International Journal of Mass Spectrometry 185/186/187 (1999) 241–251

Isomerization and dissociation processes of protonated benzene and protonated fulvene in the gas phase

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Received 29 May 1998; accepted 10 July 1998

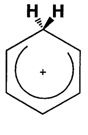
Abstract

The protonation energetics of benzene and fulvene are investigated through the use of molecular orbital ab initio G2(MP2) calculations using B3LYP/6-31G* optimized geometries. Calculated proton affinities of benzene and fulvene are 752 and 842 kJ mol^{-1} assuming formation of benzenium ion **1** and Cα-protonated fulvene **3**, respectively. Isomerization reactions of protonated benzene and protonated fulvene were investigated at the same level of theory. The isomerization of benzenium ion **1** into protonated fulvene implies as a first step the formation of bicyclo[3,1,0]-hexenyl cation, **5**, that may eventually evolve to yield methylene-protonated fulvene **2** and Cα-protonated fulvene **3**. The latter yields the C_β-protonated species **4** through a relatively low activation barrier. The energy required by the dissociation of benzenium ion via a 1,1-H_2 extrusion process is equal to its endothermicity. The excess energy of the dissociating species **1** having a lifetime of 10^{-5} s is sufficiently low to explain the absence of an appreciable kinetic energy release during the separation of the products. (Int J Mass Spectrom 185/186/187 (1999) 241–251) © 1999 Elsevier Science B.V.

Keywords: Protonated benzene; Protonated fulvene; Benzenium cation; Bicyclo[3,1,0]-hexenyl cation; G2(MP2) molecular orbital calculation

1. Introduction

One important question in the gas-phase chemistry of aromatic molecules concerns the structure and the energy of their protonated products. The prototypical case of benzene has been extensively studied over the years because of its relevance to electrophilic aromatic substitution [1]. Both theoretical [2,3] and experimental [2,4–10] data indicate that benzenium ion **1** is the most favoured protonated form of benzene and that its face protonated form **1″** is less stable by far. The loss of identity of the seven hydrogen atoms of the protonated benzene has been interpreted by a facile interconversion of ions **1** via the side protonated structure **1′**.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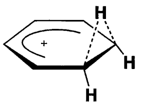
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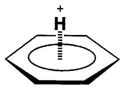
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If 1,2-hydride shifts such as **1** → **1′** → **1** are important reaction channels in benzenium ions chem-

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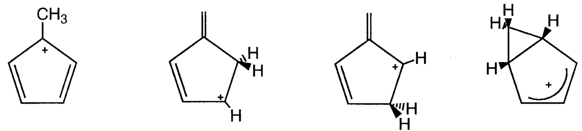
* Corresponding author.

Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

PII S1387-3806(98)14109-X



2 **3** **4** **5**

Scheme 1.

istry, other types of rearrangements are, however, possible and have been suspected in some cases. For example, isomerization of benzenium ion **1** into protonated fulvene was suggested from photodissociation decay of protonated benzene [7,8]. Similarly, parallel formation of protonated fulvene, besides **1**, seems to occur when $[C_6H_7]^+$ ions are generated by dissociative ionization of cyclohexadiene [4,7] and methylcyclopentene [4] or by ion-molecule reactions involving allene [4], propyne [4], allyl bromide [8], vinyl chloride [5], and butadiene [11]. However, no firm conclusion can be drawn from these data because most of the structural, mechanistic, and energetic details concerning the participation of protonated fulvene into the chemistry of protonated benzene are lacking.

Benzenium ions **1** undergo one major unimolecular dissociation leading to $[C_6H_5]^+$ phenyl cations. This H_2 loss is the exclusive fragmentation of metastable ions **1** and it is associated with a very small kinetic energy release (T is less than, or close to, 4 kJ mol^{-1}) [2].

To the best of our knowledge, no rigorous calculation on the stationary points for protonated fulvene as well as their possible interconversion into protonated benzene have been reported to date. In an attempt to explore this question we have carried out ab initio molecular orbital calculations using the G2(MP2) theory and the B3LYP variant of density functional theory on a series of $[C_6H_7]^+$ ions that includes benzenium ion **1** and the protonated forms of fulvene **2**–**5** (Scheme 1). Details on the energetics associated with the loss of H_2 from benzenium ion **1** will also be given.

2. Computational

In order to obtain reliable descriptions of the C_6H_6 and $C_6H_7^+$ systems under study, a high level ab initio molecular orbital technique is required. Among the different alternatives, the G2 theory of Pople and co-workers [12a] is one of the most powerful as long as it provides calculated thermodynamic properties, in particular proton affinities [13], in excellent agreement with the experimental outcomes. The treatment of systems of the size considered here becomes computationally demanding at the G2 level. Hence, we have decided to use the alternative G2(MP2) theory [12b] which constitutes a cheaper approach but still provides estimates of the proton affinities and relative energies of isomers within a few kJ mol^{-1} in most cases.

Standard G2(MP2) procedure is based on the use of MP2/6-31G* optimized geometries and zero point energy (ZPE) corrections evaluated at the HF/6-31G* level. In the present application of the theory, we have used optimized geometries obtained using the B3LYP density functional approach and a 6-31G* basis set expansion. It has been shown that, in general, B3LYP optimized geometries do not differ significantly from the MP2 optimized ones. Moreover, the B3LYP harmonic vibrational frequencies—and as a consequence the estimation of the ZPE—are much better than the HF ones. ZPEs calculated at the B3LYP/6-31G* level were scaled by the empirical factor 0.98 [14]. To establish unambiguously which local minima are connected by each transition state, we have used an internal reaction coordinate (IRC) approach.

All calculations have been carried out using the GAUSSIAN 94 series of programs [15]. The B3LYP/6-31G* optimized geometries of the different stationary points of the potential energy surface examined in this study were schematized in Fig. 1. The corresponding total energies calculated at the B3LYP/6-31G* and G2(MP2) levels were summarized in Table 1. This table also includes the ZPE corrections and the relative potential energies at 0 K (ΔE).

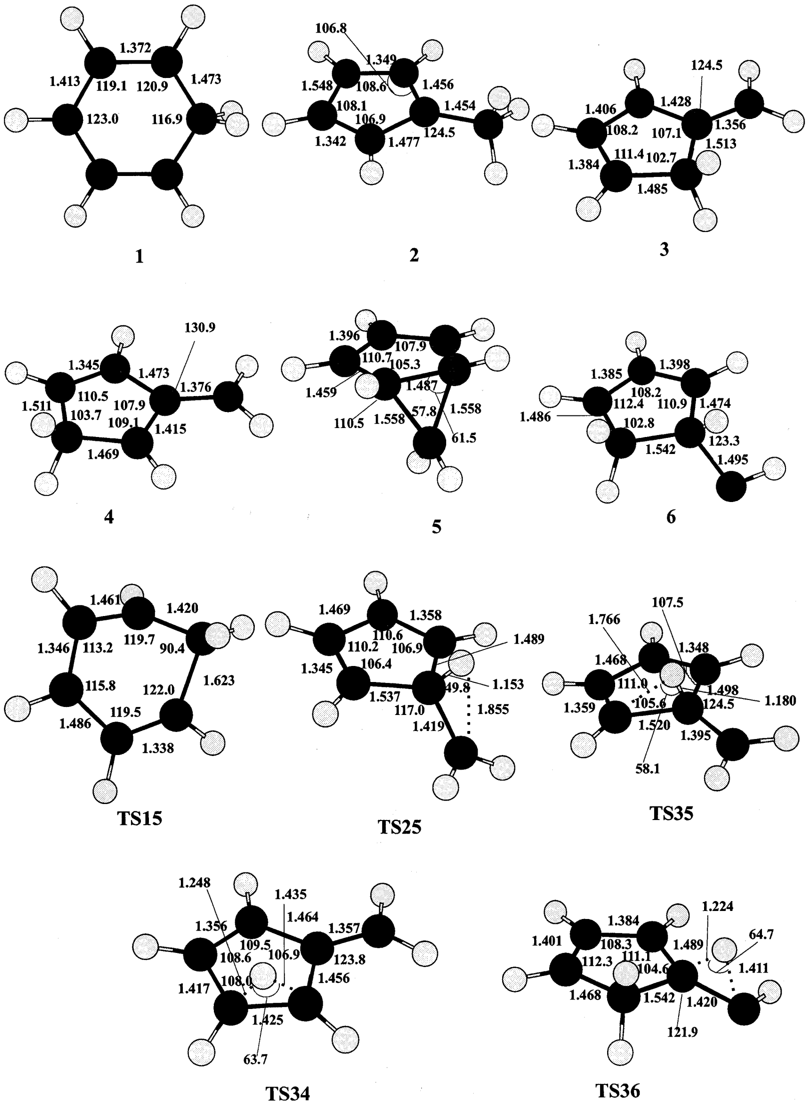


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Fig. 1. Optimized geometry (B3LYP/6-31G*) of the relevant stationary points of the $[C_6H_7]^+$ potential energy surface (bond lengths in Å, bond angles in degrees).

3. Results and discussion

3.1. Protonation of benzene and fulvene

3.1.1. Structures

As summarized in the introduction, convincing evidence points to **1** being the most stable structure for protonated benzene. The most recent and thorough theoretical study of this system shows that the other suggested species, **1**′ and **1**″, are first- and second-order saddle points, respectively, on the corresponding potential energy surface [3]. Structure **1**′ has been identified as the transition structure for 1,2-hydride ion migration in **1**. Its energy at 298 K (G2(MP2) level) [3] is 34 kJ mol^{-1} above **1**. This value is in close agreement with the experimental estimates of 30–40 kJ mol^{-1} based on ^{13}C NMR studies of **1** in solution [16] and 32 kJ mol^{-1} based on gas phase radiolysis of terbutyl–toluenyl ion [17]. The second-

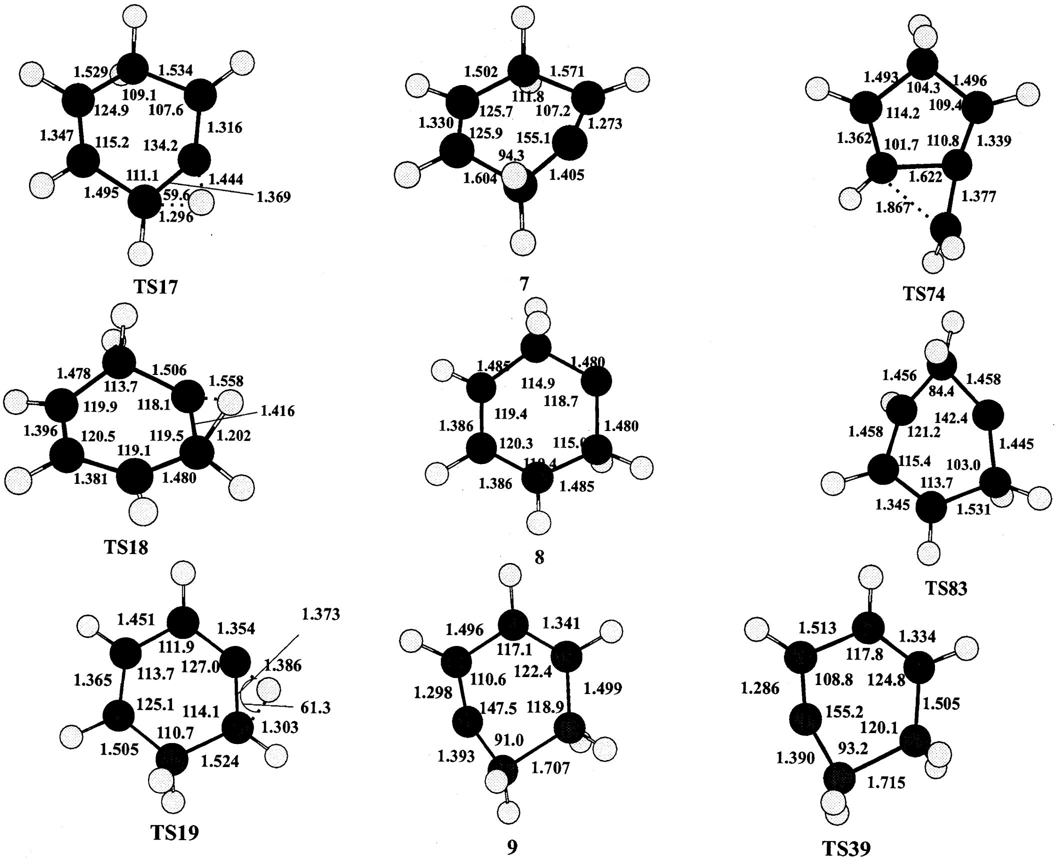


Fig. 1. *(continued)*

order saddle point **1**″ (B3LYP/6-31G (d,p) degenerate imaginary frequencies = 1690 cm^{-1}) is situated 199 kJ mol^{-1} above the stationary point **1** [G2(MP2) level, corrected for 298 K thermal energy] [3].

As expected, the most stable form of protonated fulvene is that in which the proton is attached to the α carbon, **3**. The energy difference calculated between structures **1** and **3** (40 kJ mol^{-1}, Table 1) combined with Δ_fH°(**1**) = 862 kJ mol^{-1}, allows us to propose a heat of formation of 902 kJ mol^{-1} for ion **3**. This value is in good agreement with an estimate done by Lias and Ausloos (895 kJ mol^{-1}, Table 2) [4]. Surprisingly enough, the second most stable structure originating from protonation of fulvene corresponds to the bicyclo[3,1,0]-hexenyl cation, **5**. In fact, protonation at the ipso carbon of the fulvene molecule results in a cyclization where the methylene group becomes bonded to one of the CH neighbouring groups. We shall see later that this structure also plays a central role in the isomerization process between protonated benzene and protonated fulvene. A heat of formation Δ_fH°(**5**) = 944 kJ mol^{-1} may be deduced from the calculation with reference to Δ_fH°(**1**) = 862 kJ mol^{-1}. Protonation of fulvene at the β site or at the methylene group leads to the less stable species **4** and **2** which are lying 103 and 121 kJ mol^{-1}, respectively, above **1**. Using Δ_fH°(**1**) = 862 kJ mol^{-1}, our G2(MP2) calculations give Δ_fH°(**4**) = 965 kJ mol^{-1} and Δ_fH°(**2**) = 983 kJ mol^{-1}. For the latter structure **2**, a heat of formation of 1012 kJ mol^{-1} has been reported [18], although an estimate ranging from 890–954 kJ mol^{-1} has been suggested by Lias and Ausloos [4] (Table 2). Our result offers a compromise between these two estimates.

Table 1
Total (*E*) and zero point (ZPE) energies (Hartree), relative energies including ZPE (ΔE, kJ mol^{-1})[a]

Species	B3LYP/6-31G*		G2(MP2)	
	E	ZPE	E	ΔE[c]
Benzene	−232.24866	0.10106	−231.77240	0
Fulvene	−232.19132	0.09832	−231.72286	130
Phenyl cation	−231.26635[b]	0.08483	−230.79259[b]	
H_2	−1.17548[b]	0.01017	−1.16585[b]	
Phenyl cation + H_2				257
1	−232.55629	0.11099	−232.05639	0
2	−232.50001	0.10748	−232.01033	121
3	−232.54059	0.11049	−232.04115	40
4	−232.51201	0.10936	−232.01706	103
5	−232.51515	0.11096	−232.02523	82
6	−232.39073	0.10572	−231.90252	404
7	−232.46625	0.10838	−231.97694	209
8	−232.41396	0.10649	−231.92254	351
9	−232.46175	0.10860	−231.97378	216
TS15	−232.47771	0.10858	−231.99112	171
TS17	−232.41729	0.10469	−231.93427	321
TS18	−232.40293	0.10457	−231.91492	371
TS25	−232.45450	0.10533	−231.96916	229
TS35	−232.45442	0.10486	−231.97281	219
TS34	−232.49665	0.10687	−232.01080	120
TS36	−232.37649	0.10328	−231.89010	437
TS74	−232.45131	0.10724	−231.96312	245
TS83	−232.39290	0.10563	−231.90927	386
TS19	−232.42445	0.10537	−231.93966	306
TS39	−232.46086	0.10811	−231.97192	222

[a] Values obtained using B3LYP/6-31G* optimized geometries.

[b] Values obtained using B3LYP/6-31+G* optimized geometries.

[c] Differences in zero point and 298 K energies are identical within ±1 kJ mol^{-1}, thus the relative energies ΔE also applies to 298 K.

Several other local minima were identified during our survey of the isomerization potential energy surface. They do not correspond to structures expected to be produced directly from protonation of benzene or fulvene and thus they will be described later, during the analysis of the isomerization processes.

3.1.2. Protonation energies

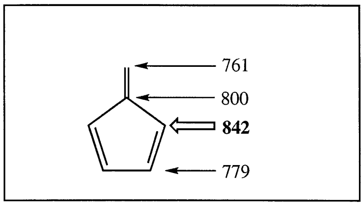
From the values reported in Table 1, it can be seen that the energy difference between benzene and fulvene decreases dramatically upon protonation. In fact, while the difference in G2(MP2) energies between benzene and fulvene is 130 kJ mol^{-1} at either 0 K or 298 K (a value in reasonably good agreement with the difference in experimental heats of formation of 141

Table 2
Thermochemical data (kJ mol^{-1}) relevant to the C_6H_6/$[C_6H_7]^+$ system

Species	$\Delta_f H^\circ_{298}$	Reference or note
Benzene	83	[25]
Fulvene	224	[25]
Protonated benzene	854	[25]
	862	[a]
Methylene-protonated fulvene	1012	[18]
	891–954	[4]
α-protonated fulvene	895	[4]
Phenyl cation	1127	[25]
	1132	[b]

[a] From the recently reevaluated proton affinity of benzene: 751.5 kJ mol^{-1} [19].

[b] Using the adiabatic ionization energy of the phenyl radical: 8.32 ± 0.04 eV [26] and $\Delta_f H^\circ$(phenyl radical) = 329 kJ mol^{-1} [25].



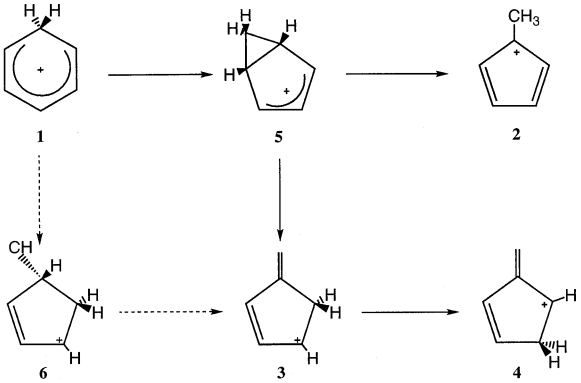
Calculated G2(MP2) proton affinities (kJ/mol) of fulvene according to the protonation site

Scheme 2.

kJ mol^{-1}, Table 2), the energy gap between the most stable protonated forms is only 40 kJ mol^{-1}. Hence, fulvene behaves as a stronger base in the gas phase than benzene.

The proton affinities of benzene and fulvene may be deduced from the data reported in Table 1 by including the usual corrections due to the translational energy of the proton and the PV term at 298 K. It is worth noting that our G2(MP2) estimated proton affinity of benzene (752 kJ mol^{-1}) is in fairly good agreement with the experimental value (751 kJ mol^{-1}) [19], so we may reasonably assume that our estimated proton affinity value of fulvene (Scheme 2 summarizes the estimated G2(MP2) proton affinities for the protonation of fulvene at its four different basic sites) to be close to the experimental value.

It is worth noting that a direct experimental determination of the proton affinity of fulvene is presently not available. However, indirect indications may be derived from previously published data. Lias and Ausloos [4], Gäumann et al. [7,8] and we [11] suspected the formation of a nonbenzenium structure in admixture with ion **1** when $[C_6H_7]^+$ ions are formed by fragmentation of cyclohexadienes or by ion-molecule reactions with allene, propyne, or butadiene. In each case the proton affinity of the conjugate base, estimated by bracketing experiments, lies around 850 ± 10 kJ mol^{-1}. In view of our estimate of the proton affinity of fulvene (842 kJ mol^{-1}, assuming protonation at the α carbon, Scheme 2), it is tempting to interpret these data by the formation of the Cα-protonated form of fulvene, **3**.



Scheme 3.

3.2. Isomerization processes

Extensive, if not complete, hydrogen equilibration is observed in $[C_6H_7]^+$ ions produced by methane [2,5,9] or water [10] chemical ionization of benzene. An isomerization mechanism obviously explaining these results is the 1,2-hybride ion migration **1** → **1**′ → **1**. This process is indeed the easiest isomerization reaction of benzenium ion **1** and will not be reinvestigated here.

As explained before, we shall emphasize the isomerization routes connecting benzenium **1** with the various forms of protonated fulvene. We have considered several mechanisms which can be classified into two categories depending upon the order of occurrence of the two elementary steps involved during the isomerization process: ring contraction and hydrogen shifts. In both cases, no direct isomerization pathways connecting species **2**, **3**, and **4** with protonated benzene **1** have been identified.

From an energetic point of view, we found that the most favourable isomerization mechanisms are those that involve, as a first step, the formation of the five-membered ring from protonated benzene **1** (Scheme 3).

Ring contraction of **1** to produce a five-membered cycle may occur between positions C_1 and C_3, or positions C_2 and C_4, or positions C_2 and C_6 (Scheme 3). In the two former cases we found that the C–C bond formation is associated with a concomitant C–C

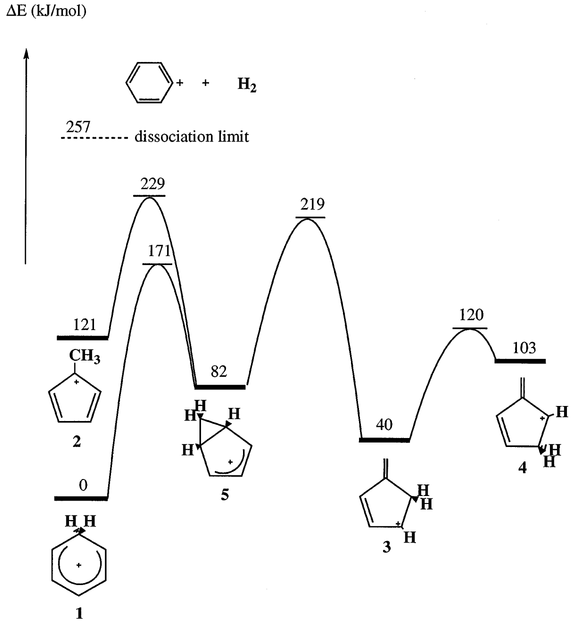
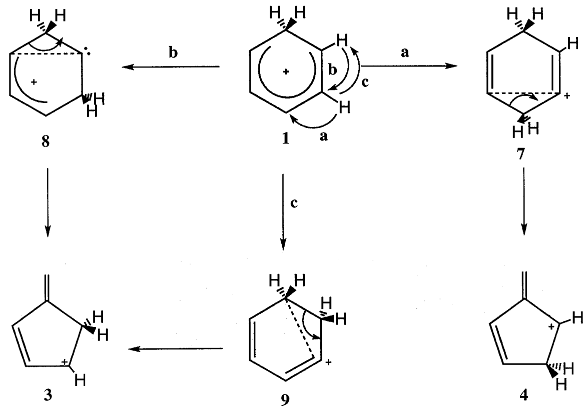


Fig. 2. Energy diagram for isomerizations processes of benzenium ion and protonated fulvene (G2(MP2)//B3LYP/6-31G* level): reactions involving "ring contraction first."



Scheme 4.

bond breaking leading to the low-stability local minimum **6**. This latter species is 404 kJ mol^{-1} above **1** and its possible participation to the isomerization processes may thus be discarded. The former reaction, in which the C_2–C_6 bond is created is much more favourable; it gives rise to the ipso-protonated fulvene **5** through the transition structure **TS15**. This process needs 171 kJ mol^{-1} (Fig. 2).

Once **5** is formed, a 1,2-H shift toward the methylene group leads to the isomer **2** via the transition structure **TS25** (relative energy 229 kJ mol^{-1}, Fig. 2). It is important to mention that we have not been able to locate any transition structure connecting the local minimum **2** with the two remaining protonated forms of fulvene **3** and **4**. All attempts collapse to species **5** which appears to play a pivotal role in the overall isomerization processes of protonated benzene and protonated fulvene. Returning to structure **5**, there are two ways to attain the most stable form of protonated fulvene **3**: (1) a 1,2-H shift from C_2 to C_6 accompanied by the C_1–C_6 bond breaking, or (2) a 1,2-H shift from C_2 to C_3 accompanied by the C_1–C_6 bond breaking. The former reaction is less energy demanding; it passes through the transition structure **TS35**, 219 kJ mol^{-1} above **1**.

The 1,2-hydride shift connecting the Cα to the Cβ protonated forms of fulvene, **3** and **4**, is the reaction associated with the transition structure of lowest energy among those considered in Scheme 3. This reaction may be formally compared with the degenerate 1,2-hydride shift on protonated benzene **1**, for which an energy barrier of 34 kJ mol^{-1} has been calculated [3]. In the present case, the transition structure **TS34** is 120 kJ mol^{-1} above **1**; this corresponds to a critical energy of 80 kJ mol^{-1} for the reaction **3** → **4** that implies an endothermicity of 63 kJ mol^{-1}.

Let us now consider the second kind of isomerization mechanisms which transform protonated benzene **1** into protonated fulvene. This set of reactions involves a 1,2-hydrogen shift as a first step; it is followed by a suitable ring contraction that may give rise to structures **3** or **4** (Scheme 4).

Starting from protonated benzene **1**, three 1,2-H shifts **a**, **b**, and **c** can generate six-membered rings **7**, **8**, and **9** which constitute local minima on the potential energy surface (Fig. 3). Structures **7** and **9** are of comparable energies (~210 kJ mol^{-1}) although structure **8** turns out to be a high energy species lying 140 kJ mol^{-1} above **7** and **9**. The three structures **7–9**

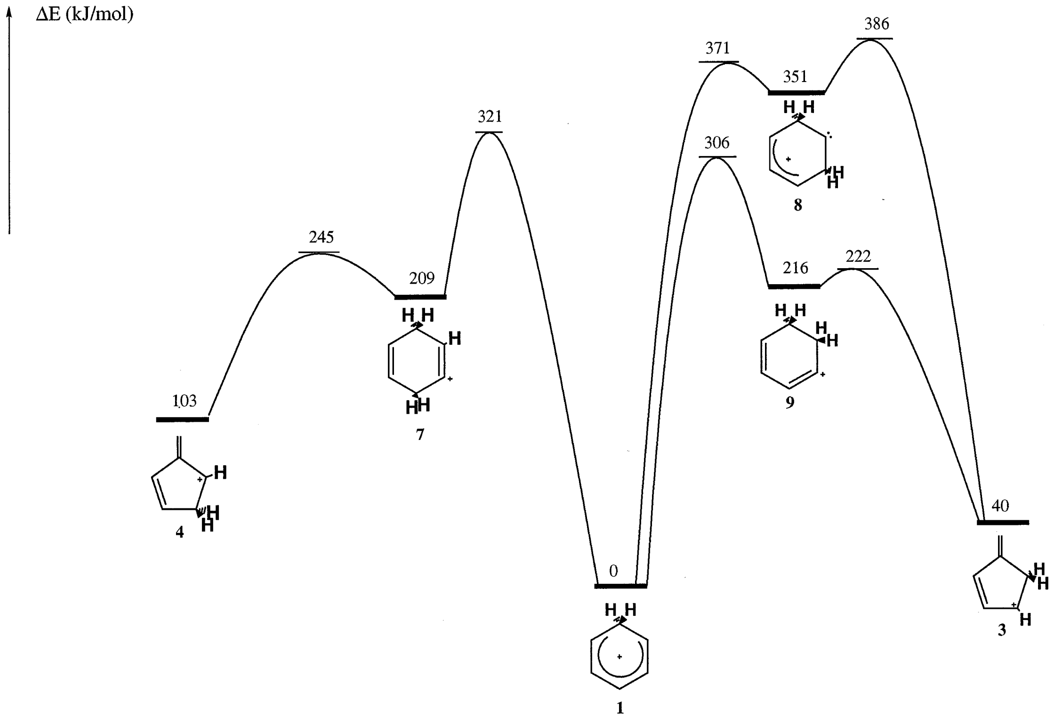


Fig. 3. Energy diagram for isomerizations processes of benzenium ion and protonated fulvene [G2(MP2)//B3LYP/6-31G* level]: reactions involving "hydrogen shift first."

evolve toward **3** and **4** by ring closure steps which need only a small amount of energy (6–37 kJ mol^{-1}). As shown in Fig. 3, the most favourable routes connecting **1** with **4** and **3** pass through structures **7** and **9**. In both cases the initial 1,2-H shift constitutes the energy determining step. Participation of structure **8** seems to be unlikely.

It is apparent that the activation barriers associated with the mechanisms presented in Scheme 4 are sizably higher than those involved in the reactions given in Scheme 3. Moreover, only the latter processes involve transition structures less energetic than the dissociation products $[C_6H_5]^+ + H_2$. Hence, we can conclude that the isomerization from protonated benzene towards protonated fulvene implies as a first step the formation of a bicyclo[3,1,0]-hexenyl cation, **5**, that may eventually evolve to yield isomers **2** and **3**. The latter yields the Cβ-protonated species **4** through a relatively low activation barrier.

3.3. Dissociation of protonated benzene

As recalled in the Introduction, the major dissociation process of protonated benzene is the loss of a hydrogen molecule. This reaction has been interpreted by a 1,1-elimination mechanism leading to the phenyl cation plus H_2 [2]. The endothermicity of this process, as deduced from experimental data, is equal to 270 kJ mol^{-1} (Table 2). Our computation gives an energy difference of 257 kJ mol^{-1} (Table 1) in close agreement with the experimental reaction enthalpy.

The second conclusion derived from the calculations is that the dissociation is a continuously endothermic process; no activation barrier is associated with the reverse reaction. In fact all attempts to locate the transition structure associated with the dissociation process failed, thus we decided to calculate point by point the corresponding potential energy profile. Considering the fact that we need to describe situa-

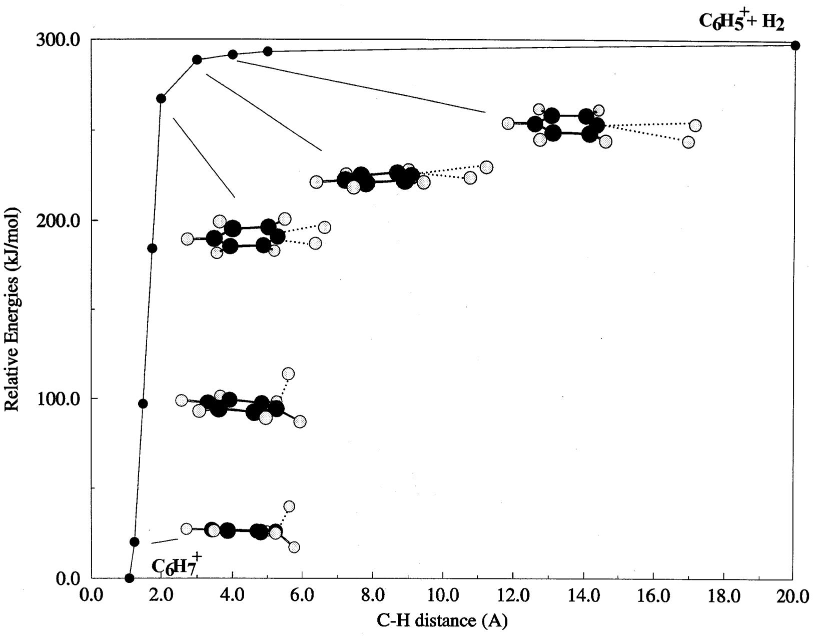


Fig. 4. Potential energy profile for dissociation of benzenium ion to $[C_6H_5]^+ + H_2$ (G2(MP2)//B3LYP/6-31+G* level without ZPE correction).

tions in which the distance between the two fragments is quite large, the geometry optimizations were carried out using a 6-31G+(d) basis set expansion rather than the 6-31G(d) used in the previous parts. To avoid any symmetry constraint the potential energy profile plotted in Fig. 4 was obtained for fixed values of the distance between the carbon and one of the H atoms of the CH_2 subunit of **1**. This procedure also ensures that no other mechanism than the 1,1-elimination may be feasible from **1**. At short C–H separation it was observed that the two hydrogens of the initial CH_2 moiety are almost symmetrically located (above and below) with respect to the $C_6H_5^+$ plane. At longer distances, the native H_2 molecule undergoes a significant tilt so that one of the hydrogens is farther away from the unsubstituted carbon of the $C_6H_5^+$ moiety than the other (see Fig. 4). The final energies used to construct the diagram of Fig. 4 were obtained at the G2(MP2) level using the B3LYP/6-31+G(d) optimized geometries.

Consistent with the previous discussion, the potential energy curve does not show any maximum between the local minimum **1** and the products $C_6H_5^+ + H_2$. We can then conclude that the energy required for the H_2 loss from benzenium ion **1** is simply given by the thermochemical dissociation limit [20]. Another point that can be noted is that the energy of the system increases very rapidly when the C–H distance increases: more than 90% of the dissociation energy is consumed when the C–H bond separation attains 2.0 Å. This is in line with the small polarizability of the hydrogen molecule (0.8 $Å^3$) that limits the extent of the ion-induced dipole interaction.

The extremely low kinetic energy released during the dissociation of metastable ions **1** (probably less than 4 kJ mol^{-1}) is in agreement with a continuously endothermic process. This observation also means that ions **1** of lifetime $\approx 10^{-5}$ s possess negligible internal energy. This seems surprising in view of the large critical energy of the fragmentation. Thus, in order to control this point we calculated the rate constant k(E) for the reaction $\mathbf{1} \rightarrow C_6H_5^+ + H_2$ in the RRKM framework [21]. Owing to the “loose” nature of the transient structure leading to the dissociation product, the orbiting transition state theory has been chosen [22]. All the parameters needed by the calcu-

Table 3
Parameters used in the RRKM calculations[a]

Benzenium ion					
Vibrational frequencies (cm^{-1})	3240	3240	3220	3220	3210
	2970	2970	1655	1590	1500
	1490	1430	1370	1320	1220
	1210	1160	1160	1070	1050
	1020	1010	1000	1000	900
	850	800	660	600	590
	420	330	220		
Rotational constant (cm^{-1}	0.1425				
Phenyl cation					
Vibrational frequencies (cm^{-1})	3250	3240	3230	3190	3190
	1800	1490	1490	1360	1300
	1200	1150	1110	1080	1000
	980	980	940	890	850
	700	660	520	460	420
	390	380			
Rotational constant (cm^{-1})	0.1597				
H_2					
Vibrational frequency (cm^{-1})	4465				
Rotational constant (cm^{-1})	60.62				
Polarizability (Å^3)	0.8				

[a] Vibrational frequencies and rotational constants are obtained using the B3LYP/6-31G* optimized geometries.

lation [23] are gathered in Table 3 and the resulting k verses E curve is presented in Fig. 5.

It is apparent from examination of Fig. 5 that the rate constant exhibits a rapid rise with internal energy E close to the threshold. The value of $k = 10^5\ s^{-1}$, associated with the dissociation of metastable ions, is attained for $E = 2.86$ eV, i.e. for an excess of energy above the fragments, E_{excess}, of only 0.2 eV (19 kJ mol^{-1}). From the latter, the contribution of the translational energy of the fragments may be estimated using the simple relationship proposed by Klots [24]. For a statistically dissociating system at a total energy E_{excess}, the average translational, rotational, and vibrational energies may be expressed in term of an operational temperature T^*. In this formulation, the average translational energy is simply the term RT^* and the total energy E_{excess} is given by:

$$E_{excess} = RT^* + (r - 1)RT^*/2 + \sum_{i=1}^{v} h\nu_i / \left[\exp(h\nu_i/RT^*) - 1\right]$$

The parameters r and v represent the rotational and vibrational degrees of freedom of the products, the ν_i's are the vibrational frequencies of the reaction products. By using $E_{excess} = 19$ kJ mol^{-1} and the frequencies quoted in Table 3, one calculates a mean translational energy of 3 kJ mol^{-1} for the $C_6H_5^+ + H_2$ system generated from metastable ion **1**. This is in agreement with experiments and confirms the validity of the models used here in the description of this 1,1-elimination process.

4. Conclusions

The present study explored the protonation energetics of benzene and fulvene and the most probable pathways connecting protonated benzene to the various forms of protonated fulvene. The stability and the central role played by the ipso protonated fulvene, the bicyclo[0,1,3]-hexenyl ion **5**, a species that has escaped the previous investigators, has been fully established. The most favourable route from protonated benzene **1** to the Cα-protonated fulvene **3** (the most

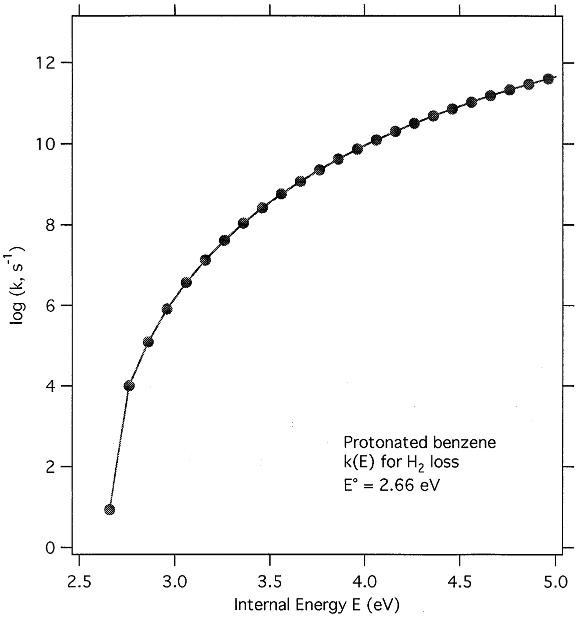


Fig. 5. Theoretical rate constant for dissociation of benzenium ion to $[C_6H_5]^+ + H_2$ (RRKM calculations, see text).

stable protonated form of fulvene) passes through **5**. Similarly the formation of the methylene protonated fulvene **2** needs the intermediacy of **5**. The level of calculation used (G2(MP2) on B3LYP/6-31G* optimized geometries) is sufficiently accurate to provide good protonation energies: 752 kJ mol^{-1} for benzene and 842 kJ mol^{-1} for fulvene. The dissociation of protonated benzene via a 1,1-H_2 extrusion process has been examined and it appears that the energy required by the reaction is simply given by its endothermicity. The excess energy of the dissociating species **1** having a lifetime of 10^{-5} s (the so-called metastable ions) is sufficiently low to explain the absence of an appreciable kinetic energy release during the separation of the products.

References

[1] F. Cacace, Acc. Chem. Res. 21 (1988) 215.
[2] D. Kuck, Mass Spectrom. Rev. 9 (1990) 583.
[3] M. Glukhovtsev, A. Pross, A. Nicolaides, L. Radom, J. Chem. Soc. Chem. Commun. (1995) 2347 and references cited therein.
[4] S. Lias, P. Ausloos, J. Chem. Phys. 82 (1985) 3613.
[5] A.W. McMahon, F. Chadikun, A.G. Harrison, R.E. March, Int. J. Mass Spectrom. Ion Processes 87 (1989) 275.
[6] J.A. Herman, K. Herman, T.B. McMahon, Can. J. Chem. 69 (1991) 2038.
[7] Z. Zhu, T. Gäumann, Org. Mass Spectrom. 28 (1993) 1111.
[8] T. Gäumann, G. Zhao, Z. Zhu, Rapid Commun. Mass Spectrom. 8 (1994) 1.
[9] R.S. Mason, C.M. Williams, P.D.J. Anderson, J. Chem. Soc. Chem. Commun. (1995) 1027.
[10] (a) C.H. DePuy, R. Gareyev, S. Fornarini, Int. J. Mass Spectrom. Ion Processes 161 (1997) 41; (b) B. Chiavarino, M.E. Crestoni, C.H. DePuy, S. Fornarini, R. Gareyev, J Phys. Chem. 100 (1996) 16201.
[11] G. Bouchoux, J.Y. Salpin, (unpublished).
[12] (a) L.A. Curtiss, K. Raghavachari, G.W. Trucks, J. Pople, J. Chem. Phys. 94 (1991) 7221; (b) L.A. Curtiss, K. Raghavachari, J. Pople, J. Chem. Phys. 98 (1993) 1293.
[13] (a) B.J. Smith, L. Radom, J. Am. Chem. Soc. 115 (1993) 4885; (b) B.J. Smith, L. Radom, Chem. Phys. Lett. 231 (1994) 345; (c) A.I. González, O. Mó, M. Yáñez, E. Leon, J. Tortajada, J-P. Morizur, I. Leito, P-C. Maria, J-F. Gal, J. Phys. Chem. 100 (1996) 10490; (d) J.C. Guillemin, M. Decouzon, P-C. Maria, J-F. Gal, O. Mó, M. Yáñez, J. Phys. Chem. A101 (1997) 9525.
[14] (a) C.W. Bauschlicher Jr., Chem. Phys. Lett. 246 (1995) 40; (b) B.J. Smith, L. Radom, J. Phys. Chem. 99 (1995) 6468.
[15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheesemann, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P Stewart, M. Head-Gordon, C. Gonzales, J.A. Pople, GAUSSIAN 94 Revision B, Gaussian, Inc., Pittsburgh, PA, 1995.
[16] G.A. Olah, J.S. Staral, G. Asencio, G. Liang, D.A. Forsyth, G.D. Mateescu, J. Am. Chem. Soc. 100 (1978) 6299.
[17] F. Cacace, M.E. Crestoni, S. Fornarini, J. Am. Chem. Soc. 114 (1992) 6776.
[18] S.E. Stein, Combus. Flame. 51 (1983) 257.
[19] J.E. Szulejko, T.B. McMahon, J. Am. Chem. Soc. 115 (1993) 7839.
[20] This conclusion is corroborated by a recent MP2/6-31G* study by E. DelRío, R. López, T.L. Sordo, J. Phys. Chem. A 101 (1997) 10090.
[21] T. Baer, W.L. Hase, Unimolecular Reaction Dynamics: Theory and Experiments, Oxford University Press, New York, 1996.
[22] (a) C.E. Klotz, in Kinetics of Ion-Molecule Reactions, P. Ausloos (Ed.), Plenum, New York, 1979; (b) E. Grice, K. Song, W.J. Chesnavich, J. Phys. Chem. 90 (1986) 3503.
[23] The TSTPST (QCPE 557) statistical theory package from W.J. Chesnavich, L. Bass, E. Grice, K. Song, D.A. Webb was used.
[24] (a) C.E. Klots, J. Chem. Phys. 58 (1973) 5364; (b) T. Baer, Adv. Chem. Phys. 64 (1986) 111.
[25] (a) S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (1988) (suppl 1); (b) E.P. Hunter, S.G. Lias, http://webbook.nist.gov
[26] V. Butcher, M.L. Costa, J.M. Dyke, A.R. Ellis, A. Morris, Chem. Phys. 115 (1987) 261.