10090 *J. Phys. Chem. A* **1997,** *101,* 10090−10094

A Theoretical Study of the H_2 Elimination from $C_6H_7^+$: An Example of the Role of Back-Donation in Carbocation Chemistry

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Received: September 12, 1997[⊗]

$C_6H_7^+$ has been investigated by using the ab initio method at MP2-FC/6-31G* level and single point calculations on the MP2 geometries at the MP4(SDTQ)-FC/6-31G* level. The most stable structure located corresponds to the benzenium ion $C_6H_7^+$ in which a proton is bonded to one of the carbon atoms of the benzene ring and an extension of the delocalization has taken place to include the attached proton, the π-electron density distribution being basically allylic in agreement with experimental findings. Two transition structures (TSs) for hydrogen scrambling were found on the $C_6H_7^+$ PES. The first one corresponds to the peripheral migration of a proton in the benzenium ion and determines an energy barrier of 7.8 kcal/mol at MP2 level (10.8 at MP4//MP2 level) in good agreement with experimental data. The second scrambling TS corresponds to the interchange of the two hydrogen atoms bonded to the same carbon atom in the ring of the benzenium ion and presents an energy barrier of 59.2 kcal/mol at MP2 level (62.6 at MP4//MP2 level). The H_2-elimination is an endoergic process that proceeds through a very late TS and an intermediate very close in energy to it that finally renders the products, $C_6H_5^+ + H_2$, without any energy barrier. The activation energy for this process (70.3 and 70.1 kcal/mol at MP2 and MP4//MP2 levels, respectively) is practically its endoergicity (71.1 kcal/mol at MP2 level and 70.8 kcal/mol at MP4//MP2 level) in accordance with the experimental finding of null energy release as relative motion between the fragments. A configuration analysis of the wave function of $C_6H_7^+$ along the reaction coordinate for H_2-elimination clearly shows that the back-donation from the NHOMO of $C_6H_5^+$ to the LUMO of H_2 plays a fundamental role in the bonding structure of the benzenium ion. The H_2 elimination takes place through deactivation of the back-bonding at an early stage in the process.

Introduction

An important characteristic of unimolecular decompositions is the energy release as relative motion between the fragments.[1] The relative amount of kinetic energy release is determined by the dynamics of the process and therefore constitutes a proof of the shape of the potential energy surface (PES) in the exit valley. Large translational energy releases have been experimentally observed for some eliminations of H_2 from small organic ions.[2] It has been inferred that these reactions are 1,2-eliminations proceeding via concerted symmetry-forbidden routes. In such routes intended crossings are foiled and, consequently, kinetic energy is released. In contrast, many of the H_2 eliminations proceed without relatively large releases of kinetic energy and have been interpreted as 1,1-eliminations proceeding through symmetry-allowed mechanisms. Therefore, kinetic energy release has been applied as a mechanistic criterion in studying H_2 loss from some simple cations.[2b]

Arenium ions are intermediates in electrophilic substitution reactions as well as in many acid-catalyzed transformations of aromatics. Thus a considerable effort has been devoted to the determination of the electronic structure of arenium ions and their reactivity through both experimental and theoretical methods. The simplest arenium ion, the benzenium ion ($C_6H_7^+$, C_{2v}), may be produced by numerous methods in the mass spectrometer (e.g. via fragmentation of benzyl alcohol[3]); the cation has also been produced via protonation of benzene in a chemical ionization source. The process $C_6H_7^+ \rightarrow C_6H_5^+ + H_2$ has been experimentally established in a mass spectrometer to occur without release of kinetic energy.[2b] Consequently, it has been proposed that this is a H_2 1,1-elimination reaction proceeding via a concerted symmetry-allowed route in which the two electrons of the NHOMO of $C_6H_7^+$ are able to pass into the π system to complete the aromatic sextet of the phenyl cation.

In this work we present an *ab initio* study of the $C_6H_7^+$ PES focusing our attention on the mechanism of the H_2 elimination from the benzenium ion ($C_6H_7^+$, C_{2v}). A detailed analysis of the electronic rearrangement involved will be performed in order to rationalize the experimental findings and get a deeper understanding of the mechanism of the process.

Methods

Ab initio calculations were performed with the Gaussian 94 series of programs.[4] Stable species were fully optimized and transition states located using Schlegel's algorithm[5] at the MP2-FC/6-31G* theory level. All the critical points were further characterized and the ZPVE was evaluated by analytical computations of harmonic frequencies at MP2-FC/6-31G* and scaled by a factor of 0.94.[6] Single-point calculations on the MP2 geometries were also carried out at the MP4(SDTQ)-FC/6-31G* level.

Reaction paths passing through the TSs located in this work were studied by MP2/-6-31G* Intrinsic Reaction Coordinate (IRC) calculations using the Gonzalez and Schlegel method[7] implemented in Gaussian 94.

The *ab initio* wave functions were analyzed by means of a theoretical method developed by Fukui's group[8] based on the expansion of the molecular orbitals (MOs) of a complex A−B in terms of those of its fragments. A configuration analysis is performed by writing the MO wave function of the combined system in terms of various electronic configurations

$$\Psi = C_0\Psi_0 + \sum_q C_q\Psi_q$$

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

S1089-5639(97)02989-7 CCC: $14.00

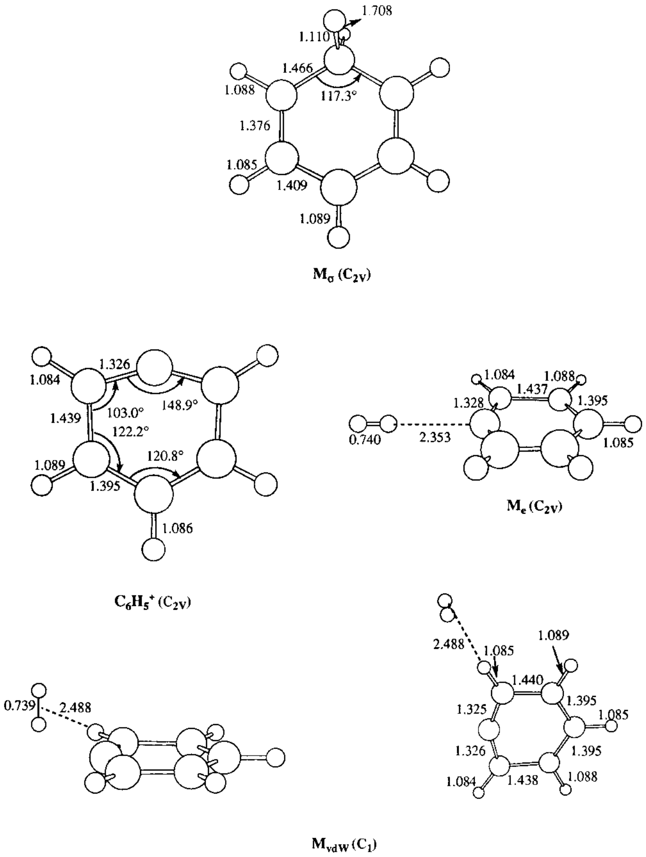


Figure 1. MP2-FC/6-31G* minimum geometries located on the $C_6H_7^+$ PES. Distances are given in angstroms.

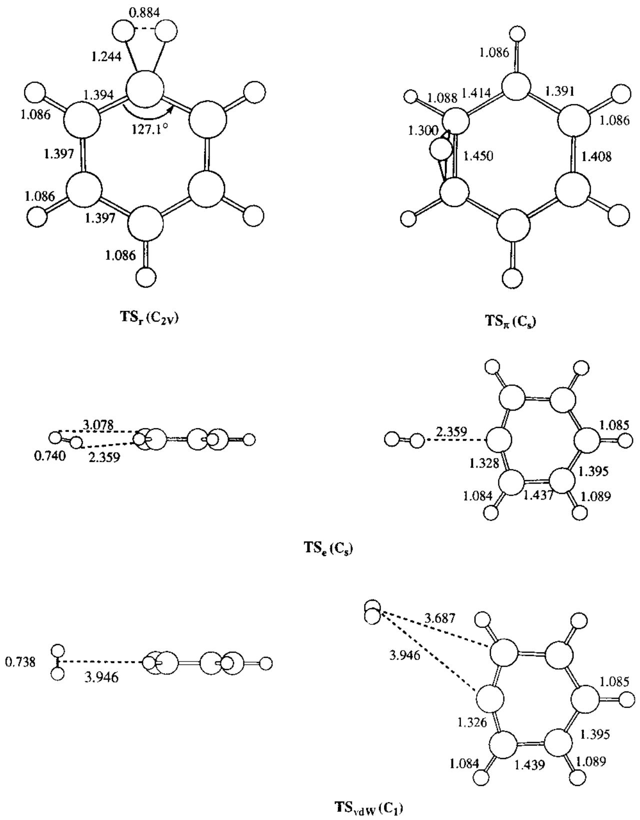


Figure 2. MP2-FC/6-31G* transition states located on the $C_6H_7^+$ PES. Distances are given in angstroms.

where Ψ_0 (zero configuration, AB) is the state in which neither electron transfer nor electron excitation takes place, and Ψ_q stands for monotransferred configurations $\Psi_{o\to u'}$, in which one electron in an occupied MO, o, in one of the two fragments A or B is transferred to an unoccupied MO, u', of the other fragment (A^+B^-, and A^-B^+ configurations), monoexcited configurations, $\Psi_{o\to u}$, in which one electron in an occupied MO, o, of any of the two fragments is excited to an unoccupied MO, u, of the same fragment (A^*B and AB^* configurations), and so on. This configuration analysis which has proved useful for understanding the physicochemical features of chemical interactions was performed by means of the ANACAL program.[9]

Results and Discussion

Figures 1 and 2 show the optimized geometry of the critical points located on the $C_6H_7^+$ PES. Table 1 presents the relative energies corresponding to the structures in Figures 1 and 2. Unless otherwise specified, the relative energies given in the text hereafter correspond to the MP2-FC/6-31G* level.

The most stable structure located on the MP2-FC/6-31G* PES is the σ complex of C_{2v} symmetry (benzenium ion), $\mathbf{M}_\sigma$, (see Figure 1) in which a proton is bonded to one of the carbon atoms of the benzene ring with a C−H bond distance of 1.110 Å. The protonated carbon atom presents a distorted sp^2 hybridization indicating that an extension of the delocalization has taken place to include the attached proton. Population analysis shows that the π-electron density in the benzenium cation is preferentially accumulated at the meta positions of the ring relative to the protonated carbon atom. These computational facts are in accord with the experimental results obtained by Olah and collaborators.[10b]

Two TSs for hydrogen scrambling were also located on this MP2 PES (see Figure 2). The first one, $\mathbf{TS}_\pi$, corresponds to a π complex of C_s symmetry in which the proton is bonded simultaneously to two of the carbon atoms of the benzene ring with a C−H distance of 1.300 Å. This $\mathbf{TS}_\pi$ presents an energy barrier of 7.8 (10.8 at MP4//MP2 level) kcal/mol including the MP2 ZPVE correction, and connects two neighbor σ complexes along a peripheral migration of the proton. The experimental activation energy for this process deduced from the temperature dependence of the NMR spectrum in superacid solution has been reported to be 8−10 kcal/mol.[10] The second scrambling TS, $\mathbf{TS_r}$, has a C_{2v} symmetry, and presents the two hydrogen atoms bonded to the same carbon atom of the ring in the molecular plane with a value of the two C−H distances of 1.244 Å. This TS connects the σ complex, $\mathbf{M}_\sigma$, with its mirror image with respect to the molecular plane; i.e., it allows the interchange of the two hydrogen atoms bonded to the same carbon atom in the σ complex by a rotation movement. The energy barrier associated with this TS is 59.2 (62.6 at MP4//MP2 level) kcal/mol.

Let us now consider the H_2 elimination from the σ complex (benzenium ion). Along the reaction coordinate for this process a TS, $\mathbf{TS_e}$ (see Figure 2), was located with a C_s symmetry in which the distance between the two leaving hydrogen atoms is 0.740 Å (the H_2 bond length at MP2-FC/6-31G* level is 0.738 Å). The already practically formed hydrogen molecule presents an angle of about 7° relative to the symmetry axis of the $C_6H_5^+$ moiety. The shortest distance between the bare carbon atom of $C_6H_5^+$ and the H_2 molecule is 2.359 Å. This $\mathbf{TS_e}$ is 70.3 (70.1 at MP4//MP2) kcal/mol less stable than the benzenium ion. Thus our best estimation of the activation energy for the H_2 elimination from $C_6H_7^+$ is 61.0 kcal/mol including the ZPVE correction, to compare with the experimental value of 65 kcal/mol.[2b] $\mathbf{TS_e}$ connects the benzenium ion, $\mathbf{M}_\sigma$, with an intermediate of C_{2v} symmetry, $\mathbf{M_e}$ (see Figure 1), in which the bond distance between the two leaving hydrogen atoms is 0.740 Å. The hydrogen molecule is now placed along the symmetry axis

TABLE 1: Total Energies (hartree), Scaled (0.94) Zero-point Energy Corrections, ZPVE (kcal/mol), and Relative (kcal/mol) Energies (ZPVE not included) Corresponding to the Most Important Structures Located on the $C_6H_7^+$ Potential Energy Surface

	total energies			relative energies	
species	MP2-FC/6-31G*	MP4(SDTQ)-FC/6-31G*//MP2-FC/6-31G*	ZPVE	MP2-FC/6-31G*	MP4(SDTQ)-FC/6-31G*//MP2-FC/6-31G*
$\mathbf{M}_\sigma$ (C_{2v})	−231.75031	−231.83197	66.0	0.0	0.0
$C_6H_5^+$ (C_{2v}) + H_2	−231.63700	−231.71915	56.2	71.1	70.8
$\mathbf{M}_\mathbf{e}$ (C_{2v})	−231.63826	−231.72029	57.0	70.3	70.1
$\mathbf{M}_\mathbf{vdW}$ (C_1)	−231.63773	−231.71985	56.9	70.6	70.3
$\mathbf{TS}_\mathbf{r}$ (C_{2v})	−231.65599	−231.73226	63.2	59.2	62.6
$\mathbf{TS}_\pi$ (C_s)	−231.73538	−231.81220	64.4	9.4	12.4
$\mathbf{TS}_\mathbf{e}$ (C_s)	−231.63826	−231.72029	56.9	70.3	70.1
$\mathbf{TS}_\mathbf{vdW}$ (C_1)	−231.63746	−231.71961	56.6	70.8	70.5

TABLE 2: Coefficients of the Most Important Electronic Configurations of Fragments (A = $C_6H_5^+$, B = H_2), and Net Charge Transfer (CT) from H_2 to $C_6H_5^+$ for the Chemically Important Structures along the H_2 Elimination from the $C_6H_7^+$

species	AB	A^-B^+ LU←HO	$A^{2-}B^{2+}$ LU←HO	$A^-B^\pm$ LU←HO NHO→LU	A^*B^* LU LU ↑ ↑ NHO HO	A^+B^- NHO→LU	AB^* LU ↑ HO	CT B→A
$\mathbf{M}_\sigma$	0.0524	−0.1765	0.1971	0.1328	0.0616	−0.0394	0.0000	0.61
RL	0.0325	−0.1346	0.2016	0.1140	0.0794	0.0384	0.0000	0.61
TSL	0.9098	−0.2517	0.0000	0.0000	0.0000	−0.0061	0.1374	0.17
$\mathbf{TS}_\mathbf{e}$	0.9918	−0.0535	0.0000	0.0000	0.0000	0.0000	0.0580	0.01

TABLE 3: Most Important Changes in the Occupation Numbers, $\Delta\nu$, of the MOs of the Chemically Important Structures along the H_2 Elimination from the $C_6H_7^+$

	$\Delta\nu$				
	A: $C_6H_5^+$			B: H_2	
species	HO-4	NHO	LU	HO	LU
$\mathbf{M}_\sigma$	−0.23	−0.60	1.37	−1.35	0.66
RL	−0.20	−0.56	1.29	−1.33	0.67
TSL	0.00	0.00	0.21	−0.17	0.02
$\mathbf{TS}_\mathbf{e}$	0.00	0.00	0.01	−0.01	0.00

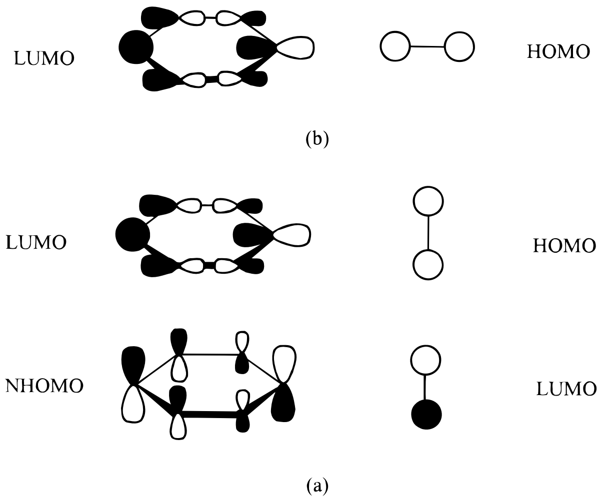


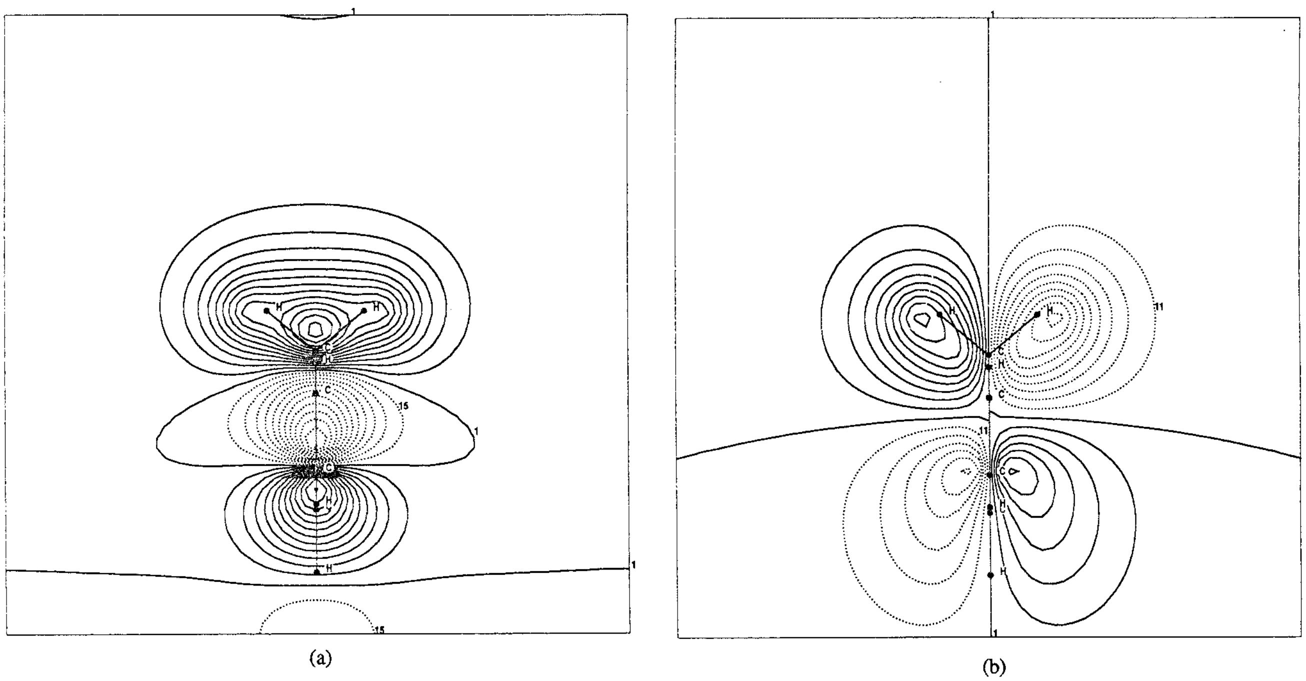
Figure 3. Interaction between H_2 and $C_6H_5^+$ when the hydrogen molecule is (a) perpendicular to the symmetry axis of $C_6H_5^+$, and (b) along the symmetry axis of $C_6H_5^+$.

of $C_6H_5^+$. The distance between the carbon atom of the ring and the nearest hydrogen atom of the H_2 molecule is 2.353 Å. $\mathbf{M}_\mathbf{e}$ has practically the same MP2 and MP4//MP2 energy as $\mathbf{TS}_\mathbf{e}$ and evolves without any energy barrier to the products $C_6H_5^+$ + H_2 which are 71.1 (70.8 at MP4//MP2 level) kcal/mol above $\mathbf{M}_\sigma$.

An extensive search for different paths for the H_2 elimination was performed without success. Then, according to the present calculations, the H_2 elimination is a 1,1 process, and the energy barrier for the H_2 elimination from $C_6H_7^+$ cation is practically the endoergicity of the process. As a consequence, our calculations predict that no kinetic energy release is to be expected for this reaction in agreement with experimental findings.[2b]

A minimum energy van der Waals structure of C_1 symmetry, $\mathbf{M}_\mathbf{vdW}$, was also located in which the distance between the two hydrogen atoms of the H_2 moiety is 0.739 Å, and the H_2 bond is completely perpendicular to the C−H bond next to the bare carbon atom of $C_6H_5^+$ (see Figure 1). This $\mathbf{M}_\mathbf{vdW}$ structure is 70.6 (70.3 at MP4//MP2 level) kcal/mol less stable than the benzenium ion and is connected with $\mathbf{M}_\mathbf{e}$ through a TS of C_1 symmetry, $\mathbf{TS}_\mathbf{vdW}$, which is 0.5 (0.4 at MP4//MP2 level) kcal/mol above $\mathbf{M}_\mathbf{e}$ ($\mathbf{M}_\mathbf{vdW}$, $\mathbf{TS}_\mathbf{vdW}$, and $\mathbf{M}_\mathbf{e}$ have practically the same energy when the ZPVE is included).

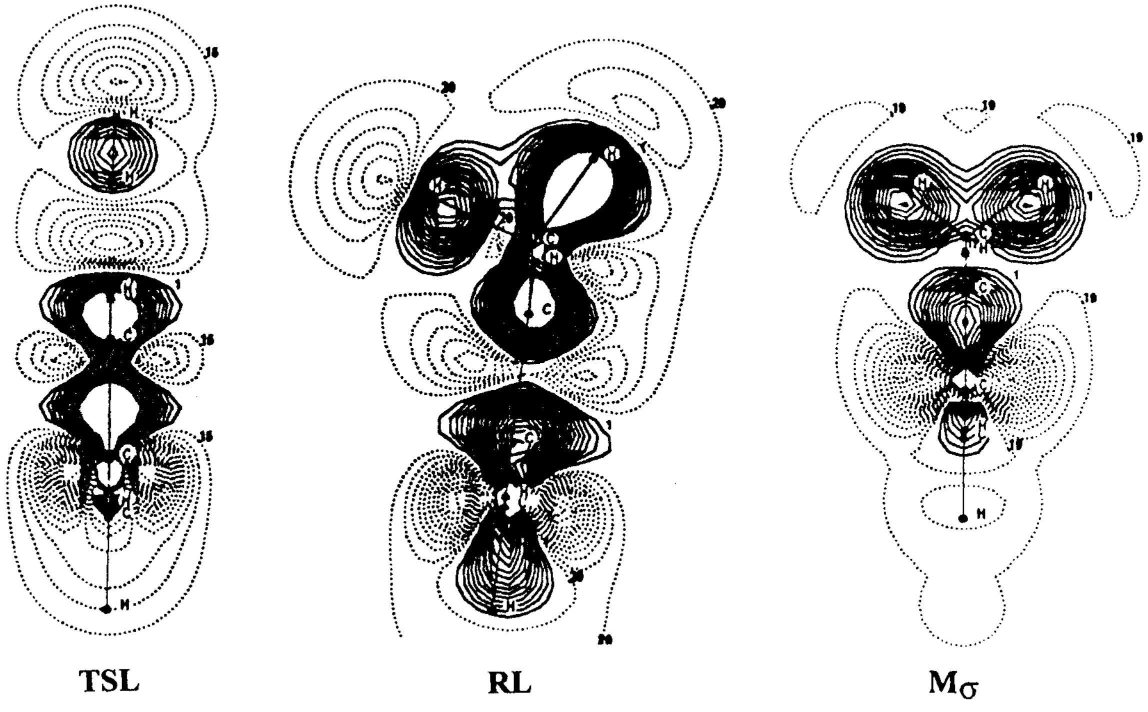
To get a deeper understanding of the redistribution of electrons and the evolution of the energy of the system for the H_2 loss from $C_6H_7^+$, a configuration analysis of several structures along the reaction path was performed. Table 2 displays the coefficients of the most important electronic configurations of $C_6H_5^+$ and H_2 fragments in the supermolecule $C_6H_7^+$ at the σ complex, $\mathbf{M}_\sigma$, at $\mathbf{TS}_\mathbf{e}$, and at two structures, **RL** (reactant-like) and **TSL** (TS-like), located between them along the reaction coordinate. At $\mathbf{M}_\sigma$ the wave function is basically a mixture of the monotransference A^-B^+ (A = $C_6H_5^+$; B = H_2), the ditransference $A^{2-}B^{2+}$, from the HOMO of H_2 to the LUMO of $C_6H_5^+$, and the simultaneous cross ditransference from the HOMO of H_2 to the LUMO of $C_6H_5^+$ and from the NHOMO of $C_6H_5^+$ to the LUMO of H_2, designated as $A^\mp B^\pm$, with small contributions from the zero configuration, AB, the diexcitation A^*B^* (NHOMO−LUMO; HOMO−LUMO) and the monostransference A^+B^- (NHOMO−LUMO). As a result there is a net charge transfer from the hydrogen moiety to the $C_6H_5^+$ fragment of 0.61e according to a Mulliken population analysis. The cross ditransference $A^\mp B^\pm$ and the monostransference A^+B^- (NHOMO−LUMO) determine the presence of a strong back-donation from the cation to the H_2 fragment. This back-donation is also clearly reflected in Table 3 where the most important changes in the occupation numbers of the MOs ($\Delta\nu$) of the two fragments are collected. We see in this Table 3 that the NHOMO of the cation has lost 0.60e and the LUMO of the hydrogen molecule has gained 0.66e. Thus at $\mathbf{M}_\sigma$ the HOMO(H_2)−LUMO($C_6H_5^+$) interaction between the fragments is augmented by a strong back-bonding through the LUMO(H_2)−



(a)

(b)

Figure 4. Contour plots of (a) the HOMO-3 (reflecting the interaction between the HOMO of H_2 and the LUMO of $C_6H_5^+$), and (b) the HOMO-1 (reflecting the interaction between the NHOMO of $C_6H_5^+$ and the LUMO of H_2) of the benzenium ion $C_6H_7^+$. Full and dashed lines distinguish between amplitudes of different signs.



TSL **RL** **M$_\sigma$**

Figure 5. Plot of the molecular density minus spherically averaged atomic density showing where the electrons have come from (dotted contours) and gone to (solid contours) when the bonds are formed at protonated benzene, $\mathbf{M}_\sigma$, and at two points of the reaction coordinate for the H_2 elimination from $C_6H_7^+$, **RL** and **TSL**, where the hydrogen molecule presents an angle of about 73° relative to the symmetry axis of $C_6H_5^+$, and is located along it, respectively.

NHOMO($C_6H_5^+$) interaction (see Figure 3a) which leads to the cleavage of the H−H bond and makes possible the formation of the two C−H bonds from which the hydrogen molecule will be eliminated. It is interesting to note here that a related important structure is the nonclassical form of the phenonium ion.[11] Figure 4 displays the contour plots of the MOs of the $C_6H_7^+$ supermolecule reflecting the interaction between (a) the HOMO of H_2 and the LUMO of $C_6H_5^+$, and (b) between the LUMO of H_2 and the NHOMO of $C_6H_5^+$. These contour plots clearly show that the back-donation from the NHOMO of $C_6H_5^+$ to the LUMO of H_2 determines an electron density corresponding to the formation of two C−H bonds whereas the HOMO(H_2)−LUMO($C_6H_5^+$) interaction would lead rather to a three-center bonding between the fragments. This is manifest in $\mathbf{TS_r}$ where because of zero overlap between the NHOMO of $C_6H_5^+$ and the LUMO of H_2 a three-center interaction takes place between the two fragments and the H_2 molecule is almost formed (see Figure 2).

The system evolves along the reaction coordinate for the H_2 elimination through structures such as **RL** where one of the C−H bonds has elongated and the net charge transfer from the hydrogen molecule to the phenyl cation has a value of 0.61e. At **RL** the configuration mixture is qualitatively the same as that at $\mathbf{M}_{\sigma}$ (see Table 2). When the π overlap between the LUMO of H_2 and the NHOMO of $C_6H_5^+$ (see Figure 3a) is very small, the back-donation disappears, and the leaving hydrogen molecule forms along the symmetry axis of the phenyl cation remaining only the HOMO(H_2)−LUMO($C_6H_5^+$) interaction between the fragments (see Figure 3b). This is the situation at **TSL** where the wave function is the zero configuration AB, with some contribution from the monotransference A^-B^+-(HOMO−LUMO) and the monoexcitation AB^*(HOMO−LUMO), and the net charge transfer from H_2 is 0.17e (see Table 2). Figure 5 presents the evolution of the molecular electronic density from $\mathbf{M}_{\sigma}$ through **TSL** showing clearly the formation of the leaving H_2 molecule. Finally, at $\mathbf{TS_e}$ the wave function is practically the zero configuration, AB, with very small contributions from the monostranference A^-B^+(HOMO−LUMO)) and the monoexcitation AB^*(HOMO−LUMO). In agreement with this a net charge transfer of only 0.01e takes place from H_2 to the phenyl cation. Thus, our analysis supports a previous interpretation[2b] according to which in the H_2 elimination from the benzenium ion, the four electrons of the two σ C−H bonds involved in the reaction rearrange in such a way that the two electrons of the HOMO-3 of $C_6H_7^+$ (see Figure 4a) pass into the HOMO of the H_2 molecule, while the two electrons of the NHOMO of $C_6H_7^+$ (see Figure 4b) pass into the π system of the phenyl cation.

In summary, according to our calculations the H_2 loss from the benzenium ion, $C_6H_7^+$, is an endoergic 1,1-elimination process whose energy barrier equals practically its endoergicity in agreement with experimental findings. The presence of a strong back-donation through the LUMO(H_2)−NHOMO($C_6H_5^+$) interaction is essential to the formation of the benzenium ion. The elimination of the H_2 molecule takes place through deactivation of that back-bonding at an early stage in the process. The two electrons implied in the HOMO(H_2)−LUMO($C_6H_5^+$) interaction between the fragments pass into the bonding MO of the eliminated hydrogen molecule, while the two electrons implied in the LUMO(H_2)−NHOMO($C_6H_5^+$) interaction pass into the π system of the phenyl cation.

Acknowledgment. The authors are grateful to Prof. Agustí Lledós for helpful comments and suggestions, and to DGICYT (Spain) for financial support (PB94-1314-C03-01). E. del R. also thanks to the DGICYT for a grant.

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