3LYP/6-311G(d,p) level of theory to see the basis-set effects on the structures. Analytical frequencies and zero-point corrections were calculated at the same level of theory in each case. The differences in geometry obtained with the two basis sets were marginal, and the corresponding energy differences were also very small. It was ensured that the transition states really had one, and only one, imaginary frequency and that the minima had none. The structures that were determined in this way were used to calculate single-point energies at the B3LYP/cc-pVTZ level of theory, using the B3LYP/6-311G(d,p) geometries and ZPE corrections, but the improved basis set did not lead to any notable energy changes. The studied species were also geometry optimized at the MP2/6-31G(d) level of theory. These calculations mostly gave geometries very similar to the DFT structure. Also here single-point energies at the MP2/cc-pVTZ level of theory using the MP2/6-31G(d) structures, with ZPE corrections from the MP2/6-31G(d) were calculated. Comparing the MP2 and DFT methods, we found no systematic differences, and the two approaches lead to identical qualitative conclusions.

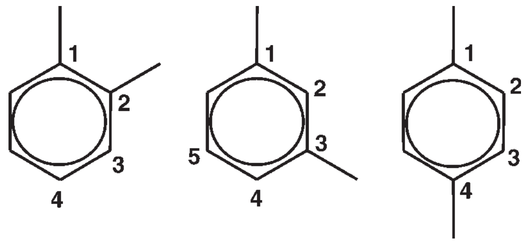
To ensure that the transition states that were found actually connect the desired minima, either intrinsic reaction coordinate (IRC) calculations[10] as implemented in Gaussian98, or small perturbations of the transition state structures along the reaction coordinate followed by ordinary optimizations, were performed.

RESULTS

Proton affinities and relative stabilities of the xylenes

The three xylene isomers have several different protonation sites available. In total, there are nine different ring protonated xylene isomers. In addition, the isomeric 1,1-dimethylbenzenium cation should be considered. Table 1 shows the possible protonation positions in the three

Table 1. Theoretical and experimental proton affinities (kJ mol^{-1})



o-xylene *m*-xylene *p*-xylene

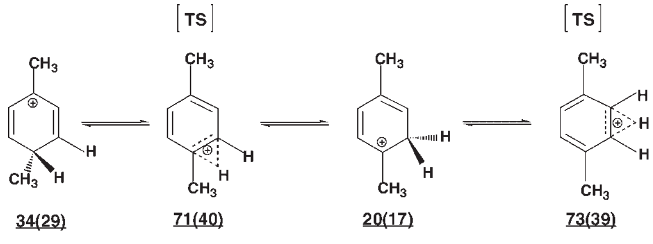
Species/ H$^+$-position	B3LYP PA	B3LYP Rel. energy	MP2 PA	MP2 Rel. energy
o-Xylene				
1	787	45	742	36
3	806	25	760	17
4	812	20	764	13
m-Xylene				
1	772	56	732	46
2	822	6	772	6
4	828	**0**	778	**0**
5	793	36	750	28
p-Xylene				
1	794	34	749	29
2	808	20	761	17
1,1-Dimethylbenzene	—	79	—	58

Proton affinity, experimental[15]	Energy (kJ mol^{-1})
o-Xylene	796
m-Xylene	812
p-Xylene	794

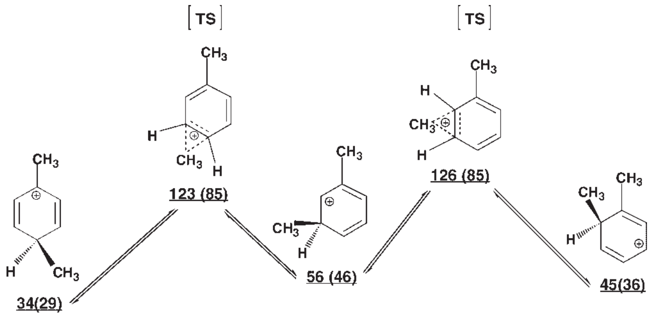
different xylenes and the calculated proton affinities at the B3LYP and the MP2 level for these positions. The relative energies of the different protonated species are also indicated. The experimental proton affinities of the three different xylenes are also included. The B3LYP proton affinities are higher by 40–50 kJ mol^{-1}, than the corresponding MP2 values, and they are closer to the experimental values. The relative stabilities of the isomers are, however, largely independent of the calculation scheme. Both calculation schemes predict that the most stable isomer is the *m*-xylene protonated in the position marked 4, 1,3-dimethyl-4*H*-benzenium. From resonance considerations, this is also plausible since the formal positive charge is on tertiary carbons in two out of three different resonance forms. *m*-Xylene protonated in position 2 is only 6 kJ mol^{-1} less stable. The 1,1-dimethylbenzenium cation does not become a xylene if a proton is removed. The energy of this isomer relative to the most stable one is considerably higher, 78 and 58 kJ mol^{-1} at the B3LYP and MP2 levels, respectively. See Refs 11–14 for earlier works on proton affinities of benzene derivatives. In the following (except when stated otherwise), all energies will be given relative to the most stable isomer of the protonated xylenes, i.e. *m*-xylene protonated in position 4 as shown in Table 1.

Hydrogen and methyl group shifts

In Scheme 1 the possible ring hydrogen shifts in protonated *p*-xylene are given, together with the energies (kJ mol^{-1}) of the stable ions and the transition states (marked by TS), all relative to the most stable protonated xylene, as given in Table 1. The first member of each pair of numbers was calculated according to the B3LYP methodology; the second, in parentheses, was obtained when MP2 was utilized, abc(xyz). The corresponding alkyl shifts are given in Scheme 2. The barriers for the isomerizations in Schemes 1 and 2 are low compared with those of the isomerization and fragmentation reactions discussed below. Because of the relatively small barriers for methyl and hydrogen migrations on the benzenium ring, all of the ten isomeric xylenium cations will be in equilibrium before scrambling reactions and ethene elimination take place. Kuck has given a survey of previous work on hydrogen and methyl group migration in alkylbenzenium ions.[4]



Scheme 1. Minima and transition states for ring hydrogen migrations on protonated *p*-xylene



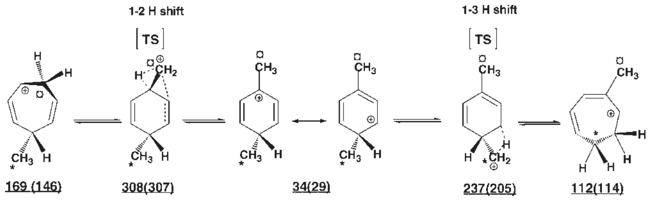
Scheme 2. Minima and transition states for ring methyl group migrations on protonated xylenes

There are few reports on measured activation energies for hydrogen or methyl group migration on gas-phase arenium rings in the literature. Cacace *et al.* investigated 1,2-hydrogen shifts in gas-phase *tert*-butylbenzenium ions, and reported a value 32 kJ mol^{-1} at 47–120 °C.[16] When the energies given in Scheme 1, and the barriers at 0 K that are implied, are compared with the experimental assessment, the values obtained from B3LYP seem to agree well (though a bit high), and the MP2 values appear too low. Büker *et al.* recently obtained an experimentally based estimate for the barrier for methyl group migration on an arenium ring.[17] The barrier was estimated to be about 83 kJ mol^{-1}. The barriers (0 K) that can be extracted from the energies given in Scheme 2 are (B3LYP) 89, 67, 70, 81 kJ mol^{-1}, in excellent agreement with Büker *et al.* The values that are obtained from the MP2 energies in Scheme 2 again appear to be low; they are 56, 39, 39 and 49 kJ mol^{-1}.

Ring expansion of protonated methylbenzenes

If a dimethylbenzene is to split off an ethene molecule, it is reasonable to assume that an isomerization, so that an ethyl group is formed, must first take place. This process can take place via expansion to a seven-membered carbon ring that can later re-contract, or via contraction to a five-membered ring. It will be seen, however, that although formation of an ethyl group may be advantageous for ethene formation it may not be a prerequisite. There are reaction steps that do not require fully formed ethyl groups in order to form ethene. The expansion path is treated first.

Experimentally, the position of the proton on the benzene ring is difficult to control. At the microscopic level, however, the position of the proton plays an important role in the ring expansion step. A ring expansion can take place in two rather different ways. They are illustrated in Scheme 3, where a protonated *p*-xylene is taken as an example. In the left part of the scheme the top methyl group is 'inserted' into the benzene ring in conjunction with a 1,2-hydrogen shift. In the transition state a hydrogen atom on the methyl group is transferred into the top ring C-atom while simultaneously the



Scheme 3. Examples of ring expansion mechanisms, both by 1,2-hydrogen and 1,3-hydrogen migrations from a methyl group, on an *ipso*-protonated *p*-xylene. Note the much lower barriers for the 1,3-hydrogen shift. To keep track of the methyl group carbons that enter the ring, they are marked with the symbols *, ¤

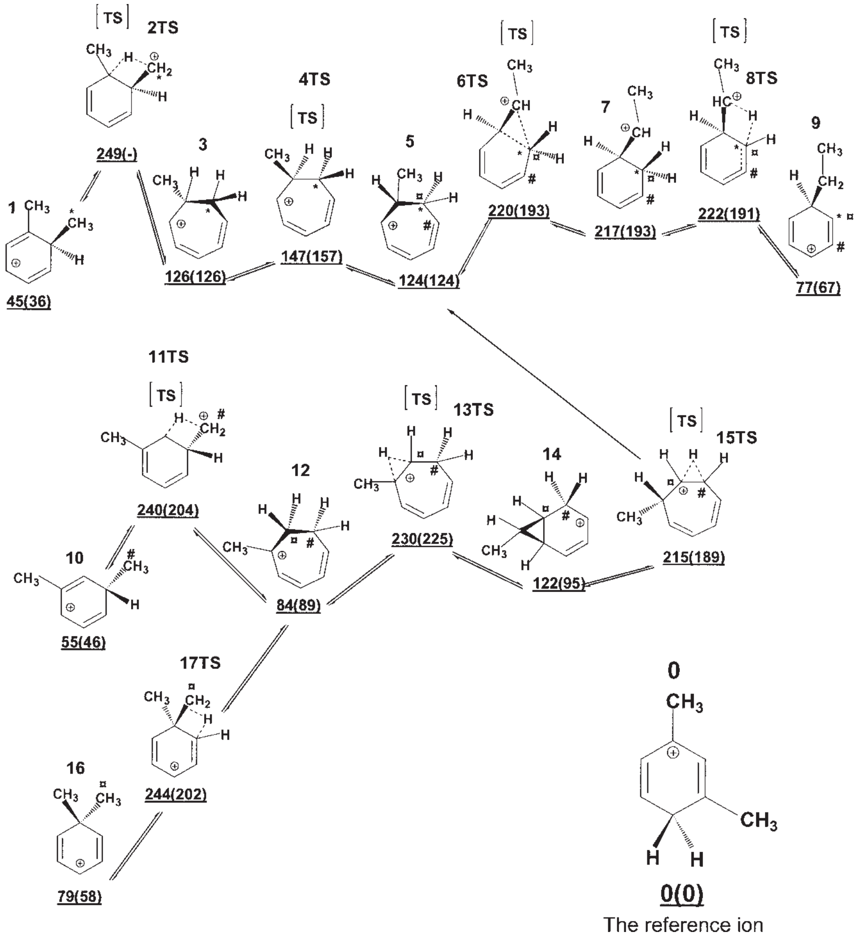
resulting CH_2-group is inserted into the adjoining (to the left or right) ring C—C bond. The other mechanism for ring expansion is shown to the right in Scheme 3. In this case the proton is in the *ipso*-position to the methyl group. A hydrogen atom is transferred to the ring via a 1,3-shift. The remaining CH_2 group is inserted into one of the adjoining ring C—C bonds.

The energies of the transition states and the resulting PMCHs are indicated in the schemes, again relative to the most stable protonated *m*-xylene isomer. The energy barrier connected with the 1,2-hydrogen shift is much higher than the corresponding barrier when the expansion takes place via a 1,3-hydrogen shift. The large difference between the two paths is independent of the particular methodology that is used. B3LYP and MP2 produce similar results. Corresponding calculations carried out on the reference ion 1,3-dimethyl-4*H*-benzenium (ion **0** in Scheme 4) concurred completely and showed the same difference between a 1,2- and a 1,3-shift. This shows that unless the protonated xylene has a very high energy, ring expansions take place via 1,3-hydrogen shifts.

Protonated methylcycloheptatriene species and interconversion between them

We have shown above that when a xylene molecule is protonated, the energy that is required for isomerization to the other isomers is fairly small. Consequently ring expansion to a PMCH can take place from any of the protonated xylene isomers, as they will all be present.

If we start out from cycloheptatriene and first form the protonated species (three different isomers) and then



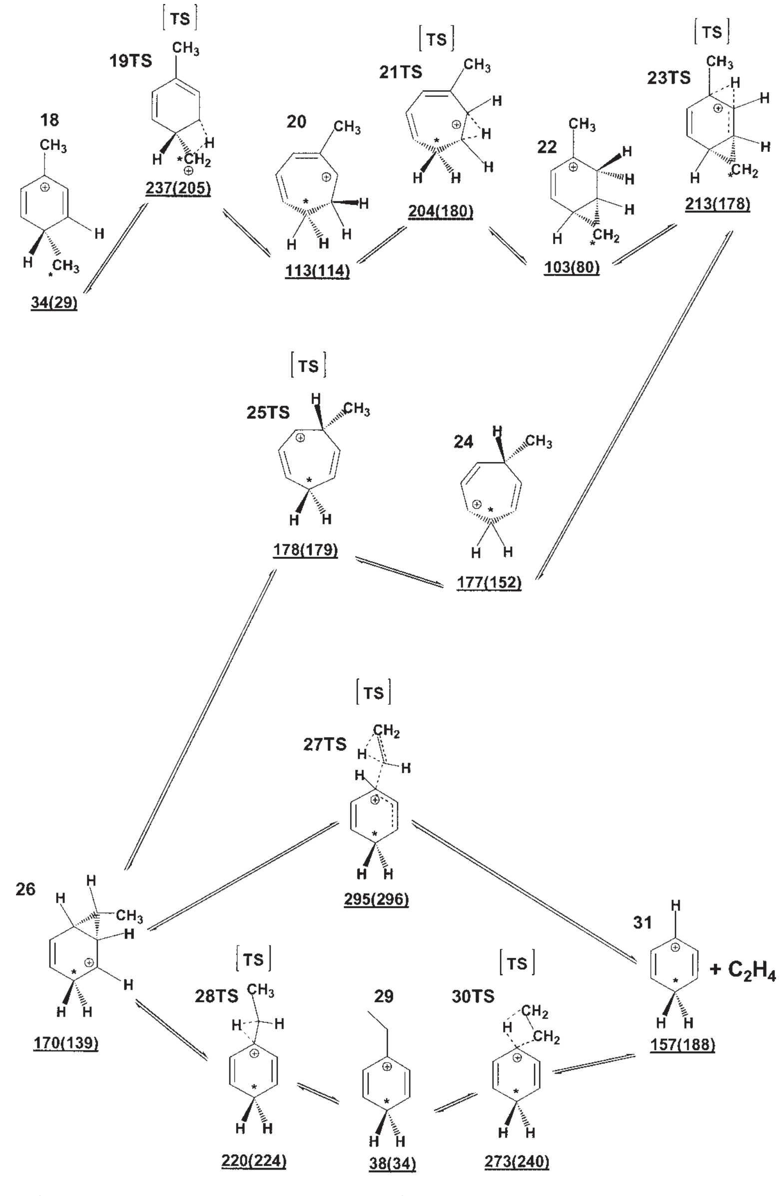
Scheme 4. *Ipso*-protonated ethylbenzene formation from protonated *o*-xylene, *m*-xylene and 1,1-dimethylbenzenium via an initial ring expansion step. The reference ion, 1,3-dimethyl-4*H*-benzene, **0**, is also shown. To keep track of the methyl group carbons that enter the ring, they are marked with the symbols *, #, ¤

replace a hydrogen atom by a methyl group, we find that there are 15 isomers. Three of these isomers arise because the PMCH is non-planar, and when a methyl group replaced a hydrogen in a CH_2 group, the methyl group could come in an axial or equatorial position.

We have computed the structures and energies of a number of these isomers, and also determined transition states for converting one isomer into another. Because the barrier for expanding a six-ring into a seven-ring system is much lower if the expansion proceeds in conjunction with a 1,3-hydrogen shift, rather than a 1,2-shift, we have only investigated the seven-membered ring species that result from 1,3-shifts.

Extending an *ipso*-protonated ethylbenzene to a seven-membered ring via a 1,3-hydrogen shift leads to formation of a —$CH(CH_3)$—CH_2— group in the ring. *o*-Xylene gives this group directly, whereas the other xylenes produce seven-ring ions that require several isomerization steps to produce this ring constituent. The calculations have, however, shown that the expansion of a protonated ethylbenzene can take place via 1,2-hydrogen shifts as well as by 1,3-hydrogen shifts, so ethyl group formation (by a contraction) can proceed also in conjunction with 1,2-hydrogen shifts. The transition state energies are not necessarily very different in this case.

The species that have been investigated are shown in Schemes 4 and 5. The energies are given in the same way as is used in Scheme 1. Ring expansions and further reactions from the *o*- and *m*-xylenium ions, as well as the 1,1-dimethylbenzenium ion are given in Scheme 4. *p*-Xylenium reactions are given in Scheme 5. The formulae are given as resonance forms. The plus sign has been



Scheme 5. Ethylbenzenium formation and ethene elimination from a *p*-xylenium ion via a ring expansion mechanism. To keep track of the methyl group carbon that enters the ring, it is marked with the symbol *

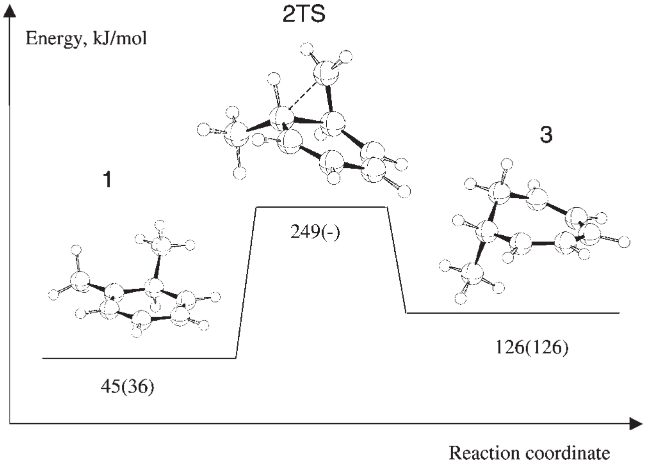


Figure 1. Structures and energies for ring expansion from an *ipso*-protonated *o*-xylene to a seven-membered ring. The dotted line indicates the C—C bond that forms during the reaction

placed so that it should be easy to see which hydrogen shift is coming next. We have also marked the carbon atoms of the methyl groups that enter the ring system by the symbols, *, #, ¤. An impression of the geometry of the species **1**, **2TS** and **3** in the first reaction step is obtained from Fig. 1, which is based on the precise atomic positions.

It is seen that ring expansion of **1** and **10** via a 1,3-hydrogen shift can be done in two ways. An important result in Scheme 4 is that the transition state energies for ring expansion are essentially independent of which isomer is expanded. The energy differences between **2TS**, **11TS**, **17TS** and **19TS** are within 12 kJ mol^{-1}, and can hardly be used to discriminate between different reaction paths. In Scheme 4 the inserted methyl group is inserted in the bond toward the other methyl group. It could also be inserted in the other bond. We have looked at this possibility, but there was no appreciable difference. The transition state energies from **1** and **10** were 239(205) and 237(203) kJ mol^{-1}, respectively, when insertions were done to the other side. It should be noted that we were not able to find, in spite of considerable effort, the **2TS** transition state when using the MP2 method. As was the case for hydrogen and methyl group migrations on the ring, MP2 predicts a lower transition barrier for ring expansion than DFT does.

There are some notable differences in energy between the primary expansion products, **3**, **12** and **20**. The differences are in line with what could be expected from a qualitative reasoning. Ion **12** is lowest in energy, and here the formal positive charge is on a tertiary carbon. Ions **3** and **20** are not very different (but **3** has a slightly higher energy) and the formal charges are on secondary carbons. The higher energy of **3** can be rationalized when the energies of the various xylenium ions of Table 1 are considered. In each case the highest energy is observed when the proton is in *ipso*-position to the methyl group as it is in **3**. Also here, expansion via insertion away from the other methyl group has little effect. From the *o*-xylene ion **20** is obtained. *m*-Xylene produces an ion with energy 88(93) kJ mol^{-1} that, after a few hydrogen or methyl shifts, is converted into one of the species in Schemes 4 or 5.

There are three species in Schemes 4 and 5 that have been assigned a bicyclic character, i.e. **14**, **22** and **26**. In **14** and **22** it is seen that unless such a bicyclic structure is formed, the electron deficient C-atom is isolated between two methylene groups, —CH_2—CH^+—CH_2— [or —$CH(CH_3)$—CH^+—CH_2—]. By establishing a bridge structure the positive charge becomes distributed over a larger area, and this broader charge distribution evidently reduces the ion's energy more than the cost of creating a strained three-atom ring. The same argument does not apply for **26**. In this case the bicyclic structure has an isolated secondary cationic C-atom. The energy of **26** is very high, and among the non-transition states, it is only surpassed by **24**. At first sight there is nothing to distinguish **24** from **3**, **5**, **12** or **20**, but the energy is 50 to 80 kJ mol^{-1} higher than that of these ions. When the geometric structure is studied it becomes clear that the structure of **24** is highly strained. The sp^2 atoms should be parts of planar structures. This is not the case here. By going from **24** to **26**, an isolated cationic C-atom is created. In addition, the methyl group is axially oriented. The sp^2 hybridized C-atoms of **26** are, however, seen to be far less strained. Parts of the ion fit in with a planar system. A similar ring collapse (to a bicyclo[4.1.0]heptane skeleton) has been reported in the case of protonated cycloheptatriene.[18]

Schemes 4 and 5 show two different paths leading to the formation of an ethyl group. The path from **5** via **7** to **9** is the expected route, with **7** as a very shallow minimum. The path from **26** to **29** was unexpected. It is worth noting that the transition state energy of **28TS** is practically the same (actually 2 kJ mol^{-1} lower) as found for **8TS**. When **5** is transformed into **9** via **7** the reaction proceeds via 1,2- and 1,3-shifts that could be relatively facile. The reaction from **26** to **29** involves a C—C bond breaking. It was therefore somewhat unexpected that the transition state energy is actually slightly lower than **8TS**. When the geometric structure of **26** is studied more closely it becomes less surprising. The two C—C bonds of the quasi-cyclopropane ring are markedly different in length, and hence strength. The bond closest to the cationic carbon is 1.62 Å, a rather stretched and weakened single bond, whereas the other bond is only 1.44 Å, and thus has considerable double bond character. Analogously, an ethyl group formation could possibly take place also from **14**. The two three-ring bonds are here equally different. This reaction has not been investigated.

We have found a transition state, **30TS**, for eliminating ethene from **29**. The energy of **30TS** [273(240) kJ mol^{-1}] is the second highest in Schemes 4 and 5, but only 25 to

40 kJ mol^{-1} higher than the expansion transition states. Ion **9** is also an ethylbenzenium, but ethene elimination requires a hydrogen shift (facile) to the *ortho*-position first. A four-membered TS could then be crossed. We have not found this transition state, but expect it to have nearly the same energy as **30TS**. Scheme 5 also shows a different path for splitting off ethene. Ion **26** can give ethene directly via transition state **27TS**. The main difference from **28TS** is that here there is a 1,2-shift of one of the methyl hydrogens and formation of a formally primary carbocation. The energy connected with this one-step reaction is considerably higher than in the two-step process. It is 294(296) kJ mol^{-1}, compared with 273(240) for **30TS**.

Carbon and hydrogen atom scrambling

When we constructed Schemes 4 and 5 we kept track of the methyl C-atoms that entered the ring system by marking them (*, #, ¤). The energy barrier for actually splitting off an ethene molecule is higher than any of the other barriers. Hence all the isomerization reactions in Schemes 4 and 5, including ring re-contractions, are likely to have taken place several times before ethene formation. An extended scrambling of C- and H-atoms is therefore to be expected. Experimentally, an incomplete scrambling is observed.[1] The theoretical barrier for fragmentation could be too high. In addition, the fragmentation reaction is likely to have a high activation entropy. Entropy effects are not considered here.

Ring contraction

Ethene could also be eliminated from protonated xylenes via an initial ring contraction step. This is mechanistically shown for *ipso*-protonated *p*-xylene. A ring contraction of protonated *p*-xylene, **18**, could, according to common views, be expected to proceed as indicated by Fig. 2. Our computations did, however, indicate that the secondary carbenium ion in Fig. 2 is not stable, i.e. it does not correspond to a minimum on the potential energy surface of the system. Computations have shown that contraction of **18** leads to formation of a bicyclic species (bicyclo[3.1.0]hexane skeleton). Scheme 6 shows this. An impression of the geometry of the species **18**, **37TS** and **38** in the first reaction step in this scheme is obtained from Fig. 3, which is based on the precise atomic positions. Bouchoux *et al.* reported the formation of bicyclo[3.1.0]hexenyl ions in reactions between a 1,3-butadiene radical cation and acetylene.[19] Their existence was predicted by quantum chemical calculations.[20]

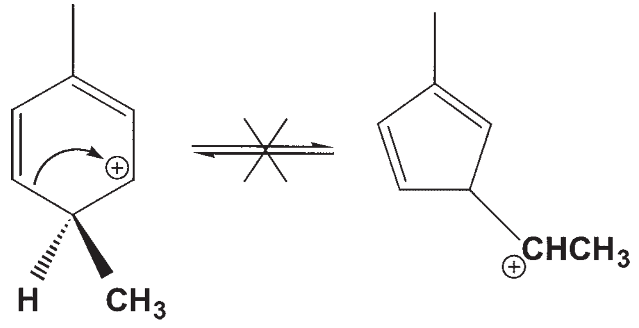


Figure 2. The reaction usually proposed for ring contraction

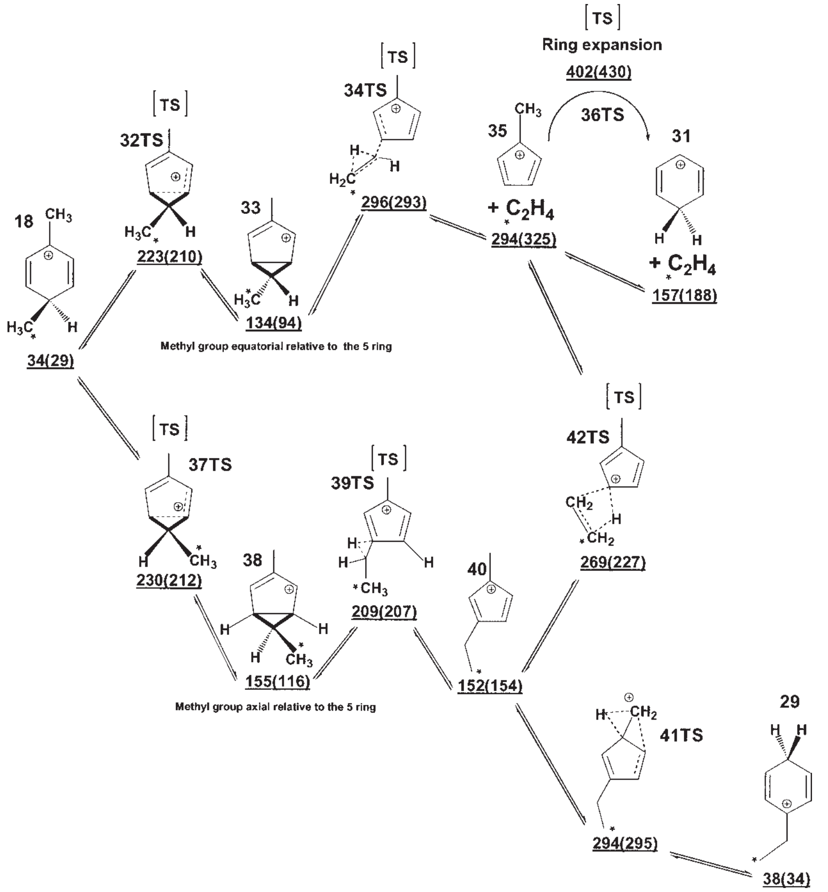
Other species that appear to be important intermediates and transition states in the reaction paths for elimination of ethene are also shown in the scheme and there are two different bicyclic structures. The methyl group of the three-membered ring can be in an equatorial (**33**) or axial (**38**) position on the cyclohexane ring. As expected, **33** with an equatorial methyl group has the lower energy. It is about 20 kJ mol^{-1} lower than that of **38** where there is an axial methyl group. The difference between the transition state (**32TS** and **37TS**) energies is in accord with the product energies and the Hammond principle. It is worth noting that the barriers for ring contraction are slightly lower than the expansion barriers discussed above.

The two conformers **33** and **38** can react further in two ways. They could split off ethene directly in a one-step reaction and form **35**, or isomerize and form an ethyl group on the cyclopentadienyl ring, species **40**. Presumably the products **35** and **40** could be formed by any of the precursors **33** or **38**. We have, however, not been able to find a transition state similar to **34TS**, forming **35**, from **38** nor a transition state, such as **39TS**, that forms **40** from **33**.

The transition state **34TS**, which involves the breaking of several bonds, has a very high energy, 296(293) kJ mol^{-1}. The energy is, however, only marginally higher than that of the final product, methylcyclopentadienyl cation, **35**, and ethene. The conversion of **33** into **35** plus ethene is a complex concerted reaction, but we have not been able to locate any stable intermediates (no minima on the potential energy surface, PES). The conversion of **38** into **40** is, as could be expected, a rather facile reaction with a barrier that is only 55 kJ mol^{-1}. The energy of **39TS** is lower than that of **37TS**.

The ethyl-methylcyclopentadienyl (**40**) cation can react along two different pathways. It can isomerize via a ring expansion and form an ethylbenzenium ion, **29**, or it can split off ethene and be transformed into **35**. The energy that is required for the two reactions was found to be the same. The high energy of **41TS** could perhaps be expected because the expansion proceeds via a formally primary cation.

The other reaction pathway warrants some further discussion. The transition state, **42TS**, does not have a very high energy, it is only 269(227) kJ mol^{-1}. This energy is, however, considerably lower than the energy of the final product, **35** plus ethene. We believe that the



Scheme 6. A ring contraction mechanism leading to ethyl group formation and ethene elimination from protonated *p*-xylene. To keep track of the methyl group carbon, it is marked with the symbol *

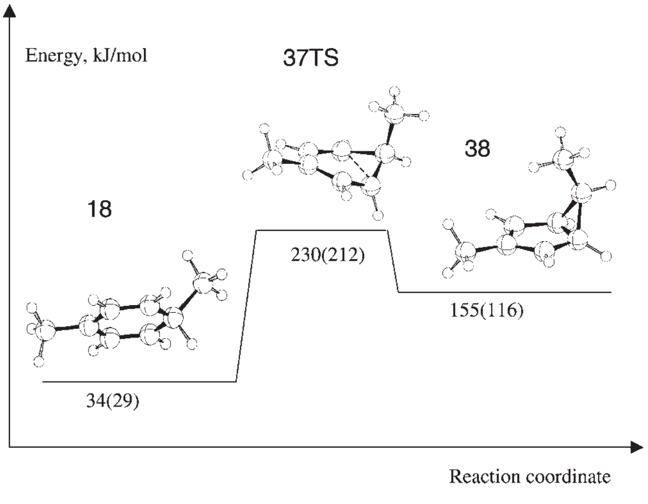


Figure 3. Structures and energies for ring contraction from an *ipso*-protonated *p*-xylene to a bicyclic five- and three-membered ring species. The dotted line indicates the C—C bond that forms during the reaction

cause for this anomaly is that there is a (formal) intermediate, which might be a π-bonded complex that has an energy below that of **42TS**. By separating the complex components, ethene and **35**, the energy becomes 294(325) kJ mol^{-1}. The IRC calculations showed that ethene was dispelled from the ion. Attempts to find the complex resulted in formation of ordinary chemical bonds to the ethene molecule.

H-atom exchange between a methyl group and ring H-atoms

The gas-phase isotopic labeling experiments carried out by Mormann and Kuck, where one of the methyl groups was fully deuterated (CD_3—C_6H_5—CH_3^+), show that there is exchange between the hydrogen atoms originally on the methyl groups and the ring hydrogen atoms.[1] This hydrogen exchange results in the formation of methane molecules that do not have the isotopic composition that would be expected for a simple loss of methane taking place by a combination of a methyl group and the *ipso*-positioned proton. The larger fraction of the eliminated methane did not show any hydrogen atom scrambling and had the atomic composition CD_3H or CH_4. However, 9% of the methane was found to have the composition CH_2D_2, and 6.8% to have the composition CH_3D.

We have found a transition state for hydrogen scrambling that is in accord with the observed scrambling between a methyl group and the ring. Figure 4 shows this transition state on an *ipso*-protonated *p*-xylene. We

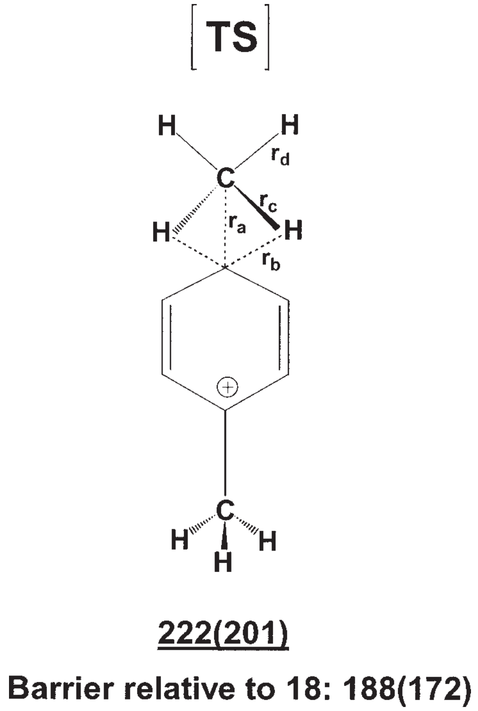


Figure 4. Schematic drawing of the transition state of the hydrogen exchange reaction on an *ipso*-protonated *p*-xylene

can see that in this transition state a methane molecule is almost completely formed. The C—C distance, $r_a = 1.948(1.862)$ Å, and the C—H bond lengths, $r_b = 1.722(1.664)$ Å, are so long that they show an almost free methane molecule, whereas the C_{methyl}—H bond lengths, $r_c = 1.113(1.114)$ Å and $r_d = 1.090(1.092)$ Å show that the hydrogen atoms are strongly bonded to the methyl group C-atom. The normal mode corresponding to the imaginary frequency shows that there is an exchange between the hydrogen atoms. The energy of the transition state is 222(201) kJ mol^{-1}, and it has a C_v symmetry.

We have not carried out a detailed study of the mechanism for methane elimination, but we have calculated the reaction energy for methane elimination from **18** at 0 K by the G3 method of Gaussian98, and found 241 kJ mol^{-1}. At 298 K this gives a reaction enthalpy of 247 kJ mol^{-1}. This value is 12 kJ mol^{-1} above the reported experimental value, 235 kJ mol^{-1}.[1] The energy change (ZPE corrected) for this reaction was also calculated at B3LYP and MP2 levels of theory, with the result 222(235) kJ mol^{-1}, corresponding to a reaction enthalpy of 228(242) kJ mol^{-1} at 298 K. The calculated reaction energy for splitting off a methane molecule is therefore somewhat higher than the barrier for hydrogen exchange between a methyl group and the ring. Hydrogen 1,2-shifts on the benzene ring are facile. The hydrogen, and respective deuterium, positions on the benzene ring thus be fully randomized. The calculations are therefore in full accord with the experimental result that there is exchange between the methyl groups and hydrogen atoms on the ring. Owing to the facile migration on the ring, there will also be exchange between the two methyl groups. The experimental results reported by Kuck and co-workers indicate that methane expulsion and hydrogen exchange take place at approximately equal rates.[1,21] The theoretical calculations lead to the same conclusion.

DISCUSSION

A conclusion to be drawn from the results presented above is that the system is very complex, and that definite conclusions about a precise reaction path are not warranted. Schemes 4–6 show that the barriers for the final elimination of an ethene molecule are higher than any other barriers, with a possible exception for the cost of expanding the cyclopentadienyl cation, **40**, to ethylbenzenium, **29**.

The calculations predict that the contraction of the benzenium ring, with formation of a bicyclo[3.1.0]hexane framework, **33** or **38**, requires less energy than a ring expansion to any of the compounds **3**, **12** or **20**. However, in general, the energies of the five-ring systems are higher than the expanded ring systems. The barriers for back reaction are therefore much lower, and the fraction of ions formed by ring contraction must be fairly low. The final barriers for eliminating ethene, or converting **40** into ethylbenzenium, are fairly high. The calculations therefore predict that if ethene is formed from xylenium ions, the formation has taken place via PMCH species. Furthermore, ethene formation through **33** or **38** would not be expected to lead to scrambling. This is borne out by Scheme 6.

In addition to exploring the chemistry of xylenium ions, this work has shown that when discussing the MTH reaction mechanism, ring expansion of alkylarenes should be taken into account. There is, however, a very important difference between the acid catalyzed MTH reaction and gas-phase arenium chemistry with isolated particles. The catalyst is also a proton acceptor, so neutral and more stable products (neutral arenes) can be obtained in one-step reactions. This lowering of product energies could also lead to lower barriers.

Supplementary material

Additional information containing all optimized geometries and absolute energies of the species that were treated in this work is available at the epoc website at http://www.wiley.com/epoc.

Acknowledgment

Thanks are due to the Norwegian Research Council for financial support through grants 135867/431 and 149326/

431, and a grant of computer time through the NOTUR project (accounts No. NN2147K and NN2878K).

REFERENCES

1. Mormann M, Kuck D. *Int. J. Mass. Spectrom.* 2002; **219**: 497–514.
2. Mormann M, Kuck D. *J. Mass. Spectrom.* 1999; **34**: 384–394.
3. Kuck D. *Int. J. Mass. Spectrom.* 2002; **213**: 101–144.
4. Kuck D. *Mass. Spectrom. Rev.* 1990; **9**: 583–630.
5. Chang CD. In *Shape-Selective Catalysis: Chemicals Synthesis and Hydrocarbon Processing*, Song C, Garces JM, Sugi Y (eds). ACS Symposium Series 738, ACS: Washington D.C., 2000.
6. Stöcker M. *Microporous Mesoporous Mater.* 1999; **29**: 3–48.
7. Haw JF, Song W, Marcus DM, Nicholas JB. *Acc. Chem. Res.* 2003; **36**: 317–326.
8. Arstad B, Nicholas JB, Haw JF. *J. Am. Chem. Soc*. 2004; **126**: 2991–3001.
9. Frisch MJ, Trucks GW, Schlegel HB, Scuseria MA, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck DK, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzales C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98, Revision A.11.* Gaussian: Pittsburgh, PA, 1998.
10. Gonzalez C, Schlegel HB. *J. Phys. Chem.* 1990; **94**: 5523–5527.
11. Devlin III JL, Wolf F, Taft RW, Hehre WJ. *J. Am. Chem. Soc.* 1976; **98**: 1990–1992.
12. Eckert-Maksić M, Klessinger M, Maksić ZB. *J. Phys. Org. Chem.* 1995; **8**: 435–441.
13. Eckert-Maksić M, Klessinger M, Maksić ZB. *Chem. Eur. J.* 1996; **2**: 1251–1257.
14. Kuck D. *Angew. Chem., Int. Ed. Engl.* 2000; **39**: 125–130.
15. NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/).
16. Cacace F, Crestoni ME, Fornarini S. *J. Am. Chem. Soc.* 1992; **114**: 6776–6784.
17. Büker HH, Grützmacher HF, Crestoni ME, Ricci A. *Int. J. Mass. Spectrom.* 1997; **160**: 167–181.
18. Salpin JY, Mormann M, Tortajada J, Nguyen MT, Kuck D. *Eur. J. Mass. Spectrom*. 2003; **9**: 361–376.
19. Bouchoux G, Yanez M, Mo O. *J. Phys. Chem. A* 2000; **104**: 5778–5786.
20. Bouchoux G, Yanez M, Mo O. *Int. J. Mass. Spectrom*. 1999; **185–187**: 241–251.
21. Kuck D. Schneider J, Grützmacher HF. *J. Chem. Soc., Perkin Trans. 2* 1985; **2**: 689–696.