Catalysis Letters Vol. 109, Nos. 1–2, June 2006 (© 2006)
DOI: 10.1007/s10562-006-0052-8

Intermediates in the methanol-to-hydrocarbons (MTH) reaction: a gas phase study of the unimolecular reactivity of multiply methylated benzenium cations

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Received 21 December 2005; accepted 5 January 2006

In order to reach a deeper insight into the reaction mechanism of the zeolite catalyzed methanol to hydrocarbons reaction (MTH), the proposed reaction intermediates, i.e., a series of multiply methyl-substituted benzenium ions has been generated in the gas phase by chemical ionization. The fragmentations of the corresponding long-lived (metastable) ions have been investigated. While expulsion of H_2 dominates for the lower homologues, elimination of methane dominates for the higher homologues, accompanied by increasing amounts $CH_3^{\bullet}$. Loss of larger fragments relevant to the MTH-reaction, in particular ethene, propene and even butene, is also observed in minor amounts. This latter finding is consistent with a proposed reaction cycle in the MTH reaction known as the *paring mechanism*, and the feasibility of this mechanism has thus been demonstrated. The metastable gas-phase ions studied here are considerably more energetic than those residing in a zeolite catalyst, but they were found to decompose with markedly higher selectivity towards alkenes as compared to those activated by collision-induced dissociation (CID).

KEY WORDS: gas phase ion chemistry; mass spectrometry; methylbenzene; methanol-to-hydrocarbons; zeolite; heptamethylbenzenium.

1. Introduction

Protonated zeolites have found widespread applications in several acid-catalyzed hydrocarbon transformation processes. Early research often invoked carbocationic species as intermediates in order to rationalize the observations made, but it is now generally accepted that zeolite acid strength is more in line with conventional acids rather than superacids, as there are only a few observations of persistent carbenium ions in zeolites. Recently, Bjørgen *et al.* [1,2] have shown that the tetramethylbenzenes and penta- and hexamethylbenzene are protonated on ring carbons when introduced into the wide-pore β-zeolite, whereas the lower methylbenzenes do not form such cations. The polymethylbenzenes form, upon protonation, species demonstrated to be key intermediates in several reactions catalyzed by acidic zeolites.

Isomerization of methyl-substituted benzenes by methyl shifts most likely proceeds via the corresponding methylbenzenium ions (so-called Pfeiffer/Wheland intermediates [3]). Transalkylation or disproportionation may also involve arenium cations, although mechanisms involving diphenylmethane-type intermediates are presently favored [3]. DFT/MP2-modeling performed by Arstad *et al.* [4] has indicated that polymethylbenzenium cations are energy minima on the potential energy surface during the methylation of methylbenzenes with methanol. This could also hold for other potential methylating agents. Also, mounting evidence pointing towards methylbenzenes as crucial intermediates in the reaction where methanol is converted into a mixture of hydrocarbons (MTH) has been collected over the last few years [5,6]. Increased insight into the specific features of the MTH-reaction mechanism has been the main motivation for the present work.

Our understanding of the mechanism of the MTH-reaction during steady state conversion has become greatly improved over the last decade, as the so-called *hydrocarbon pool* mechanism [7–10] has gained increasing acceptance. This is an indirect mechanism, believed to proceed via repeated methylations and subsequent alkene loss from organic reaction centers trapped within the zeolite voids. The exact chemical nature of the hydrocarbon pool is incompletely known and might vary with the reaction conditions and catalyst type, but polymethylbenzenes, and in particular the higher congeners, have been shown to function as such reaction centers [11–17]. The well-known induction period of the MTH-reaction, during which the degree of conversion increases to the steady state level, is not considered in the present report.

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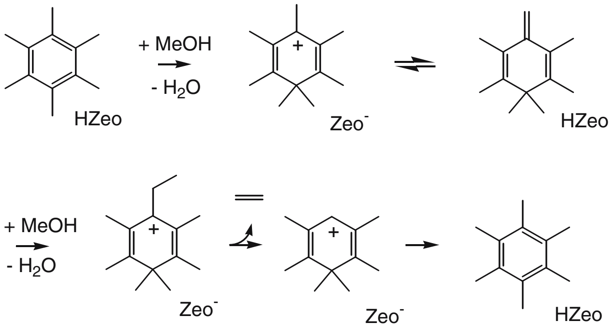


Scheme 1.

The manner in which alkenes are lost from the polymethylbenzene intermediates is a central issue in MTH-chemistry. Haw and co-workers [17,18] have suggested the mechanism outlined in Scheme 1. Deprotonation of a polymethylbenzenium species results in the formation of an exo-cyclic double bond, which can by methylated once or several times. The resulting alkyl groups will then be split off as alkenes, thereby regenerating a polymethylbenzene and completing a catalytic cycle. This multi-molecular mechanism type has been named *the side-chain methylation mechanism*.

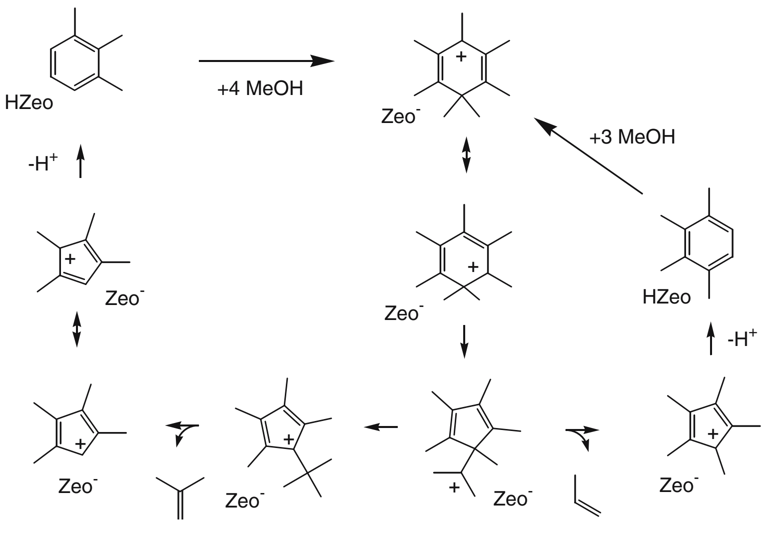
In parallel, ongoing work by Kolboe and co-workers [19–21] has indicated that a monomolecular mechanism might lead to alkene formation from polymethylbenzenium species. Extensive isotopic labeling experiments were carried out by Bjørgen *et al.* [20], and the results were in accordance with the pathway for alkene formation outlined in Scheme 2. A fairly complex series of ring contractions and/or expansions leads to the growth of higher alkyl groups, which are lost as alkenes. A similar reaction scheme was proposed by Sullivan *et al.* [22] in 1961 to explain the formation of aliphatics from hexamethylbenzene on a bifunctional catalyst. In line with the naming introduced by Sullivan *et al.* we shall designate all such monomolecular routes leading to alkene loss from polymethylbenzenium species as *the paring mechanism*, regardless of the specific elementary steps involved.

In order to further elucidate the role of multiply methyl-substituted benzenium ions in the MTH-reaction, we found it worthwhile to investigate their intrinsic reactivity in an environment free of the surrounding catalyst framework, that is, in the highly diluted gas phase of a mass spectrometer. Hence, a series of protonated or methylated polymethylbenzenes (Scheme 3) was investigated by use of mass-analyzed kinetic energy (MIKE) spectrometry, a well-established technique sampling relatively long-lived, "metastable" ions [23,24]. A number of reports on the gas-phase reactivity of protonated methylbenzenes already exist and have been reviewed [25–28]. Of particular relevance to the present study are those on metastable toluenium ions [29] and, more recently, *para*-xylenium [30,31] ions and protonated cycloheptatrienes [32], carried out besides those on various methyl-substituted α, ω-diphenylalkanes [33]. Also, Arstad *et al.* recently published a detailed theoretical study on xylenium ions [34]. The results reported here are compared with relevant literature data and discussed with respect to the mechanism of the MTH-reaction.

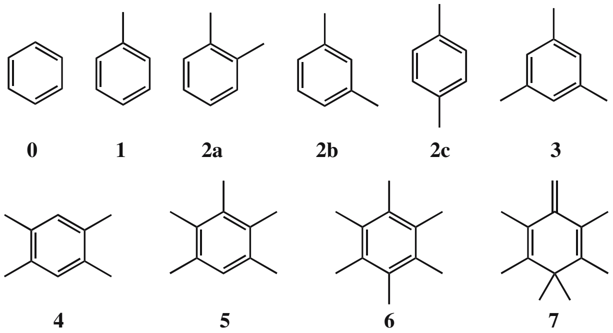
2. Experimental

2.1. Chemicals

Compounds **0–6** (Scheme 3) were commercially available, at purities >98%. Compound **7** (1,2,3,3,4,5-hexamethyl-6-methylene-1,4-cyclohexadiene, denoted HMMC) was synthesized as the end product of a Friedel-Craft alkylation of pentamethylbenzene with chloromethane. Details have been given previously [21].



Scheme 2.



Scheme 3.

2.2. Calculations

Thermochemical data were obtained for compound **7** and ions [**7** + H]$^+$ and [**7** + CH$_3$]$^+$ using the G3MP2 computational scheme as implemented in Gaussian 03 [35]. These species have C_s symmetry within this computational scheme.

2.3. Mass spectrometry

Mass spectra were recorded by use of either a Fisons Prospec-Q instrument, which is a hybrid mass spectrometer with EBEHQ configuration normally running at an acceleration voltage of 4 kV, or a Fisons Autospec instrument, which has an EBE configuration and runs at 8 kV. For chemical ionization (CI), a tight ion source was used to ensure sufficiently high-pressure conditions. Methane was used as the reagent gas in the protonation experiments, providing predominantly the proton donors CH_5^+ and $C_2H_5^+$ in approximately equal abundances. Methylation experiments were carried out by use of chloromethane as the reagent gas, which provides mainly the methyl donor $CH_3ClCH_3^+$ plus minute amounts of CH_3ClH^+. The precursor ion of interest was selected using the first two stages (EB). Ionic products from spontaneous decomposition in the field-free region following B (third field-free region) were recorded with an orthogonal detector positioned in the fourth field-free region, by scanning the second electric sector (MIKE spectrometry). The spectra obtained in this manner are entitled metastable ion (MI) decomposition spectra. In separate experiments collision-induced dissociation (CID) was achieved by bringing the selected precursor ions to collide with He in the third field-free region of the Autospec instrument. The He pressure inside the collision cell was set to attenuate the intensity of the precursor ion peak to ca. 50%. Relative abundances of fragment ions from metastable ion decomposition can in some cases be different from the relative peak heights reported in Tables 1, 2: (a) detector response generally decreases with the translational energy of an ion, which, however, is largely compensated by post-acceleration, (b) peak width and probability of detection strongly depends on translational energy release, and (c) there is always some unintended CID resulting from collisions with residual gas in the analyzer region; this effect is most important in cases where only few ions give rise to MI and significantly more pronounced in the Prospec-Q as compared to the Autospec instrument.

Table 1

MIKE spectra of protonated methylbenzenes. The numbers are relative peaks heights (%) normalized to the tallest peak in each spectrum. Estimated standard deviation is ±2%. For reasons explained in the ex perimental section these peak heights can be different from the relative ion abundances

		$-H_2$	$-CH_3$	$-CH_4$	$-C_2H_4$	$-C_3H_6$	$-C_4H_8$
Compound	*m/z*	−2	−15	−16	−28	−42	−56
Benzene (0)	79	100					
Toluene (1)	93	100		16			
o-Xylene (2a)	107	100	39	70	19	< 1	< 1
m-Xylene (2b)	107	100	40	71	20	< 1	< 1
p-Xylene (2c)	107	100	40	70	20	< 1	< 1
Mesitylene (3)	121	20	61	100	12	1	< 1
Durene (4)	135	55	50	100	6	2	1
PMBz (5)	149	71	60	100	15	3	1
HMBz (6)	163	54	100	68	6	13	2

3. Results

Compounds **0**–**7** (the numbering corresponds to the number of ring substituents) were all subjected to protonation and methylation, producing a wide series of polymethylbenzenium cations in the gas phase. Their MI spectra and CID spectra were recorded (figures 1–3).

3.1. MI spectra of [M + H]$^+$ ions (table 1)

The MI spectra of the protonated methylbenzenes [**0** + H]$^+$ to [**6** + H]$^+$ are summarized in Table 1. The fragmentations of long-lived benzenium, toluenium [29] and xylenium [30] ions have been investigated previously, whereas, to the best of our knowledge, the higher methylbenzenium ions have not yet been studied using mass spectrometry.

In the case of benzenium ions, $C_6H_7^+$ ([**0** + H]$^+$), only dehydrogenation is observed:

$$C_6H_7^+ \rightarrow C_6H_5^+ + H_2. \quad (1)$$

This reaction was reported in as early as 1967 [36,37] and studied in detail for metastable ions in 1974 [38,39]. For the next higher congeners, H_2 loss is also a significant process, but it practically vanishes beyond protonated mesitylene. In addition to H_2 loss, elimination of CH_4 and C_2H_4 is observed for all [M + H]$^+$ ions beyond protonated toluene. Moreover, some loss of $CH_3^\bullet$ occurs in varying relative amounts, but the major contribution to the corresponding [M-15]$^+$ peaks has to be traced to the naturally occurring isotopomer of the molecular radical cations, [$^{13}C_1$]-M$^{+\cdot}$ (see below).

Table 2

MIKE spectra of adducts between H^+/CH_3^+ and methylbenzenes (Prospec data). The numbers are relative peaks heights normalized to the tallest peak in each spectrum. For reasons explained in the experimental section these peak heights can in some instances be quite different from the relative abundances. An asterik indicates that overlap with a broad and more intense neighboring peak does not allow for precise quantification of the signal. Some likely fragments are displayed. Other possibilities may exist, in particular for the larger mass losses. Compared to the Autospec data (Table 1) there are more low mass fragment ions in these spectra, due to the smaller size of the Prospec which results in higher analyzer pressure under CI conditions giving significant unwanted CID. The smaller size also leads to shorter metastable ion lifetimes and thereby higher internal energies

			$-H_2$	$-CH_3$	$-CH_4$	$-C_2H_3$	$-C_2H_4$	$-C_2H_6$	$-C_2H_7$ or $-CH_4-CH_3$		$-C_3H_4$	$-C_3H_6$	$-C_3H_8$ or $-C_2H_4-CH_4$	$-C_3H_{10}$ or $-C_2H_6-CH_4$	
Compound		m/z	−2	−15	−16	−27	−28	−30	−31	−32	−40	−42	−44	46	−47
Benzene (0)	H^+	79	100			11[a]	13[a]				5[a]				
	CH_3^+	93	100		33		10					7			
Toluene (1)	H^+	93	100		44		11	5				8			
	CH_3^+	107	39		100		19	10				10	6		
o-Xylene (2a)	H^+	107	35		100		11	8				7	5		
	CH_3^+	121			100		14	20				13	12		
p-Xylene (2c)	H^+	107	21		100		11	6				8	*		
	CH_3^+	121	6		100		16	17				13	12		
Mesitylene (3)	H^+	121	6		100		10	13				9	8		
	CH_3^+	135		10	100		17	11				5	7		
Durene (4)	H^+	135		10	100		7	12				4	7		
	CH_3^+	149		36	100		14	19[b]		*		5	6		
PMBz (5)	H^+	149		27	100		10	16[b]		*		5	5		
	CH_3^+	163		100	100		19	30[b]		*		7		8[b]	
HMBz (6)	H^+	163		100	100		14	28[b]		*		10		9[b]	
	CH_3^+	177		100	33		27	18[b]		*		18		7[b]	
HMMC (7)	H^+	177		100	13		14	< 5	9			40			
	CH_3^+	191					100					4			

			$-C_4H_6$	$-C_4H_8$ or $-C_2H_4-C_2H_4$	$-C_4H_{10}$				$-C_5H_{10}$	$-C_5H_{12}$								
Compound		m/z	−54	−56	−58	−60	−66	−68	−70	−72	−80	−82	−84	−86	−94	−96	−98	−100
Benzene (0)	H^+	79																
	CH_3^+	93	4															
Toluene (1)	H^+	93	5															
	CH_3^+	107	*	7				4										
o-Xylene (2a)	H^+	107	*	4			*	3										
	CH_3^+	121		7	*			*	5		*	4						
p-Xylene (2c)	H^+	107	*	4			*	3										
	CH_3^+	121		5	*			*	4		*	3						
Mesitylene (3)	H^+	121		3	*			*	2		*	2						
	CH_3^+	135		3	4				2			*	1		*	1		
Durene (4)	H^+	135		4	4				1			*	1		*	1		
	CH_3^+	149		*	6				*	3			2				2	
PMBz (5)	H^+	149		*	5				*	2			1				1	
	CH_3^+	163		*	5				*	5			1	2			1	
HMBz (6)	H^+	163		5	6				*	7			*	3			2	
	CH_3^+	177		8		5			*	4			*	4			*	2
HMMC (7)	H^+	177		33														
	CH_3^+	191		4														

[a] The relative areas of the peaks resulting from ethene and vinyl losses are around 10:1. Some CID is inferred.

[b] The peak is composite, making it difficult to quantify the relative contribution from two neighboring peaks.

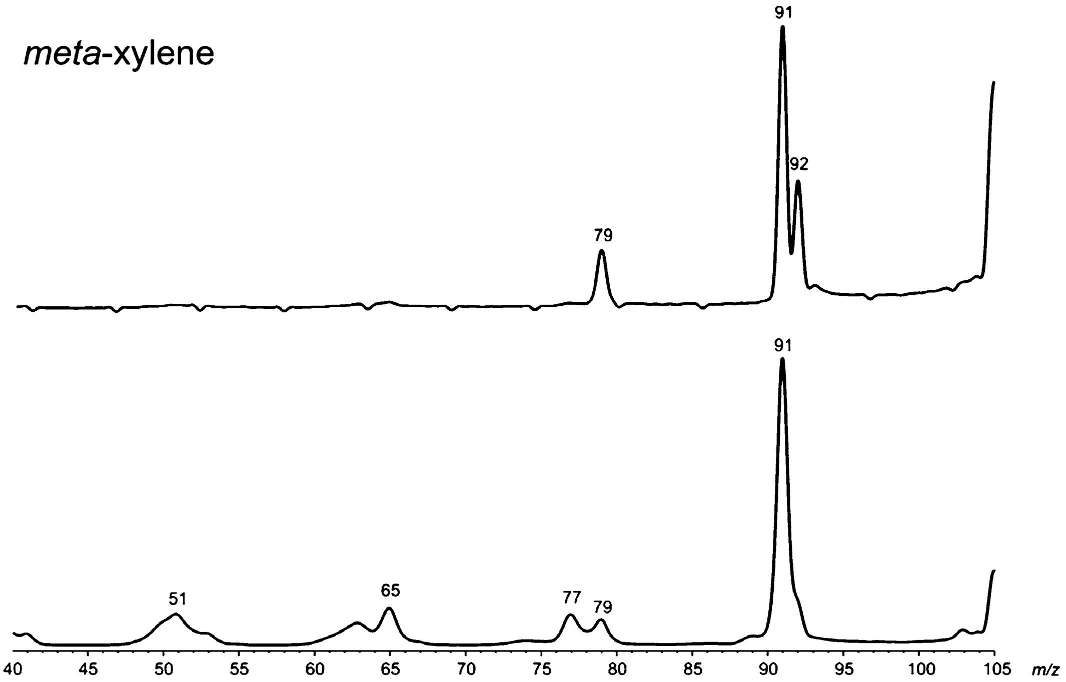


Figure 1. MI spectrum (top) and CID spectrum (bottom) of protonated meta-xylene [**2b** + H]$^+$.

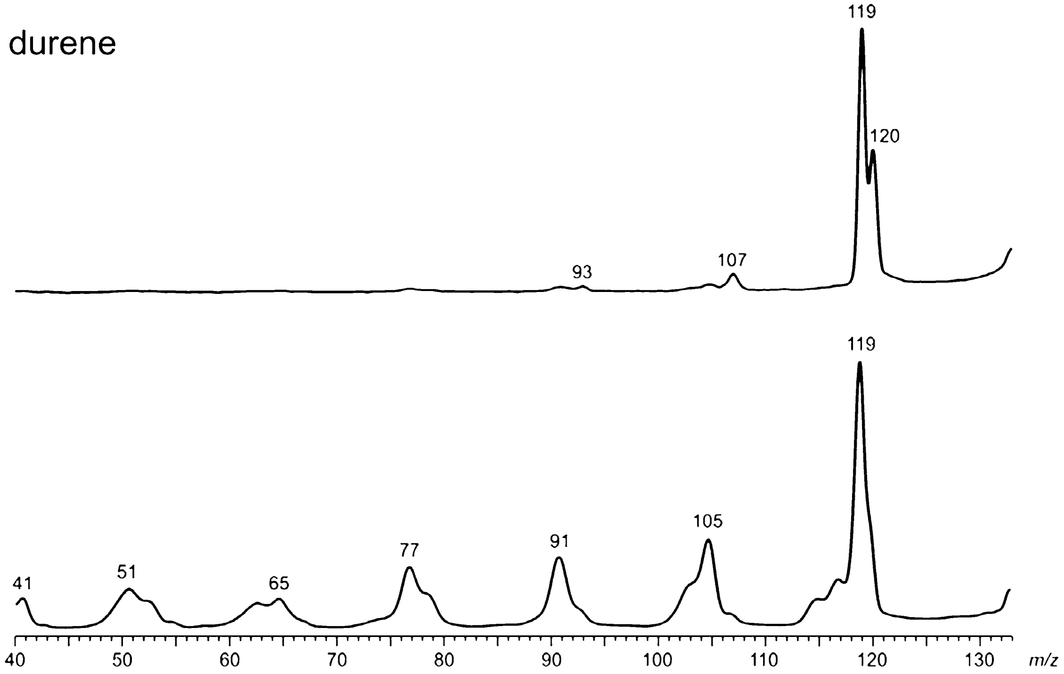


Figure 2. MI spectrum (top) and CID spectrum (bottom) of protonated durene [**4** + H]$^+$.

Protonated toluene is an intermediate case, expelling only methane in addition to dihydrogen. Most interestingly, there is an obvious tendency for increased alkene loss with increasing number of methyl groups in the [M + H]$^+$ ions. Even more noticeable, larger congeners eliminate also propene and even butene, the former reaction even overtaking ethene loss for protonated hexamethylbenzene, [**6** + H]$^+$. These clear trends in reactivity will be discussed in Section 4. It is also noted that the xylenium ions generated from the three isomeric xylenes give rise to identical MI spectra, reflecting that the three constitutional isomers ions have similarly easy access to the same regions of their common potential energy surface, in accordance with quantum chemical calculations [34]. Thus, it can be safely assumed that the MI spectrum of the

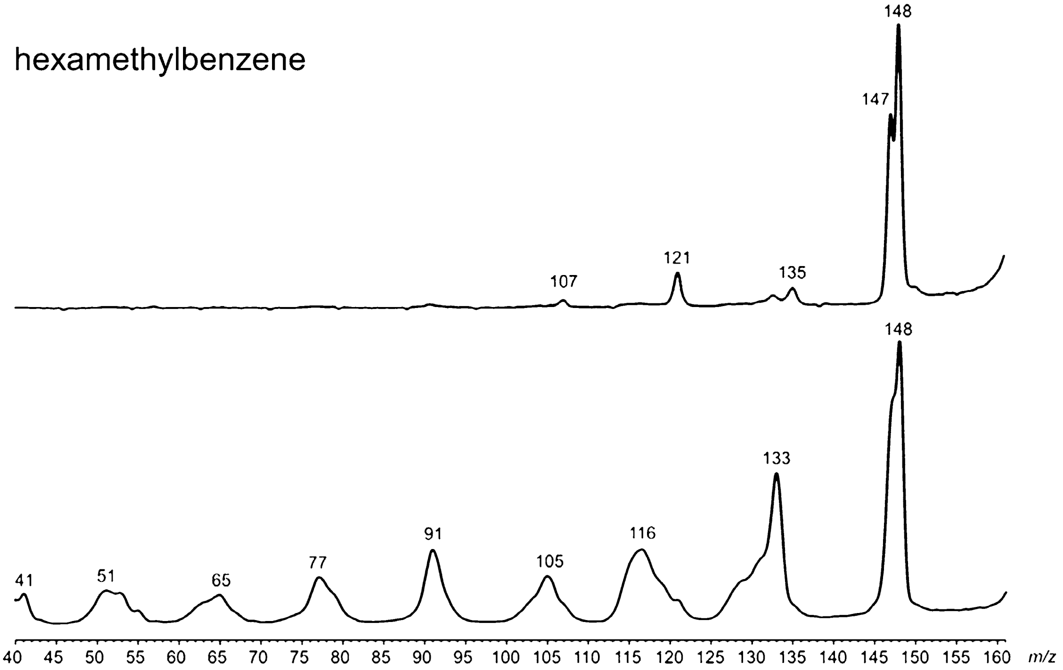


Figure 3. MI spectrum (top) and CID spectrum (bottom) of protonated hexamethylbenzene [**6** + H]$^+$.

tetramethylbenzenium ions [**4** + H]$^+$, generated from durene in the present study, is also representative for the MI spectra of protonated isodurene and 1,2,3,4-tetramethylbenzene (prehnitene).

Besides the [M + H]$^+$ ions formed by protonation, the presence of radical cations in the ion source could be inferred from the CI(CH$_4$) mass spectra. As a consequence, all of the [M + H]$^+$ ion beams contain fractions of the corresponding molecular radical cations [^{13}C$_1$]-M$^{+\bullet}$. Loss of ^{12}CH$_3^\bullet$ and, in minor amounts, ^{13}CH$_3^\bullet$ from the latter ions gives rise to fragment ions that are isobaric with the [M + H-CH$_3$]$^{+\bullet}$ and [M + H-CH$_4$]$^+$ fragments, respectively, thus obscuring the decomposition behavior of the [M + H]$^+$ ions of interest. However, separate determination of the MI spectra of the [^{12}C$_1$]-M$^{+\bullet}$ allowed us to assess the contributions originating from the [^{13}C$_1$]-M$^{+\bullet}$ ions and ascertain that, in fact, the protonated methylbenzenium ions lose a methyl radical along with methane. Interestingly, the abundance ratios of {[M + H - CH$_3$]$^{+\bullet}$}/{[M + H - CH$_4$]$^+$} are small (<0.05) for protonated toluene, [**1** + H]$^+$, and increase markedly up to protonated hexamethylbenzene, [**6** + H]$^+$, for which a ratio of 0.25 ± 0.10 has been determined. The occurrence of the methyl loss from the higher congeners is corroborated by the finding that the MI spectra of the corresponding [M + CH$_3$]$^+$ adduct ions (see Section 3.3) generated by methyl cationization exhibit the peaks for CH$_3^{\cdot}$ and CH$_4$ loss in similar ratios, although the contributions due to ion beam contamination is excluded there. In fact, the same tendency for increasing CH$_3^{\cdot}$ loss the with increasing number of methyl groups is observed with the [M + CH$_3$]$^+$ ions as well.

3.2. Collision-induced dissociation (CID) spectra of [M + H]$^+$ ions

Upon introduction of He into the collision chamber, increased fragmentation of the [M + H]$^+$ ions was observed, both with regard to the total abundance of fragment ions and the nature of the fragments formed. A typical feature in the CID spectra is the tendency to form smaller ions. Although we see some homolytic bond cleavage, the majority of fragment ions are even-electron species. In the low mass range, the ions C$_3$H$_3$$^+$, C$_4H_3$$^+$, C$_5H_3$$^+$ and C$_5$H$_5$$^+$ increase in significance at the expense of most of the fragments dominating the MI spectra, in particular the olefin expulsion. However, elimination of CH$_4$ is clearly enhanced relative to the loss of CH$_3^{\cdot}$ and, in the case of the lower congeners, H$_2$.

3.3. Metastable ion (MI) spectra of [M + CH$_3$]$^+$ ions (Table 2)

By employing both protonation and methylation of the respective congeners, it is possible to produce – at least nominally – the same multiply methyl-substituted benzenium ion from different starting materials. Adducts with methyl cations were produced by reaction of CH$_3$ClCH$_3$$^+$ with a given methylbenzene and compared to the next higher protonated congener. Thus, methylation of toluene and protonation of a xylene will most probably yield similar mixtures of (mainly) tautomeric arenium ions. Admittedly, the ions' internal energy distribution will depend on the mode of their formation, and so will the relative amounts of the isomeric structures. In all cases we observe quite similar fragmentation behavior between isomeric metastable ions created by protonation of a methylbenzene or methylation of the lower homologue. Minor intensity variations were observed – probably due to different energy contents – but this does not disturb the generally close similarity of the fragmentation pattern.

3.4. MI spectra of $C_{13}H_{21}^+$ (heptamethylbenzenium) ion (Table 2)

Protonation of HMMC leads to the heptamethylbenzenium ion [**7** + H]$^+$, for which no proton is likely to be bonded directly to the aromatic ring. Instead, there are two methyl groups bonded to one of the ring carbon atoms. This distinctive structural feature is clearly reflected in the observed fragmentation pattern since, by contrast to the lower congeners, methyl loss is the by far dominating fragmentation channel. We also notice the corresponding fragment ion with *m/z* 162 to be a major component in the ion source spectrum. There is also a clearly enhanced tendency for loss of alkenes from the parent ion, evident from major peaks at *m/z* 149, 135 and 121 indicating the elimination of C_2H_4, C_3H_6 and C_4H_8 (or/and twice C_2H_4) in a ratio of ca. 2:5:4.

3.5. MI spectra of the $C_{14}H_{23}^+$ ion [7 + CH_3]$^+$ (Table 2)

Methylation of HMMC is likely to occur mainly at the exocyclic double bond, resulting in an ion containing an ethyl group. Hence, the [**7** + CH_3]$^+$ ion has an initial structure somewhat different from the previously described ions. Loss of the ethyl group in the form of ethene is the principal feature of the fragmentation pattern, giving rise to an ion with *m/z* 163. Also, two minor peaks are seen at *m/z* 149 (loss of C_3H_6) and 135 (loss of C_4H_8). These are the only fragmentation reactions observed for [**7** + CH_3]$^+$ ion; interestingly, loss of methane or methyl is found to be insignificant for this ion.

4. Discussion

4.1. Internal energy of the metastable ions

The internal energy distribution of the reacting ions is not known and it is evident that thermodynamic equilibrium is not attained in the low-pressure plasma of the ion source. Therefore, it is likely that the ions leaving the ion source have not experienced many thermalizing collisions with neutral molecules. However, the dynamics of the processes in which [M + H]$^+$ and [M + CH_3]$^+$ ions are formed determine how much of the available energy that ends up as internal energy of these arenium ions. Proton transfer is considered to be efficient in bringing about of 80% the enthalpy released into the [M + H]$^+$ ion [40–44], so we assume that a large fraction of the difference in proton affinity between the methylbenzene (M) and the corresponding base of the protonating cation, i.e., methane or ethane, is transferred along with the proton:

$$CH_5^+ + M \rightarrow [M + H]^+ + CH_4 \tag{2}$$

$$C_2H_5^+ + M \rightarrow [M + H]^+ + C_2H_4. \tag{3}$$

There is also possibility for protonation directly by $CH_4^{+\cdot}$, which has the potential for bringing even more energy into the [M + H]$^+$ ions. With regard to the methylation process, less is known about energy deposition during methyl cation transfer:

$$CH_3ClCH_3^+ + M \rightarrow [M + CH_3]^+ + CH_3Cl. \tag{4}$$

Since it is likely that a straightforward S_N2 type mechanism is in operation, it is assumed that also here a majority of the available energy will end up in the ionic product. Table 3 lists the enthalpy changes for both proton transfer (PT) and methyl cation transfer (MT). It is noticed that for the lower homologues the methyl cation transfer energy lies in-between the two proton-transfer enthalpies, whereas the enthalpy of the methyl cation transfer is closer to the lowest proton-transfer

Table 3
Thermochemical data (kJ mol^{-1})

Compound [M]	ΔH_f° [M]	IE [M]	PA [M]	ΔH_f° [MH$^+$]	ΔH°, PT[a]	ΔH°, MT[b]
Benzene (**0**)	83	892	750	863	199, 70	112
Toluene (**1**)	50	852	784	796	233, 104	122
o-Xylene (**2a**)	19	826	796	753	245, 116	165
p-Xylene (**2c**)	18	815	794	754	243, 116	165
Mesitylene (**3**)	−16	811	836	678	285, 156	169
Durene[c] (**4**)	−43	818	846	641	295, 166	171
Pentamethylbenzene (**5**)	−67	765	851	612	300, 171	166
Hexamethylbenzene (**6**)	−77	758	861	592	310, 181	178
HMMC (**7**)	(−5)		(955)	(570)	(404, 275)	
CH_4	−75		551	904		
C_2H_4	52		680	902		
$CH_3ClCH_3^+$	743					
CH_3Cl	-82	1087				
CH_3	146	950				
$C_7H_7^+$ (benzylium)	900					
$C_7H_7^+$ (tropylium)	850					
$C_6H_5^+$	1149					
$C_5H_5^+$ (vinylcyclopropenyl)	1082[d]					
C_2H_6	−84					
C_3H_4	20					
Cl	121					

Data taken from NIST web page, those in parentheses are quantum chemical data obtained at the G3MP2 level of theory.

[a] STP enthalpy change for proton transfer to compound from methonium ion, CH_5^+ (first entry) and $C_2H_5^+$ (second entry).

[b] STP enthalpy change for methyl cation transfer to compound from dimethylchloronium ion, $CH_3ClCH_3^+$.

[c] Data for the 1,2,3,5-tetramethylbenzene isomer was used.

[d] *Ab initio* estimate from M.N. Glukhovtsev, R.D. Bach and S. Laiter *J. Phys. Chem.* 1996, **100**, 10952–10955.

enthalpy for the higher homologues. This indicates a broader, possibly bimodal, distribution for proton transfer.

However, it is important to realize that most of the energetic ions decompose already before leaving the ion source. The metastable ions studied here are by far lower in energy, and therefore closer to the fragmentation thresholds.

4.2. Thermochemistry

Dehydrogenation of protonated benzene (equation 1) has been reported to occur with negligible translational energy release [38]. Consequently, there is no reverse barrier, as confirmed by in MP2 calculations [45]. The calculated forward barrier of 294 kJ mol^{-1} is in good agreement with the experimental thermochemical minimum of 272 kJ mol^{-1}. The absence of a reverse barrier is in perfect compliance with the fact that LUMO of the phenyl cation has the character of an empty *p*-orbital that points out in a radial orientation from the periphery of the ring and, as a result, strong σ-electron accepting properties. The benzenium ion corresponds to a side-on adduct of the phenyl cation and H_2 having C_{2v} symmetry [46], and H_2 loss proceeds with monotonically increasing potential energy towards the dissociation limit. Isolable arenium ions are known, and the benzenium ion itself, $C_6H_7^+$, has been inferred from NMR spectroscopy of superacidic solutions [47] and on the basis of X-ray crystallography [48].

A detailed thermochemical analysis for the higher homologue $C_7H_9^+$ is instructive [49–51] but, unfortunately, complete reaction data for the larger ions are not available. For $C_7H_9^+$ ions the following thermochemical requirements are valid:

$$C_7H_9^+ \rightarrow C_7H_7^+ + H_2 \quad \Delta H^\circ = 54^\circ \mathrm{kJ\,mol^{-1}} \qquad (5)$$

$$C_7H_9^+ \rightarrow C_6H_5^+ + CH_4 \quad \Delta H^\circ = 278^\circ \mathrm{kJ\,mol^{-1}} \qquad (6)$$

$$C_7H_9^+ \rightarrow C_6H_6^{+\bullet} + CH_3^\bullet \quad \Delta H^\circ = 325^\circ \mathrm{kJ\,mol^{-1}} \qquad (7)$$

$$C_7H_9^+ \rightarrow C_5H_5^+ + C_2H_4 \quad \Delta H^\circ = 338^\circ \mathrm{kJ\,mol^{-1}}. \qquad (8)$$

It has been suggested that formation of $C_7H_7^+$ is accompanied by ring expansion although it is also consistent with a 1,2-H_2 loss from the *ipso* protonated isomer [29,50]. In the former case the fragmentation gives the tropylium ion and is endothermic by 54 kJ mol^{-1}, whereas in the latter case, the benzyl cation is formed requiring + 104 kJ mol^{-1}. However, irrespective of the structure of the $C_7H_7^+$ fragment formed, there is a significant reverse barrier to the reaction [29,38,50]. The methane loss reaction has been reported and used as a definite proof for skeletal rearrangement of the [**1** + H]$^+$ ions [25,27,29]. Starting from the *ipso*-protonated isomer a mechanism that parallels the H_2 loss from benzenium (see above) can be envisaged. It is known that a major fraction of the methane lost includes a ring carbon, as shown by ^{13}C and D labeling [25]. In fact, ca. 40% of the ions undergoes a fast and essentially reversible ring expansion/contraction, whereas the other fraction of ions suffers only slow and incomplete hydrogen exchange. Thus, the total of metastable $C_7H_9^+$ ions of the [**1** + H]$^+$ type suffer "composite scrambling" [27]. In spite of its high endothermicity, elimination of CH_4 can compete with the expulsion of H_2 because of the large activation barrier of the latter. By contrast to these reactions and in line with its even higher energy demand, elimination of C_2H_4, which would necessarily require a ring carbon atom, is not at all observed as a unimolecular fragmentation but only upon high-energy collision. $CH_3^{\cdot}$ loss from the [**1** + H]$^+$ ions is slightly less endothermic than C_2H_4 loss and only a very inferior unimolecular process in these lower methylbenzenes ions. It involves a homolytic bond cleavage and represents a violation of the "even electron rule". As we have seen, compared to elimination of H_2 and CH_4, the loss of $CH_3^{\cdot}$ becomes an increasingly favorable fragmentation channel for the higher methylbenzenium ions, and this "forbidden" process even overtakes the methane loss in the case of the heptamethylbenzenium ion [**7** + H]$^+$.

A reaction scheme consistent with the observed fragmentation behavior of the toluenium ions [**1** + H]$^+$ was also proposed for the xylenium ions [**2** + H]$^+$ [26]. In the latter ions, extensive (though somewhat reduced as compared to [**1** + H]$^+$) isomerization takes place prior to decomposition, probably again including ring expansion/contraction. Detailed B3LYP and MP2 calculations by Arstad *et al.* corroborated these conclusions [34].

4.3. Reactivity trends with increasing size and complexity of the methylbenzenium ions

Experimental reports concerning the reactions of methylbenzenes in a zeolitic environment have shown that their reactivity depends on the number of methyl substituents. Arstad and Kolboe [11] have demonstrated that HMBz (or the ionic counterpart) decomposes much more rapidly than the tri-, tetra-, and pentamethylbenzene (PMBz) congeners after having been synthesized inside the cages of the H-SAPO-34 zeotype catalyst. Moreover, Song *et al.* [15] have suggested that the ethene/propene ratio in the product stream depends on the degree of methyl substitution on the benzene rings located in the catalyst pores; the lower homologues mainly yielding ethene and *vice versa*. It is therefore necessary to assess any trends in the gas phase reactivity of the ions studied here. When analyzing the results displayed in Tables 1, 2, it must be considered that the data are normalized with respect to the largest peak by peak heights and not by peak area. The following points can be made:

1. The tendency for methane loss increases relative to dihydrogen loss with increasing number (n) of methyl groups in the range for $n \leq 6$.
2. For $n = 6$ and 7, methyl loss also increases relative to dihydrogen loss and apparently even the methane loss, reflecting the lower ionization energy of the higher methylbenzene and, in the case of ions [**7** + H]$^+$, the absence of hydrogen atoms bonded directly to the ring, which is a prerequisite for methane loss. However, the apparent overtaking of the methane by methyl loss is mainly due to [$^{13}C_1$]-$M^{\bullet +}$ contributions.
3. The relative amount of alkene loss decreases slightly in the range $3 \leq n \leq 4$ but increases again for $n \geq 5$.
4. The data do show an increase in the [propene]:[ethane] ratio with the number of methyl groups, although this trend is not perfect.
5. Butene loss (being much more likely than 2-fold ethene loss) increases in relative abundance with increasing n.
6. For ions [**7** + CH_3]$^+$, alkene loss (C_2H_4 predominating, and C_3H_6 and C_4H_8) is the only type of fragmentation observed.

The elimination of ethene is a well-known reaction for ethyl-substituted benzenium ions [25,32]. Arstad *et al.* have shown that the presence of a substituent larger than methyl (i.e., ethyl) results in a significant lowering of the barriers for propene and butene loss compared to species with methyl substituents exclusively [52]. This may be rationalized by considering that the presence of an ethyl group allows transition states involving secondary carbenium ion-like structures, rather than formally primary carbenium ion-like structures.

4.4. Bearings on MTH-chemistry

As stated in the Introduction, the unimolecular reactivity of multiply methyl-substituted benzenium ions is likely of relevance to the mechanism of hydrocarbon formation from methanol in acidic zeolites. There are, however, two factors that must be taken into account at this point before attempting to draw firm conclusions. First, the validity of a comparison of the present set of results to the reactions actually occurring within the zeolite pores should be considered. In addition to any effects caused by pore size limitations and/or the electrostatic field imposed by a surrounding zeolite on potential monomolecular ion reactions, it is conceivable that the zeolite itself is a vital participant in the reactions leading to alkene loss from polymethylbenzenium ions. For instance, it has been shown, using theoretical methods, that alkyl groups may be lost from benzenium ions in E2-type eliminations, wherein a zeolitic oxygen serves as the base [53]. If the interaction of the organic cations and the zeolite wall is essential for alkene loss, or if the mechanism outlined in Scheme 1 is prevalent, the current data would be of more indirect relevance to MTH-chemistry. This reservation does, however, not preclude us from reaching our initial goal, which is to evaluate to what extent the unimolecular reactivity of the polymethylbenzenium ions is compatible with what is otherwise known about the MTH-reaction.

Second (and less decisive), gas-phase molecules and ions made by the processes described here are by far higher in internal energy than the corresponding ions within a zeolite cavity. A precise temperature cannot be given since the metastable ions are not a canonical ensemble, but the effect is substantial. Furthermore, interaction with surrounding molecules and the zeolite framework will speed up dissipation of the energy. For this reason the ions in zeolites, once formed, will give rise to fewer reactions, favoring those of lowest critical energy.

The present set of data unequivocally demonstrates that alkenes may be split off from protonated "polymethylbenzenes" in strictly unimolecular reactions, which is the expected outcome if the paring mechanism, as outlined in the introduction, is operative. Thus, it has been demonstrated that the paring mechanism is indeed viable and not an intrinsically impossible. However, for all ions studied here (except methylated HMMC, see above) methane or dihydrogen losses are the predominating fragmentation channels, a feature that is different from efficient production of ethene and higher hydrocarbons over the zeolite. Moreover, the experimental data and the thermochemical considerations show that methane, dihydrogen, and possibly even methyl loss are the least energy demanding processes of those observed. If these observations are pursued, two interesting implications for MTH-chemistry arise.

First, the losses of dihydrogen and methane most likely involve the removal of two substituents in geminal positions on the ring. At least in the latter case, the resulting fragment ions very likely is a substituted phenyl cation, a highly reactive species consisting of a six-membered ring that lacks a hydrogen or substituent at one of the ring carbons. Such species are usually not considered to play a prominent role in the MTH-reaction. If present in a zeolite, they will display great reactivity, possibly serving as powerful hydride abstractors, or undergo intramolecular rearrangements or bond formation directly with the zeolite walls.

Second, the increasing loss of methyl radicals observed for the higher congeners, in particular, merits a short discussion. Free radicals were suggested to participate in the MTH-reaction by Zatorski and Kryzyzanowski [54] as early as in 1978. Clarke *et al.* performed ESR experiments showing that free radicals may be present when dimethylether (which is formed from methanol during the MTH-reaction) is converted over zeolite catalysts, and it was suggested that dimethylether could be a source of methyl radicals [55]. However, it has been concluded that NO does not act as a radical scavenger during methanol conversion [56]. Also, the ESR-signals are quenched by the presence of methanol [57], and the present consensus is against a radical mechanism [58]. Even so, when Kolboe recorded the ESR signals throughout the induction period over a ZSM-5 catalyst, during which the hydrocarbon pool is built up within the zeolite voids and appreciable activity is reached, it was found that when the methanol feed was stopped, a clearly detectable ESR signal due to organic free radicals appeared [57]. In light of the present data, it appears reasonable to assume that these ESR signals were caused by the loss of methyl radicals from hydrocarbon pool species (polymethylbenzenes) retained inside the catalyst pores after the methanol feed had been stopped.

5. Conclusions

The gas-phase reactivity of a series of mono-, di- and multiply methyl-substituted benzenium ions has been investigated using mass spectrometry. These ions have a characteristic fragmentation behavior which partially includes preceding deep-seated skeletal rearrangement processes. The initial scope of the study has been to evaluate the *paring mechanism*, which hypothesizes that monomolecular alkene loss from "polymethylbenzenium" ions is an important reaction in the zeolite-catalyzed methanol-to-hydrocarbons (MTH) reaction system. Loss of ethene, propene and even butene is found to occur especially for the higher congeners, and the feasibility of the paring mechanism has thus been demonstrated, without ignoring that a direct comparison between mass spectrometric data and results from catalytic studies is complicated by the differences in internal energy and environmental factors.

Acknowledgments

Thanks are due to the Norwegian Research Council for a grant of computer time through the NOTUR project (account number NN2878K) and to Dr. Bjørnar Arstad for valuable discussions concerning quantum chemical data.

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