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A Theoretical Study of the H_2 Elimination from $C_2H_5^+$

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The elimination of H_2 from $C_2H_5^+$ was investigated at MP2−FC/6-311+G(d,p), QCISD/6-311+G(d,p), and QCISD(T)/6-311++G(3df,2p)//QCISD/6-311+G(d,p) levels. This elimination is an endoergic reaction that proceeds through a late transition state in which two C−H bonds are synchronously stretched with an energy barrier close to its endoergicity, in agreement with experimental results. Back-donation from the HOMO of $C_2H_3^+$ to the LUMO of H_2 plays a crucial role in this process. This back-donation depends on the elongation of the C−C bond so that H_2 is eliminated when the synchronous stretching of the two C−H bonds is out of phase with respect to the stretching of the C−C bond.

Introduction

The elimination of H_2 from organic cations is an interesting reaction in which the excess energy may appear as kinetic energy or as internal (vibrational) energy in the products.[1−3] Some eliminations of H_2 from small organic ions presenting large translational energy releases have been interpreted as 1,2-eliminations proceeding via concerted symmetry-forbidden routes. 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.[1,2]

The H_2 elimination from $C_2H_5^+$ has been studied by different experimental techniques.[2−7] A small kinetic energy release has been detected experimentally, and so this reaction is thought to proceed by a symmetry-allowed 1,1-elimination. Two of the four electrons in the two C−H bonds implied in the process pass into the eliminated hydrogen molecule and the other two pass into the π system of the vinylium ion.[2] The experimental activation energies reported for this process are 67,[2,3] 55,[5] and 32.3−40 kcal/mol.[6] The enthalpy change in the reaction, calculated from the heats of formation,[8] is 50 kcal/mol.[6] The study of deuterium isotope effects has shown that the loss of H_2 from the ethyl cation occurs through a transition state (TS) in which two C−H bonds are synchronously stretched.[4] A MINDO/3 study of this H_2 elimination[9] has reported a TS located from a second-order saddle point structure of C_s symmetry by a displacement along the antisymmetric combination of the two C−H stretches, which is not in accord with the classically accepted formalism for a 1,1-elimination and seems to be in conflict with the results obtained in the aforementioned isotope effects study. Therefore, the aim of the present work is to further investigate the title process with ab initio methods to elucidate its mechanism and the electronic rearrangement taking place in it. Special attention will be paid to the electronic transferences between the H_2 and $C_2H_3^+$ fragments given that very recently it has been shown that back-donation plays a fundamental role in the H_2 elimination from the benzenium ion.[10]

Methods of Calculation

Ab initio calculations were carried out with the Gaussian 94 series of programs[11] using the 6-311+G(d,p) basis set.[12] Stable species were fully optimized and TSs were located using Schlegel's algorithm[13] at the MP2−FC and QCISD[14] theory levels. All the critical points were further characterized and the zero-point vibrational energy (ZPVE) was evaluated by analytical MP2−FC and numerical QCISD computations of harmonic frequencies. Single-point calculations were performed on the QCISD optimized geometries at the QCISD(T)/6-311++G(3df,2p) level.

Reaction paths passing through the TSs located in this work were studied by MP2−FC/6-311+G(d,p) Intrinsic Reaction Coordinate (IRC) calculations using the Gonzalez and Schlegel method[15] implemented in Gaussian 94.

The ab initio wave functions were analyzed by means of a theoretical method developed by Fukui's group[16] 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

$$\Psi = C_o\Psi_o + \sum_q C_q\Psi_q \qquad (1)$$

where Ψ_o (zero configuration, AB) is the state in which neither electron transfer nor electron excitation takes place, and Ψ_q stands for monotransferred configurations $\Psi_{o\rightarrow u'}$, 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), and monoexcited configurations, $\Psi_{o\rightarrow u}$, 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 with the ANACAL program.[17]

Results and Discussion

Figure 1 displays the optimized geometry of the critical points located on the $C_2H_5^+$ potential energy surface (PES). Table 1

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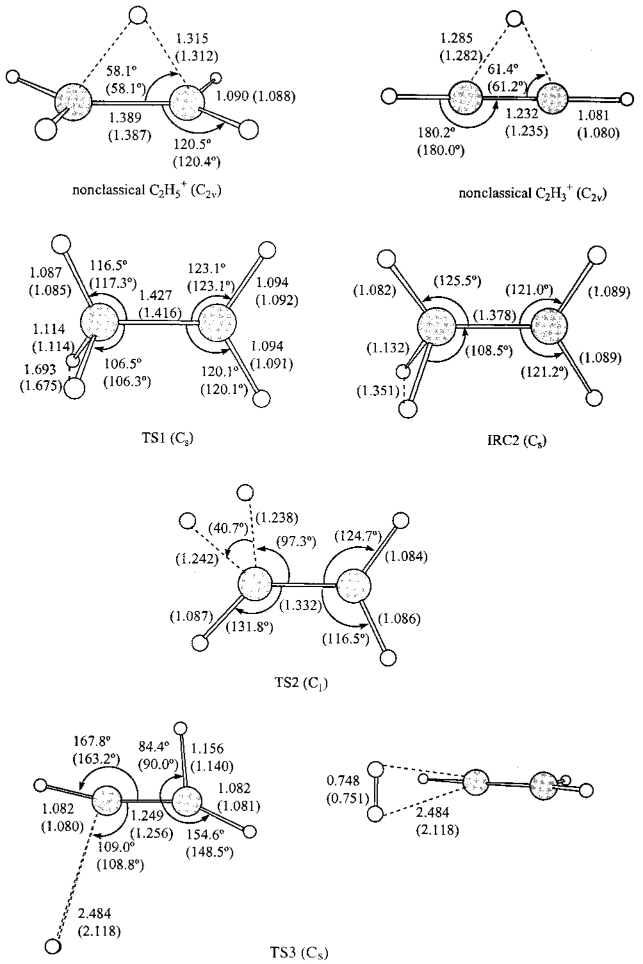

Figure 1. QCISD/6-311+G(d,p) and MP2−FC/6-311+G(d,p) (in parentheses) geometries corresponding to the most important structures located on the $C_2H_5^+$ PES. Distances are given in angstroms and angles in degrees.

presents the corresponding total and relative energies at the theory levels employed in the present work. Unless otherwise specified, the relative energies given in the text hereafter correspond to the QCISD(T)/6-311++G(3df,2p)//QCISD/6-311+G(d,p) level including the ZPVE correction at the QCISD level.

The most stable structure located on the MP2−FC and QCISD PESs is the nonclassical structure $C_2H_5^+$ of C_{2v} symmetry. A TS of C_s symmetry for hydrogen scrambling was also found (TS1). This TS allows the bridged H atom and any of the other four H atoms in the system to interchange their position through an energy barrier of 6.01 kcal/mol. At MP2−FC level, a TS of C_s symmetry was located in which a hydrogen molecule interacts with one of the carbon atoms of the $C_2H_3^+$ fragment (TS2). According to IRC calculations, this TS2 connects two $C_2H_5^+$ nonclassical structures through an energy barrier of 43.53 kcal/mol at the MP2−FC level. This TS disappears at the QCISD level.

A TS of C_s symmetry for the H_2 elimination from $C_2H_5^+$ was found on the MP2−FC and QCISD PESs (TS3). In this TS, the distance between the two leaving hydrogen atoms is 0.751 Å at the MP2−FC level (0.748 Å at the QCISD level) and the H−H bond is completely perpendicular to the $C_2H_3^+$ plane at a distance of 2.118 Å (2.484 Å) of the nearest carbon atom (see Figure 1). The geometry of TS3 is then in accord with the results of the experimental study of deuterium isotope effects on the H_2 elimination from $C_2H_5^+$.[4] The calculated energy barrier corresponding to this TS is 49.67 kcal/mol. TS3 connects the bridged structure $C_2H_5^+$ with the nonclassical structure $C_2H_3^+$ of C_{2v} symmetry plus H_2. These products are 47.63 kcal/mol less stable than the reactant, which is in reasonable agreement with the enthalpy change evaluated from the experimental heats of formation.[6] According to the present results, the energy barrier for the H_2 loss from $C_2H_5^+$ is close to the endoergicity of the process. As a consequence, our calculations predict that this process occurs with small kinetic energy release, which is in agreement with experimental findings.

To gain a deeper understanding of the electronic rearrangement taking place in the H_2 loss from $C_2H_5^+$, a configuration analysis of the most significant structures along the reaction coordinate was performed. Table 2 collects the coefficients of the most important electronic configurations of $C_2H_3^+$ and H_2 fragments in the supermolecule $C_2H_5^+$ at TS3 and at three structures, IRC1−IRC3, located along the IRC path between this TS and the reactant (see Figure 2). Table 3 displays the most important changes in the occupation numbers of the MOs of the two fragments. According to IRC calculations, the loss of H_2 from the nonclassical ethyl cation takes place as follows: the bridged H atom moves toward one of the ends of the molecule breaking the C_{2v} symmetry and displacing one of the C−H bonds from the molecular plane (IRC1). Subsequently, this H atom ends up bonded to only one C atom with a C−H bond length equal to that of the displaced C−H bond, both bonds being situated symmetrically with respect to the molecular plane with C_s symmetry (IRC2). Then, the angle between the two aforementioned C−H bonds becomes smaller and the leaving H_2 molecule starts to form (IRC3). Finally, TS3 is reached where the H_2 molecule is practically formed and is separated 2.118 Å from the $C_2H_3^+$ fragment. Concerning the evolution of the electronic density, our configuration analysis shows that the electronic transference from the HOMO of H_2 to the LUMO of $C_2H_3^+$ (A^-B^+ and/or $A^{2-}B^{2+}$) is important all along the path between the reactant and TS3 diminishing as the two fragments separate each other. At IRC1 and IRC2, the simultaneous cross ditransference $A^{\mp}B^{\pm}$ has an appreciable weight, indicating the presence of a strong back-donation from $C_2H_3^+$ to the H_2 fragment. This back-donation is also clearly reflected in the depopulation of the HOMO of the cationic fragment and the increment in the occupation number of the LUMO of H_2 (see Table 3). Consequently, at those structures, the hydrogen molecule has not yet started to form and the two C−H bonds persist. In contrast, at IRC3, the back-donation has considerably diminished, as clearly displayed by an important reduction in the depopulation of the HOMO of the vinylium ion and in the increment in the occupation number of the LUMO of H_2. Therefore, the zero configuration AB takes the leading role, indicating that the leaving hydrogen molecule is starting to form as the two fragments separate each other. Finally, at TS3 the wave function of the system is practically the zero configuration with a small contribution from the monotransference A^-B^+ from the HOMO of H_2 to the LUMO of $C_2H_3^+$. As a consequence, the net charge transfer from H_2 is very small.

The following point could be raised: Why isn't H_2 elimination through TS1 possible given that the TS for H_2 elimination, TS3, evolves according to IRC calculations through structures (e.g., IRC2) very similar to that of TS1? The answer clearly reveals the crucial role played by back-donation from the cationic fragment in this process. In effect, the relative weight of back-donation is larger at TS1 than at IRC2, as reflected in the larger loss of population of the HOMO of $C_2H_3^+$ and the

TABLE 1: Total Energies (Hartree), ZPVE (kcal/mol), and Relative Energies (kcal/mol) (ZPVE not included) Corresponding to the Most Important Structures Located on the $C_2H_5^+$ PES

	MP2−FC/6-311+G(d,p)	QCISD/6-311+G(d,p)		QCISD(T)/6-311++G(3df,2p)
species	energy	energy	ZPVE	energy
nonclassical $C_2H_5^+$ (C_{2v})	0.00 (−78.61401)	0.00 (−78.64572)	38.48	0.00 (−78.70086)
H_2 + nonclassical $C_2H_3^+$ (C_{2v})	57.68 (−78.52209)	59.42 (−78.55103)	27.90	58.21 (−78.60810)
TS1	7.93 (−78.60137)	5.87 (−78.63637)	37.63	6.86 (−78.68993)
TS2	45.65 (−78.54127)			
TS3	61.48 (−78.51604)	59.82 (−78.55039)	29.41	58.74 (−78.60725)

TABLE 2: Coefficients of the Most Important Electronic Configurations of Fragments (A = $C_2H_3^+$, B = H_2) and Net Charge Transfer (CT) from H_2 to $C_2H_3^+$ for the Chemically Important Structures on $C_2H_5^+$ PES

configuration	TS1	IRC1	IRC2	IRC3	TS3
AB	0.0523	0.0000	0.0900	0.4035	0.9360
A^-B^+ (H−L)	0.1686	0.0794	0.2274	−0.3773	0.1637
$A^{2-}B^{2+}$ (H−L/H−L)	0.1760	0.1746	0.1822	0.1221	0.0128
A^+B^- (H−L)	−0.0482	0.0000	−0.0618	−0.0936	−0.0091
$A^{\mp}B^{\pm}$ (H−L/H−L)	0.1552	0.1174	0.1561	0.0875	0.0000
CT (B→A)	0.52	0.47	0.55	0.48	0.08

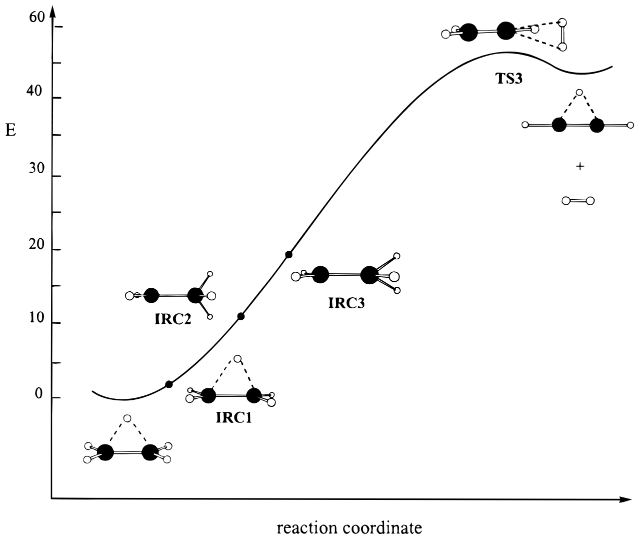

Figure 2. IRC energy profile for the H_2 elimination from $C_2H_5^+$.

TABLE 3: Most Important Changes in the Occupation Numbers, Δ*ν*, of the MOs of the Chemically Important Structures on the $C_2H_5^+$ PES

		Δν				
fragment	MO	TS1	IRC1	IRC2	IRC3	TS3
A = $C_2H_3^+$	LUMO	1.31	1.29	1.18	0.70	0.10
	HOMO	−0.80	−0.72	−0.62	−0.19	0.00
B = H_2	LUMO	0.60	0.64	0.47	0.15	0.00
	HOMO	−1.33	−1.37	−1.22	−0.71	−0.08

larger increment of population of the LUMO of H_2 occurring at TS1 (see Table 3). Therefore, given that back-donation from the vinylium ion prevents the formation of the H_2 molecule, the hypothetical leaving hydrogen atoms at TS1 are too far separated from each other to give rise to a reaction channel for H_2 elimination. A detailed analysis of the structure of TS1 and IRC2 suggests that the magnitude of the back-donation is closely related to the elongation of the C−C bond. At TS1, the C−C bond length is 0.038 Å larger than at IRC2 and therefore the energy of the HOMO of $C_2H_3^+$ is 0.0084 eV less stable at TS1 than at IRC2. As a consequence, the back-donation is larger at TS1 because of the smaller energy gap between the HOMO of $C_2H_3^+$ and the LUMO of H_2. Therefore the vibration of the C−C bond will be very important in the dynamics of H_2 elimination from the nonclassical $C_2H_5^+$ minimum structure. When the stretching of the two C−H bonds takes place simultaneously with the C−C stretching, the presence of a considerable back-donation prevents the formation of the H_2 molecule, whereas when the stretching of the C−H bonds coincides with the shortening of the C−C bond, a much weaker back-donation will allow H_2 elimination. Then, considering the reverse process, a collision of H_2 with $C_2H_3^+$ will be reactive or not depending on the phase of the C−C vibration of $C_2H_3^+$ relative to their approach. Therefore, vibrational excitation of $C_2H_3^+$ seems to be crucial for the association reaction with H_2.[6,7]

In summary, according to our calculations, the H_2 loss from $C_2H_5^+$ is an endoergic process whose energy barrier is only 2.08 kcal/mol greater than its endoergicity, which is in agreement with experimental findings. To produce the H_2 elimination, the synchronous stretching of the two implied C−H bonds must be out of phase with respect to the stretching of the C−C bond so that the back-donation from the HOMO of $C_2H_3^+$ to the LUMO of the H_2 moiety, which would prevent the hydrogen molecule from forming, is weak.

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