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Theoretical Study of Ethylbenzenium Ions: The Mechanism for Splitting Off Ethene, and the Formation of a π Complex of Ethene and the Benzenium Ion

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Structures and energies of protonated ethylbenzene and 2,6-dimethylethylbenzene have been studied by quantum chemical calculations. The main goal is to study the mechanism for splitting off ethene from protonated ethylbenzene. Data are reported for the four ethylbenzenium isomers arising depending on the position of the proton on the benzene ring: a π complex where ethene is weakly bonded to a benzenium ion and two transition states connected with the cleavage of the ethylbenzenium ion. The larger part of the data that are reported has been obtained at the B3LYP/cc-pVTZ level of theory. Energies obtained by the Gaussian-3 G3B3 composite method are also given. Computations have also been carried out at the MP2/6−311++G(d,p) level of theory. The calculated results can be reconciled with published experimental observations, and they give information about the reaction system that is not obtained by experimental techniques.

Introduction

Protonated species are essential parts of the reactions occurring in acidic environments, that is, acidic catalysis. Protonated species are easily made in superacidic media, and they have been studied by a variety of methods which include NMR spectroscopy and mass spectrometric techniques. Mass spectrometry has proved useful to study fragmentation of protonated alkylbenzenes, and much insight of general chemical interest has been obtained. Several reviews have been given by Kuck.[1,2] There are, however, many details that are not obtained by experimental techniques. Quantum chemical methods can complement experimental techniques and in some cases can give further information.

In this paper, we study protonated ethylbenzene (ethylbenzenium ion) and protonated 2,6-dimethylethylbenzene (2,6-dimethylethylbenzenium ion). The particular issue of interest is to study the mechanism for splitting off ethene and to investigate whether a π complex between an (alkyl)benzenium ion and ethene, respectively, (alkyl)benzene and an ethenium ion, can exist. The possible existence of these, and similar, π complexes has been an important part of several papers.[3−13] A study of protonated methylbenzenes has very recently been carried out by Sekiguchi et al.[14]

There are important acid-catalyzed industrial processes where addition of an alkene to an arene or, conversely, dealkylation of an alkylarene takes place. Examples include the production of ethylbenzene from benzene and ethene and the methanol to hydrocarbon reaction (MTH) (also called MTO and MTG) where methanol, when passed over certain acidic zeotype catalysts, is transformed into a mixture of hydrocarbons in the range C_2-C_{12} and water. It is now generally accepted that alkylbenzenes are essential intermediates in the MTH reaction.[15,16] The reaction proceeds by splitting off the alkene, whereby a less substituted benzene ring is formed, and the alkylbenzene is regenerated via repeated methylations by methanol and ensuing isomerizations. The MTH chemistry is the background for our interest in benzenium ion chemistry. The isomer families we have chosen are representative model compounds for the full series of ethyl(poly)methylbenzenium ions. Alkylbenzenes have a fairly high proton affinity which increases with the number of alkyl groups and, for example, tetramethylbenzene and hexamethylbenzene are fully protonated in H-beta zeolite, so benzenium ions are available in the reaction system.[17,18]

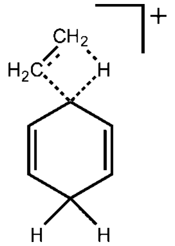

Figure 1. Schematic representation of our previously found possible mechanism for splitting off ethene from ethylbenzenium.

We have previously found a possible mechanism for splitting off an ethene molecule from an ethylbenzenium ion.[19] In that case, the parent ion was ethyl-4*H*-benzene, and the reaction proceeded as indicated in Figure 1. The activation energy for the reaction proceeding by this mechanism was 235 kJ mol^{-1} when calculated according to a B3LYP/cc-pVTZ//B3LYP/6−311G(d,p) level of theory and was 206 kJ mol^{-1} when the calculation was based on an MP2/cc-pVTZ//MP2/6−311G(d,p) scheme (in both cases, zero point energy (ZPE) corrected). The experimental reaction enthalpy for formation of benzenium and ethene from ethylbenzenium is 143 kJ mol^{-1}, and a reaction leading to benzene and ethyl carbocation has a reaction energy of 213 kJ mol^{-1}.[20] The previously calculated activation energies are so high that it seems difficult to reconcile them with experimental studies which indicate that the activation energy should not be much higher than the reaction energy.[5] This is an

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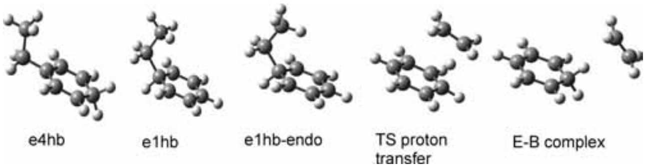

Figure 2. Pictorial representation of the stationary states in the ethylbenzenium system.

indication that the reaction does not really proceed by the previously assumed mechanism. We have, therefore, studied the system in more detail and have tried to find a different mechanism connected with a lower barrier, which then is more likely to represent the true reaction pathway.

Computational Details

The computations which are presented have all been performed using the Gaussian 03 program package.[21] Many low-level computations were carried out to find possible reaction pathways. The geometries that will be presented were obtained at the B3LYP/cc-pVTZ level of theory. Zero point energies (ZPE) were calculated at the B3LYP/6−311++G(d,p) optimized level. The integration grid was set to Ultrafine as defined by Gaussian 03. The geometry optimization convergence criterion was set to Tight.

Computations were also carried out at the MP2/6−311++G(d,p) level with ZPE calculated at the same level of theory. In the cases where the two methodologies gave qualitatively similar results, the geometries and relative energies predicted by the two methods were very similar. There were, however, cases where B3LYP and MP2 gave conflicting results. These discrepancies are treated in more detail in the Results section.

For this reason, the results description will be centered on the B3LYP results. B3LYP is, however, known to not always give very accurate energies. Energies have therefore also been computed according to the Gaussian-3/B3LYP (G3B3 keyword) methodology.

Results

A protonated ethylbenzene may have the proton attached to any of the benzene ring carbon atoms. As expected, the para-position (ethyl-4*H*-benzene) has the lowest energy (see below), and the energies will be given relative to the energy of this isomer. We shall, however, concentrate on a situation where the ethyl group splits off from the ethyl-1*H*-benzene. In this isomer, the C−C bond which binds the ethyl group is weakened. If the proton were attached to any of the other ring atoms, the mechanism for ethene elimination would be essentially the same as our previously discussed mechanism for ethyl-4*H*-benzene, and so, as found there, the barrier would be too high. The stationary states that will be discussed are shown in Figure 2. The designations used there for the structures are short forms of the following more complete descriptions: e4hb = ethyl-4*H*-benzene, e1hb = ethyl-1*H*-benzene, and e1hb-endo = ethyl-1*H*-benzene-endo (a rotational conformer of the methyl group with one hydrogen atom pointing inward, in the direction of C^4; it is a rotational transition state). TS proton transfer is a transition state where a proton jumps between an ethenium ion and benzene or, vice versa, between a benzenium ion and an ethene molecule. Finally, E−B complex is an ethene/benzenium ion complex. The atomic numbering is the same as shown in Figure 3 where the same designations as in Figure 2 are used.

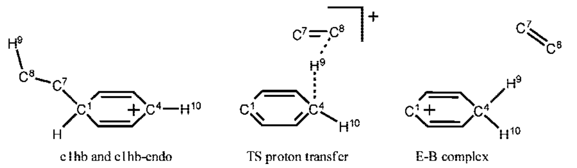

Figure 3. The atom numbering convention that is used in this paper.

A simplified description of the series of events leading to elimination of ethene from ethylbenzenium may be given as follows.

The reaction starting point is e1hb. This species has its minimum energy when one of the hydrogen atoms on the methyl group points away from C^4. However, the energy barrier for rotating the methyl group is so low that one of the hydrogen atoms will often point in the general direction of C^4. Consider the situation where the methyl group has been rotated exactly 60° from the energy minimum position. This is a transition state for rotating the methyl group. This state has been designated e1hb-endo to reflect that the C^8-H^9 is pointing inward in the direction of C^4. The reaction may further be considered to take place by breaking the C^1-C^7 bond, and the ethyl cation which is then formed moves over the benzene ring in the direction of C^4. Atom H^9 is all the time positioned between the ethyl carbon atoms (C^7, C^8) and the benzene ring. Finally, a state is reached where the C^8-H^9 bond is broken and a C^4-H^9 bond is formed. This is the transition state “TS proton transfer” in Figures 2 and 3. The newly formed ethene molecule may, after moving further on, form a weakly bound π complex with the new-formed benzenium ion or, if the translational energy of the ethene molecule is high enough, it may break away and form a free ethene molecule and a free benzenium ion.

The structure optimizations were initially performed with no geometric constraints, but when Tight convergence criteria and Ultrafine integration grid were utilized, they all exhibited very near C_s symmetry, which was thereupon made exact.

The most important geometric characteristics of the discussed species are shown in Table 1. The numbering of the atoms in the five cases is seen from Figure 3. Table 2a gives the energies of the species in Figure 2 both with and without zero point energy (ZPE) corrections. (For completeness, the energies of ethylbenzene protonated in C^2 and C^3 positions are also given, but these species are not further discussed.) The energies refer to 0 K. The table is given in two parts, a and b. Results obtained with basis set cc-pVTZ are given in part a; part b gives the results with 6/311++G(d,p). Comparison of the two parts shows that the effects of increasing the basis set are small. Table 2b also serves for comparison between ethylbenzenium and 2,6-dimethylbenzenium. Energies and geometries of the latter are given in Tables 4 and 5. In the latter case, the computations have only been carried out with the 6−311++G(d,p) basis set.

That TS proton transfer is indeed a transition state in the reaction where the C^1-C^7 bond is broken and the E−B complex is formed was verified by running intrinsic reaction coordinate (IRC) calculations. After four IRC steps in each direction, an ordinary geometry optimization (with C_s symmetry relaxed to C_1) converged to the e1hb structure in the one direction and in the other direction to the E−B complex structure. During the optimization toward e1hb, an essential retention of C_s symmetry, with a virtual formation of e1hb-endo, was observed until the final steps when a rotation of the methyl group took place and e1hb was formed. We take this to indicate that a configuration like the one shown in Figure 4, which is an intermediate

TABLE 1: Geometric Characteristics of the Ethylbenzenium Isomers: Selected Distances (Å) and Angles[a]

atom number	e4hb	e1hb	e1hb-endo	TS proton transfer	E−B complex
C^1C^7	1.484	1.578	1.581	3.546	5.451
C^7C^8	1.554	1.525	1.540	1.359	1.330
C^8H^9		1.089	1.090	1.439	2.502
C^4C^7	4.327	4.170	4.140	3.435	3.622
C^4C^8	5.061	4.402	4.342	2.889	3.581
C^4H^9			3.583	1.467	1.131
C^4H^{10}	1.104	1.083	1.083	1.083	1.099
C^7H^9				2.072	2.502
$C^1C^4C^8$				91.5	136.9
$C^1C^4H^9$				85.4	122.3
$C^1C^4H^{10}$	129.7	179.9	179.8	172.9	139.4
$C^4H^9C^8$			128.1	167.6	158.8

[a] Obtained at the B3LYP/cc-pVTZ level of theory and application of the Ultrafine integration grid. Convergence criterion set to Tight. Molecular symmetry is C_s.

TABLE 2: Energies of the Species Derived from Protonated Ethylbenzene at 0 K

(a) B3LYP/cc-pVTZ Level of Theory

species	E/hartree	ΔE^a	ZPE/hartree[b]	ΔE^c
e4hb	−311.308676	0	0.166506	0
e1hb	−311.293819	39.0	0.166801	39.8
e1hb-endo	−311.289372	50.7	0.166499	50.7
TS proton transfer	−311.252555	147.3	0.158614	126.6
E−B complex	−311.264751	115.3	0.161611	102.4
benzenium	−232.634352		0.110076	
ethene	−78.623179		0.050773	
sum B + E	−311.257532	134.3	0.160849	119.4
e2hb	−311.306210	6.5	0.166304	5.9
e3hb	311.299982	22.8	0.166050	24.0

(b) B3LYP/6-311++G(d,p) Level of Theory

species	E/hartree	ΔE^a	ZPE/hartree	ΔE^c
e4hb	−311.278665	0	0.166506	0
e1hb	−311.264326	37.6	0.166801	38.4
e1hb-endo	−311.259806	49.5	0.166499	49.5
TS proton transfer	−311.221859	149.2	0.158614	128.5
E−B complex	−311.233818	117.9	0.161611	105.0
benzenium	−232.611326		0.110076	
ethene	−78.615538		0.050773	
sum B + E	−311.226865	136.0	0.160849	121.1
e2hb	−311.27630	6.3	0.166304	5.7
e3hb	−311.270125	20.1	0.166050	21.3

[a] kJ mol^{-1}, not ZPE corrected. Relative to the most stable isomer, e4hb. [b] ZPE values from B3LYP/6−311++G(d,p). [c] kJ mol^{-1}, ZPE corrected, relative to the most stable isomer.

TABLE 3: Energies of the Species Derived from Ethylbenzenium According to Gaussian-3 (G3B3)

species	ZPE/hartree	E/hartree[a]	ΔE^b	ΔE^c
e4hb	0.161189	−310.903743	0	0
e1hb	0.161597	−310.890363	35.1	34.7
e1hb-endo	0.161458	−310.886022	46.5	44.5
TS proton transfer	0.153693	−310.851878	136.2	136.9
E−B complex	0.156511	−310.857054	122.6	124.9
benzenium ion	0.106560	−232.339891		
ethene	0.049189	−78.509285		
ethene + benzenium ion	0.155749	−310.849176	143.3	143.4

[a] G3 (0 K) energy. (These values incorporate the scaled ZPE correction.) [b] Energies relative to the most stable isomer, e4hb, kJ mol^{-1}, 0 K. [c] Energies relative to the most stable isomer, e4hb, kJ mol^{-1}, 298 K.

TABLE 4: Energies of the Species Derived from Protonated 2,6-Dimethylethylbenzene at the B3LYP/6-311++G(d,p) Level of Theory at 0 K

species	E/hartree	ΔE^a	ZPE/hartree	ΔE^b
dm-e4hb	−389.937052	1.1	0.222101	0.7
dm-e1hb	−389.937487	0.0	0.222259	0.0
dm-e1hb-endo	−389.933117	11.5	0.221916	10.6
dm-TS[c]	−389.884357	139.5	0.213054	115.3
dm-E−B complex	−389.898862	101.4	0.216170	85.4
dm-benzenium	−311.277633		0.164659	
ethene	−78.615538		0.050773	
sum dm-B + E	−389.893171	116.4	0.215432	98.4

[a] kJ mol^{-1}, not ZPE corrected, relative to the most stable isomer, dm-e1hb. [b] kJ mol^{-1}, ZPE corrected, relative to the most stable isomer. [c] dm-TS proton transfer.

structure during the optimization, represents a minimal energy pathway when ethene is split off from, or adds to, a benzenium ion.

A pictorial view of the energetics reaction system when ethene is split off from ethyl-4*H*-benzene (the most stable state) and finally forms free ethene and benzenium, or, vice versa, when ethene adds to a benzenium ion forming an ethylbenzenium ion, is given by Figure 5 (no ZPE correction). The reaction coordinate (progress of reaction) cannot be represented by one single structural parameter, so the sum of distances $C^1{-}C^7$ and

TABLE 5: Geometric Characteristics of the Species Derived from 2,6-Dimethylethylbenzenium: Selected Distances (Å) and Angles[a]

atom number	dm-e4hb	dm-e1hb	dm-e1hb-endo	dm-TS proton transfer	dm-E−B complex
C^1C^7	1.493	1.59	1.591	3.331	5.578
C^7C^8	1.558	1.528	1.543	1.364	1.333
C^8C^9	1.091	1.093	1.092	1.434	2.603
C^4C^7	4.333	4.055	4.026	3.418	3.710
C^4C^8	5.062	4.152	4.100	2.879	3.677
C^4H^9	1.106		3.287	1.453	1.126
C^4H^{10}	1.106	1.086	1.086	1.086	1.103
C^7H^9			2.210	2.098	2.594
$C^1C^4C^8$			39.6	87.4	1.386
$C^1C^4H^9$			51.0	83.3	123.9
$C^1C^4H^{10}$	129.9	179.4	179.2	174.0	137.1
$C^4H^9C^8$			132.1	171.8	159.1

[a] Obtained at the B3LYP/6−311++G(d,p) level of theory and application of the Ultrafine integration grid. Convergence criterion set to Tight. Molecular symmetry is C_s.

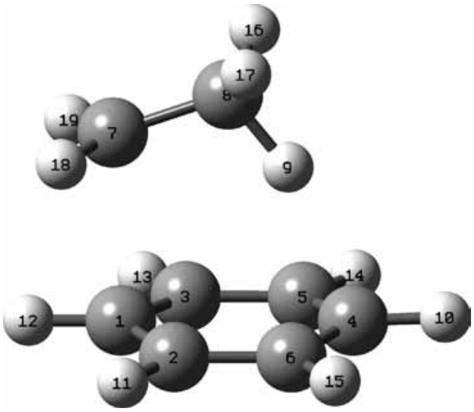

Figure 4. An intermediate step when ethene is split off from an ethylbenzenium ion, or vice versa, when ethene is added to a benzenium ion. The figure does not represent a stationary state, but it represents a stage on the minimum energy reaction path on the potential energy surface (PES).

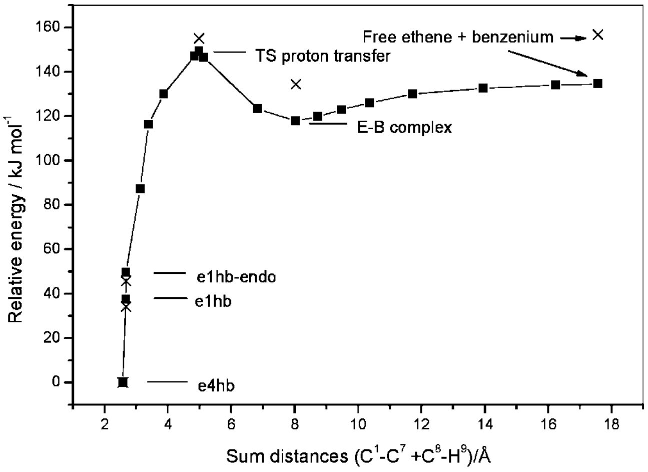

Figure 5. The potential energy in the reaction system when ethene is split off from an ethylbenzenium ion. The “sum distances” on the abscissa serve as a measure of the reaction coordinate. The stationary states are indicated. The other points that are given are not stationary states but rather are approximate values on the reaction minimum potential energy surface. The filled squares (■) connected by lines were obtained from the B3LYP computations. The crosses (×) represent the potential energy (i.e., the zero point energy correction is removed) at the stationary states as given by the G-3 method.

C^8-H^9 is used. The first part of the reaction involves only breaking of the C^1-C^7 bond, so here this distance is the important parameter; when the TS is approached and further on, the important distance is C^8-H^9. The sum describes the full process.

The B3LYP computational scheme is known to produce fairly good energy estimates, but it is also known that the composite Gaussian-3 (G-3) methods in various flavors usually give more precise results. We have, therefore, repeated the energy calculations by utilizing the G-3 B3LYP scheme (G3B3 keyword).[21] Gaussian-3, which is a composite method, is known to give precise energies. When tested against the G3/99 test set, comprising a wide range of elements and bond types with nearly 400 experimental energies known to be accurate within ±4 kJ mol^{-1}, a mean absolute deviation of about 4.5 kJ mol^{-1} has been found, and when only the hydrocarbons are considered, the mean deviation falls to less than 3 kJ mol^{-1}.[22] Computations carried out via G-3 are effectively at the QCISD(T,full)/G3Large level.[22]

The energy values obtained from B3LYP, which are given in Table 2, show a modest deviation from the G-3 values in Table 3 showing that the B3LYP energies are sufficiently accurate that they can be used for discussing the system properties and for allowing comparison between the ethylbenzenium ion and the 2,6-dimethylbenzenium ion system or other alkylbenzenium ion systems.

The results of the G-3 calculations are given in Table 3 for 0 and 298 K. The 298 K energy values are given in order to compare with the experimentally determined reaction energy. The reaction energy 143.4 kJ mol^{-1} at 298 K is seen to be quite close to the experimentally accepted reaction enthalpy value of 143 kJ mol^{-1} corresponding to a reaction energy of 145.5 kJ mol^{-1} (with an uncertainty that may well be 1−4 kJ mol^{-1}).[20] The G3B3 reaction energy at 0 K is 143.3 kJ mol^{-1}.

When these results are compared with the B3LYP/cc-pVTZ reaction energy in Table 2, which is 121.0 kJ mol^{-1} at 0 K, it appears that B3LYP gives a too low reaction energy. At 298 K, the calculated reaction energy is 124.1 kJ mol^{-1}, which is considerably less than the experimental value 145.5 kJ mol^{-1}. A more graphical impression of the similarity, and difference, between the B3LYP values and the more accurate G-3 values is obtained from Figure 5.

In the case of computations that may involve weakly bonded complexes, the MP2 method is often considered more reliable than density functional theory (DFT) methods. For this reason, we have also performed an extensive series of calculations using MP2 methodology. The results obtained for e4hb, e1hb, and e1hb-endo (6−311++G(d,p) basis set) were essentially equivalent to those described above both with regard to structures and (relative) energies. As regards the transition state for proton transfer (TS proton transfer) and the ethene/benzenium complex (E−B complex), the situation turned out to be very different. We were not able to get stationary state convergence for any of the two species. An attempt to find a stationary minimum state based on the B3LYP structure of the E−B complex ended up by giving the e1hb structure. We have earlier studied this discrepancy between the two methods in considerable detail, and also on a higher level of theory (CCSD and QCISD with basis set 6−311++G(d,p)), with the outcome that the B3LYP result is correct.[23] The E−B complex represents a local minimum on the PES in the ethene/benzenium ion system and a quantum chemical stable state. Some further aspects of this issue, for example, why does MP2 fail in this case, that could not be discussed previously because no details about the TS were given are discussed in the Supporting Information.

In an MTH reaction system, there will usually be several methyl groups on the benzenium ion. As a simple example of such a system, we have chosen to perform corresponding calculations on 2,6-dimethylethylbenzenium ions. It was expected that the more crowded environment for the ethyl group and the higher proton affinity of the resulting dimethylbenzene might influence the energies and the structures of the various species involved.

The energies and the main geometric characteristics are given in Tables 4 and 5. The naming of the species is the same as used in Figure 2 apart from adding the prefix dm (for 2,6-dimethyl) in the names. The atomic numbering is the same as used in Figure 3. The two methyl groups in positions 2 and 6 are not directly involved in bond splitting/formation, and so no details about them are given. Full structures are, however, given as Supporting Information. Apart from the replacement of two hydrogen atoms by methyl groups, there are no clear visual differences between the species shown in Figure 2 and the corresponding structures from 2,6-dimethylethylbenzenium ions. Comparison of Tables 1 and 5 shows that also quantitatively the geometries are virtually identical.

Attention may be drawn to the result that in the case of ethylbenzene the para-protonated form is more stable than the ipso-protonated one, whereas in the case of 2,6-dimethylethylbenzene, the two forms are essentially of equal energy with a slight preference for ipso-protonation. Apart from this difference, it can be seen that energies of the various species relative to e1hb, respectively and dm-e1hb are quite similar. The energy needed for splitting off ethene is, as was expected, lower: 98.4 versus 121.1 kJ mol^{-1}.

Discussion

A fairly clear impression of the mechanism for splitting off an ethene molecule from a protonated ethylbenzenium or dimethylbenzenium ion has now been obtained. It is also clear that a π complex between ethene and benzenium or dimethylbenzenium ion exists.

To our knowledge, the only preceding computational study of ethene elimination from ethylbenzenium is our earlier work on xylenium ions where a possible mechanism with an energy barrier of 235 kJ mol^{-1} was mentioned.[19] A reverse reaction, catalytic addition of ethene to benzene, was investigated by Arstad et al.[24] These works are, however, not directly comparable with the present work because different mechanisms were investigated. Leung and Harrison and Audier et al. studied dissociation of ethylbenzenium ions in the mass spectrometer. They looked in particular at various benzenium ion isotopomers and studied $C_6D_5H\text{-}CH_2CH_3^+$, $C_6H_6{-}CD_2CH_3^+$, and $C_6H_6{-}CH_2CD_3^+$.[1−5]

The main results were (1) H or D on the benzene ring showed no tendency for being exchanged with H or D on the side chain. (2) There was a clear preference for the methyl group hydrogens to be attached to the resulting benzenium ion ring, but the probability for transferring H or D from the methylene group to the benzene ring was far from negligible.

To which extent the calculated results concur with the experimental findings may require some discussion. The computational results cannot be directly compared with the experiments. The computations give information on structure and energies, whereas the experiments have given information on atomic exchange.

The computations discussed above refer to an idealized case corresponding to a molecule with C_s symmetry that moves strictly along a minimum potential energy curve on the PES. In reality, the molecular system has internal rotations and vibrations. Consequently, if the reaction were reversed after the transfer of the proton to the benzene ring, it is conceivable that the ethene molecule might pick up any of the hydrogens on the benzenium ion because the hydrogens on a benzenium ion meet only small barriers for moving around, and the ethene molecule may move rather freely around the benzenium ion in the complex. This might lead to hydrogen exchange. Further scrutiny of the issue shows, however, that hydrogen exchange is unlikely to take place to any extent.

(A) The computations indicate that such reversibility may not be very probable. The extra energy needed to separate the ethene molecule from the benzenium ion is small. According to Table 2, the B3LYP/cc-pVTZ energy of the TS at 0 K is 7 kJ mol^{-1} higher than that of the separated ion and molecule, so complete cleavage might be expected to take place once the TS is passed. On the other hand, according to G3B3 (Table 3), the TS energy is 7 kJ mol^{-1} lower than that of the separated species, so on this basis one should not expect separation of the two parts always to take place, but it should also not be a rare event. (If the energies were distributed according to a Boltzmann distribution ($n_i/n_j = \exp(-(E_i - E_j)/RT)$), sufficient energy would be available in about 6% of the cases.) It is therefore possible that once the TS is passed the reaction is not likely to be reversed and hydrogen exchange may not often take place.

(B) The barrier for hydrogen walk on a benzenium ion is not small relative to the energies involved here. We have calculated the barrier within the B3LYP/cc-pVTZ level of theory and have found the barrier to be 51.4 kJ mol^{-1}, a value that is close to the results obtained by del Rio et al. who carried out calculations at the MP2/6−31G(d) and MP4(STDQ)/6−31G(d)//MP2/6−31G(d) levels of theory.[25]

The barrier for hydrogen walk is therefore much higher than the binding energy of the ethene/benzenium ion complex, which is seen from Tables 2 and 3 to be about 20 kJ mol^{-1}. The protonic hydrogen H^9 will therefore remain attached to C^4, and if the reaction were reversed, H^9 would still become reattached to the ethyl group. Consequently, hydrogen exchange between the benzene ring and the ethyl group is not to be expected.

On basis of the description given above of the mechanism for splitting off ethene, one might conclude that it will always be a methyl group hydrogen that is becoming attached to the benzene ring. One must, however, keep in mind that in a free ethyl cation one hydrogen is situated midway between the two carbon atoms, and in any case, the energy needed for moving the protonic hydrogen from one carbon to the other is small. It is known that in a free ethyl cation the hydrogens scramble quickly.[5] The preference for transferring a methyl hydrogen to

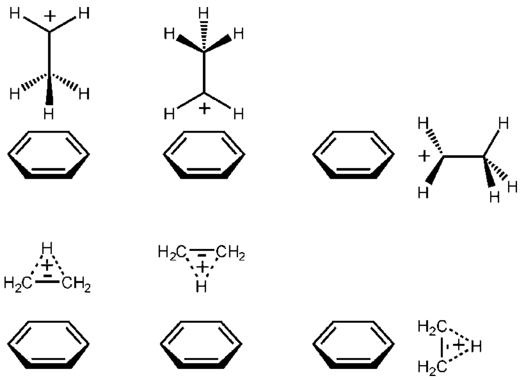

Figure 6. Configurations that were taken as starting points when we looked for possible stable C_6H_6----$C_2H_5^+$ π complexes. Stationary states for such complexes were not found.

the benzene ring is therefore in qualitative accord with the computations because then no hydrogen shift is required, but it is also not surprising that there is a nonnegligible probability that a methylene hydrogen is transferred.

Possible π complex formation in cationic arenic systems has been discussed in the literature.[1−13] The complexes may be of two types: an alkenium ion bonded to a benzene ring or an alkene bonded to a benzenium ring but without the presence of a σ-bond which binds them together. In refs 1−3 and 5, it is speculated that that the complex C_6H_6----$CH_2CH_3^+$ represents a stable state (i.e., a local minimum on PES), which may be transformed into a free benzenium ion and a free alkene when the proton is transferred from the alkenium moiety to the benzene ring. We have not been able to find a stable complex of the form C_6H_6----$C_2H_5^+$. Several configurations were tried as indicated in Figure 6.

It is difficult to prove that there is no local minimum on the PES corresponding to C_6H_6----$C_2H_5^+$, but the configurations we tried converged either to an ethylbenzenium (ethyl-1*H*-benzene) or to the benzenium ion/ethene complex discussed above or to higher order saddle points if symmetry was imposed when structure optimizations were run. It therefore seems that if there is a local minimum corresponding to the C_6H_6----$C_2H_5^+$ complex it is likely to represent a very special arrangement of the $C_2H_5^+$ group relative to the benzene molecule.

There are not many theoretical investigations devoted to the study of π complex formation of the type C_6H_6----$C_nH_{2n+1}^+$ or $C_6H_7^+$----C_nH_{2n}. Heidrich studied the possible existence of isopropyl and *tert*-butyl cation π complexes with benzene utilizing MP2 with the 6−31+G(d,p) basis set.[12] He found that at this level of theory there is a stable C_6H_6----$C_4H_9^+$ complex and that the complex C_6H_6----$C_3H_7^+$ did not represent a stable state. Berthomieu et al. have earlier studied the same system with the semiempirical AM1 method and ab initio computations at the HF/6−31G(d,p)//3−21G level and have concluded that the above complexes were stable (local minima).[7,8] Heidrich explained the opposing results regarding the C_6H_6----$C_3H_7^+$ complex as being due to the low level of theory utilized in the older investigation. The system $C_6H_6 + CH_3^+$ has been studied by Miklis et al. and Ishikawa et al. with the clear conclusion that the two species do not form a π complex; a methylbenzenium ion is immediately formed.[11,13]

We have earlier carried out a theoretical study of acid-catalyzed addition of ethene to benzene.[23] In that case, a one-step mechanism where the proton is transferred to the ethene molecule, which at the same time adds to the benzene molecule forming ethylbenzenium, was investigated. In view of the results obtained here, it may seem that it might be worthwhile to look at a mechanism where the benzene molecule is protonated first. The much higher proton affinity of benzene relative to ethene is likely to make the activation energy for such a mechanism lower than we previously found.

Conclusion

Quantum chemical calculations have been carried out on several isomers that may form when ethylbenzene or 2,6-dimethylbenzene is protonated. A mechanism whereby ethene may be split off has been found. The energy barrier for this mechanism is almost the same as the reaction energy, so no other mechanism with a lower energy barrier is likely to be found. It has been found that ethene and benzenium or 1,3-dimethylbenzenium ion may form a stable complex.

It was looked for a π complex of the type C_6H_6----$C_2H_5^+$, but in all cases, a geometry optimization led to either ethyl-1*H*-benzene or to the complex $C_6H_7^+$----C_2H_4.

The theoretical results seem to agree well with published experimental data for ethylbenzenium ions.

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Supporting Information Available: *XYZ* coordinates for the species that are discussed are given. There is a short discussion about the failure of MP2. This material is available free of charge via the Internet at http://pubs.acs.org.

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