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Rearrangements Involving the Phenonium Ion: A Theoretical Investigation

Emma del Río, María I. Menéndez, Ramón López, and Tomás L. Sordo*

Contribution from the Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, C/Julián Clavería, 8, 33006 Oviedo, Principado de Asturias, Spain

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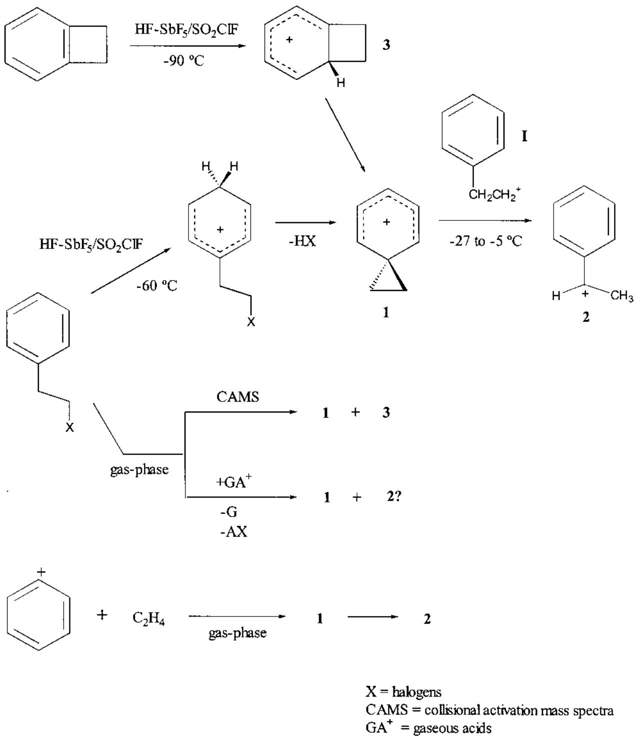
Abstract: Rearrangements involving the phenonium ion were investigated by means of a B3LYP/6-311G(d,p) study in which the effect of solvent has been incorporated by using a PCM solvation model. A rationalization of the whole set of experimental facts reported both in the gas phase and in solution was possible thanks to the characterization of protonated benzocyclobutene as a minimum energy structure and, particularly, to the important preferential stabilization in solution of the TS for the isomerization of the phenonium ion to the α-methylbenzyl ion, which reduces the Gibbs energy barrier of 26.6 kcal/mol for this process in the gas phase to a more accessible one of 18.7 kcal/mol in solution.

Introduction

The mechanism of the solvolysis of β-arylalkyl systems has been an object of study and controversy over the last 35 years.[1−4] The original proposal by Cram[1a] that the intermediates for these reactions were phenonium ions (**1** in Scheme 1) was criticized by Brown,[1e] who proposed that the experimental data could also be rationalized in terms of weakly π-bridged rapidly equilibrating ions. Further studies led to the conclusion that a continuous spectrum of species exists, from open to completely bridged ions, depending upon solvent and substitution in the ions.[5]

The characterization of alkylenebenzenium ions and their role in the mechanism of solvolysis of β-arylalkyl systems was obtained by using low nucleophilicity solvent systems, such as the superacidic media.[6] Experimental studies in superacid medium by Olah have shown that the ionization of β-phenylethyl chloride gives **1** which in turn isomerizes slowly into the more stable α-methylbenzyl cation **2** (see Scheme 1).[7] According to ^{1}H NMR spectra results the activation energy for the transformation of **1** to **2** is 13 kcal/mol.[7c] By analogy with studies in superacid media on ring opening of cyclopropyldimethylcarbinyl cations,[8] it has been suggested that the above-mentioned conversion could proceed via a highly unstable intermediate, the β-phenylethyl cation (**I** in Scheme 1).[7c] Recently protonation of benzocyclobutene under superacidic stable ion conditions has been found to be a new independent route to the generation of **1**.[9] This route would proceed through protonated benzocyclobutene (**3** in Scheme 1) which has been suggested to rearrange in a remarkably facile way to **1**.

Scheme 1



X = halogens
CAMS = collisional activation mass spectra
GA$^+$ = gaseous acids

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Several phenonium ions including the unsubstituted phenonium ion have been reported to be present in the gas phase.[10−16] In contrast with the results obtained in superacid media, experimental studies in the gas phase have reported that the ionization of β-phenylethyl halides yielded **1** and **3** (see Scheme 1) but no **2** could be detected.[10] According to collisional activation mass spectra no evidence for **I** ions of $\geq 10^{-5}$ s lifetimes has been found.[11] A posterior collisional activation study has also shown that **1** does not interconvert with **2**.[12] A more recent gas-phase study, however, reports a different behavior under high-pressure conditions where the phenonium ion is primarily obtained from the highly exothermic addition of the phenylium ion to ethylene but is rapidly converted to **2** (see Scheme 1).[13] However, thermal gaseous ethylenebenzenium ions obtained by acid-induced AX elimination from β-phenylethyl substrates (see Scheme 1) undergo **1**−**2** isomerization quite slowly, if at all.[15]

Several theoretical studies have been performed on the structure and rearrangement of phenonium ions.[17−19] The theoretical investigation of the structure of phenonium ions has recently been addressed by various works.[19] STO-3G calculations have rendered 35.4 kcal/mol for the **1**−**2** isomerization barrier.[17] These calculations have also clearly indicated that **I** in Scheme 1 (which is a primary cation) is not a minimum energy structure since it collapsed to **1** without activation when fully optimized. MP2-FC/6-31G(d)//HF/6-31G(d) calculations have revealed that **3** is a stable minimum 9.0 kcal/mol higher in energy than **1**. However, at the MP2-FC/6-31G(d) level **3** ceases to be a minimum and collapses to **1**.[9]

With the aim of obtaining a deeper understanding of the above-mentioned experimental facts and tackle the controversy that has arisen, we have undertaken a theoretical study of the gas-phase addition of the phenylium ion to ethylene, and the rearrangements interconnecting **1**, **2**, and **3** both in the gas phase and in solution using the density functional theory (DFT) and a solvation Polarizable Continuum Model (PCM).

Computational Methods

Quantum chemical computations were performed by using the Gaussian 98 series of programs[20] with the hybrid density functional B3LYP method,[21] which combines Becke's three-parameter nonlocal hybrid exchange potential with the nonlocal correlation functional of Lee, Yang, and Parr. The geometries of stable species and transition states (TSs) were fully optimized by using the 6-311G(d,p) basis set[22] and Schlegel's algorithm.[23] Harmonic vibrational frequencies were also calculated at this same theory level to characterize the critical points located and to evaluate the zero-point vibrational energy (ZPVE). B3LYP/6-311G(d,p) intrinsic reaction coordinate (IRC) calculations starting at each saddle point verified the two minima connected by that TS by using the Gonzalez and Schlegel method[24] implemented in Gaussian 98.

Thermodynamic data, ΔH, ΔS, and ΔG (298.15 K, 1 atm), were computed by using the B3LYP/6-311G(d,p) frequencies within the ideal gas, rigid rotor, and harmonic oscillator approximations.[25]

To take into account condensed-phase effects on the rearrangements of the phenonium ion, we have used a Self-Consistent-Reaction-Field (SCRF) model proposed for quantum chemical computations on solvated molecules.[26−28] The solvent is represented by a dielectric continuum characterized by its relative static dielectric permittivity ϵ_o. The solute, which is placed in a cavity created in the continuum after spending some cavitation energy, polarizes the continuum, which in turn creates an electric field inside the cavity. This interaction can be taken into account by using quantum chemical methods, minimizing the electronic energy of the solute plus the Gibbs energy change corresponding to the solvation process that is given by:[29]

$$\Delta G_{\text{solvation}} = -\frac{1}{2}E_{\text{int}}$$

where E_{int} is the solute−solvent electrostatic interaction energy:

$$E_{\text{int}} = \sum_{\alpha} V_{\text{el}}(\boldsymbol{R}_{\alpha})\boldsymbol{Z}_{\alpha} - \int V_{\text{el}}(\boldsymbol{r})\rho(\boldsymbol{r})\,\text{d}r$$

In this equation, V_{el} is the electrostatic potential created by the polarized continuum in the cavity, $\boldsymbol{R}_{\alpha}$ and $\boldsymbol{Z}_{\alpha}$ are the position vector and charge of the nucleus α, respectively, and $\rho(\boldsymbol{r})$ is the electronic charge density at point $\boldsymbol{r}$. The factor $-^{1}/_{2}$ arises in the Gibbs energy from the fact that the positive work required to polarize the medium is exactly one-half the value of the interaction energy in the linear response approximation. Addition to $\Delta G_{\text{gas-phase}}$ of the solvation Gibbs energy, evaluated neglecting the change in the relative value of the thermal corrections when going from a vacuum to the solution, gives $\Delta G_{\text{solution}}$. Within the different approaches which can be followed to calculate the electrostatic potential V_{el}, we have employed the united atom Hartree−Fock (UAHF)

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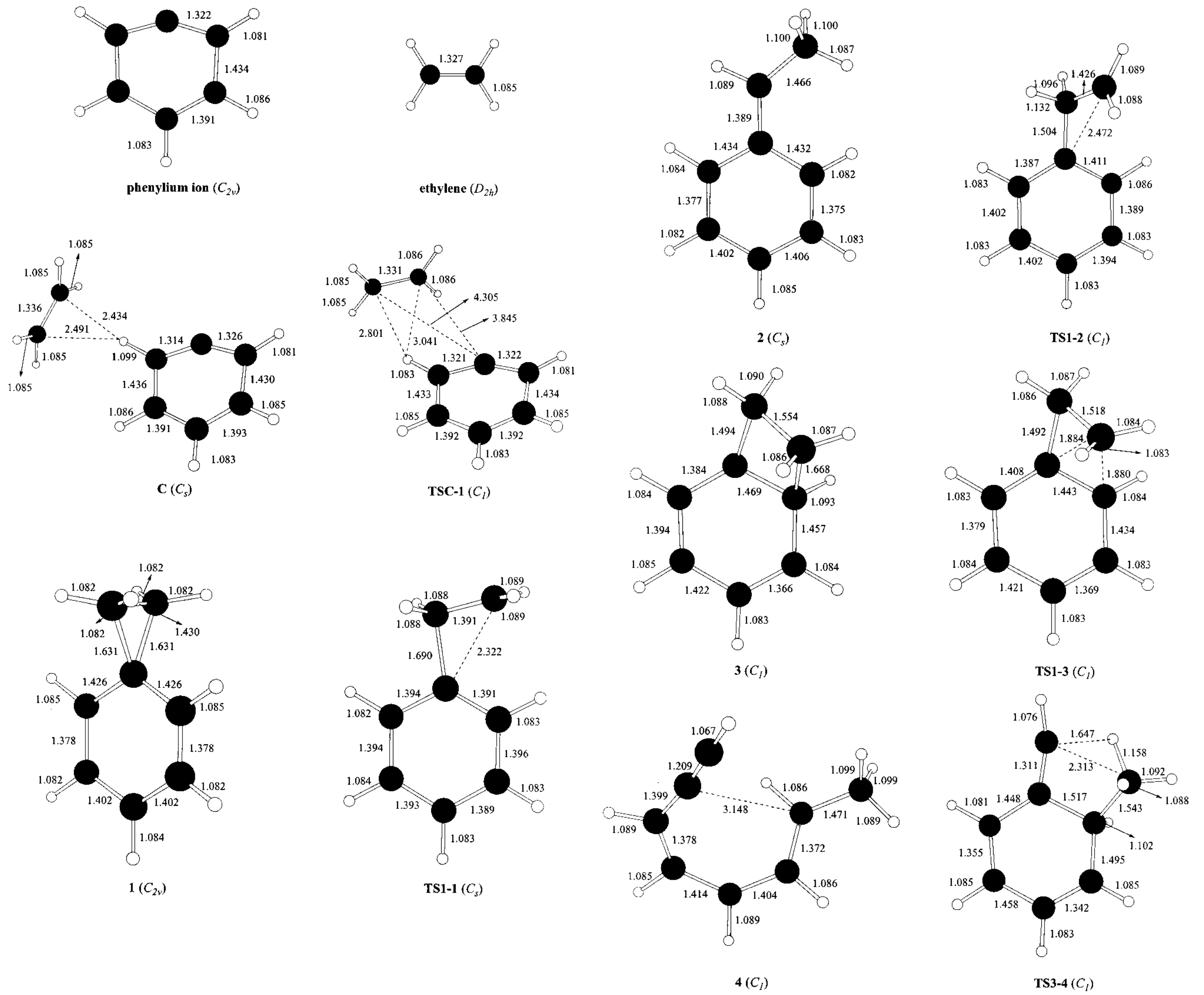

phenylium ion (C_{2v}) **ethylene** (D_{2h}) **2** (C_s) **TS1-2** (C_1)

C (C_s) **TSC-1** (C_1) **3** (C_1) **TS1-3** (C_1)

1 (C_{2v}) **TS1-1** (C_s) **4** (C_1) **TS3-4** (C_1)

Figure 1. B3LYP/6-311G(d,p) optimized geometries of the chemically important structures located along the electronic energy profile for the reaction of the phenylium ion with ethylene to give the phenonium ion and its further rearrangements. Distances are given in angstroms.

of the PCM,[27,30] taking into account electrostatic solute−solvent interactions. The solvation Gibbs energies $\Delta G_{\text{solvation}}$ along the reaction coordinate were evaluated from single-point PCM-UAHF calculations on the gas-phase geometries at the B3LYP/6-311G(d,p) level.

A relative permittivity of 40.0 has been used to simulate superacidic, low-nucleophilic media, such as HF−SbF$_5$ dissolved in SO$_2$ClF as the solvent used in the experimental work.

Results and Discussion

We will present first the energy profile for the gas-phase formation of the phenonium ion and then the gas-phase and solution energy profiles for the rearrangements of the phenonium ion. The theoretical results obtained will be discussed and compared with experiment. Figure 1 displays all the optimized structures involved in these processes. B3LYP/6-311G(d,p) absolute energies and ZPVEs of those structures are listed in Table 1S available in the Supporting Information. Table 1 collects the corresponding relative electronic energies including the ZPVE, the gas-phase ΔH, $-T\Delta S$, and ΔG values, and $\Delta\Delta G_{\text{solvation}}$ and $\Delta G_{\text{solution}}$ relative to the phenonium ion. Figure 2 displays the corresponding Gibbs energy profiles. Unless otherwise indicated we will give in the text the electronic energy including the ZPVE correction.

Table 1. B3LYP/6-311G(d,p) Electronic Energy Including the ZPVE Correction (ΔE), Enthalpy (ΔH), Entropy Contribution ($-T\Delta S$), Gibbs Energy in the Gas Phase ($\Delta G_{\text{gas-phase}}$), Electrostatic Gibbs Energy of Solvation ($\Delta\Delta G_{\text{solvation}}$), and Gibbs Energy in Solution ($\Delta G_{\text{solution}}$) with Respect to the Phenonium Ion, in kcal/mol, for the Chemically Important Structures Located along the Electronic Energy Profile for the Reaction of the Phenylium Ion with Ethylene To Give the Phenonium Ion and Its Further Rearrangements

				ΔG		
species	ΔE	ΔH	$-T\Delta S$	gas phase	solvation	solution
$C_6H_5^+ + C_2H_4$	67.7	69.0	−12.6	56.4		
C	62.2	64.1	−6.0	58.1		
TSC-1	64.3	65.8	−5.5	60.3		
1	0.0	0.0	0.0	0.0	0.0	0.0
2	−13.9	−13.6	−0.8	−14.4	2.2	−12.2
3	16.2	16.1	0.3	16.4	1.5	17.9
4	46.7	48.2	−3.6	44.6	1.4	46.0
TS1-1	35.0	35.2	−0.3	34.9	−4.2	30.7
TS1-2	26.7	26.8	−0.2	26.6	−7.9	18.7
TS1-3	16.9	16.5	1.0	17.5	2.1	19.6
TS3-4	72.6	72.8	−0.4	72.4	−1.0	71.4

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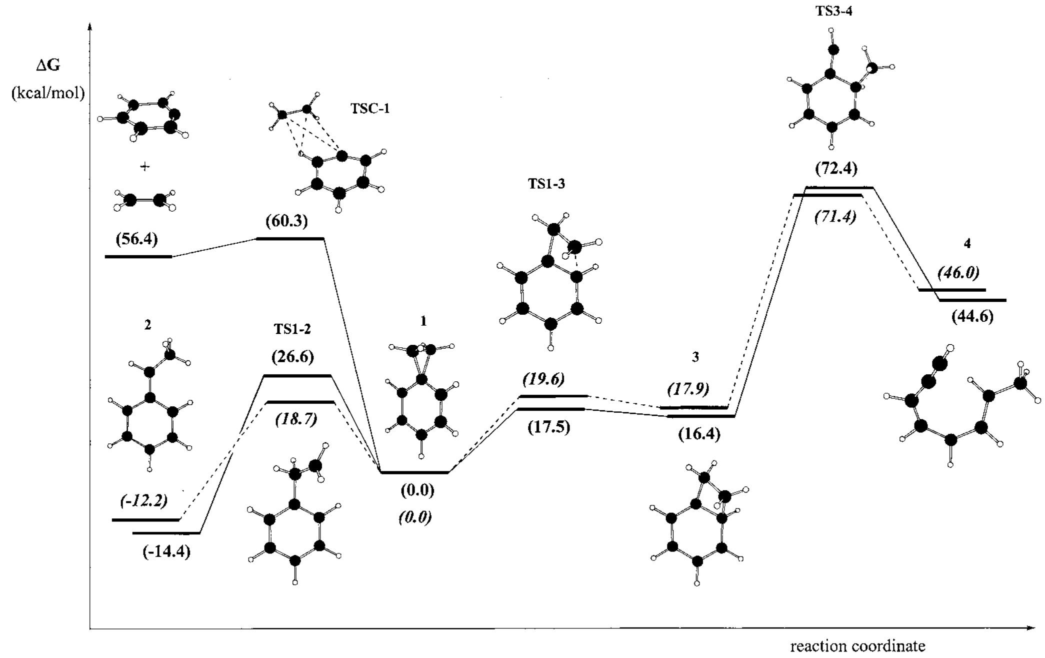

Figure 2. Gibbs energy profiles for the gas-phase reaction of the phenylium ion with ethylene to give the phenonium ion (continuous line) and the phenonium ion rearrangements both in the gas phase (continuous line) and in solution (dashed line).

Gas-Phase Addition of the Phenylium Ion to Ethylene. When $C_6H_5^+$ approaches ethylene the π electrons of the alkene interact with one of the *ortho* hydrogen atoms of the phenylium ion giving rise to a complex of C_s symmetry, **C**, 5.5 kcal/mol more stable than $C_6H_5^+ + C_2H_4$, in which the two C(ethylene)−H($C_6H_5^+$) distances are 2.434 and 2.491 Å, respectively (see Figure 1). This complex **C** evolves through a TS of C_1 symmetry, **TSC-1**, 2.1 kcal/mol above it, in which ethylene has come closer to the bare C atom of the phenylium ion, to give **1** which is 67.7 kcal/mol more stable than $C_6H_5^+ + C_2H_4$.

A statistical thermodynamic analysis of the theoretical results was performed at 298.15 K and 1 atm (see Table 1). Figure 2 displays the corresponding Gibbs energy profile. We see that the relative thermal corrections are not very important, ΔH values differing from the relative electronic energy values by 1.3−1.9 kcal/mol. Owing mainly to the entropy contribution **C** becomes a transient structure in the Gibbs energy profile. In Gibbs energy, **TSC-1** determines a barrier of 3.9 kcal/mol and the Gibbs energy change for the process of formation of **1** is −56.4 kcal/mol.

Rearrangements of the Phenonium Ion. The phenonium ion, **1**, presents an orthogonal conformation of C_{2v} symmetry with a C−C bond distance of 1.631 Å between the bare carbon atom of the phenylic fragment and the two carbon atoms of the ethylenic moiety. This carbocation can isomerize to its mirror image through a TS, **TS1-1**, with an energy barrier of 35.0 kcal/mol. **TS1-1** presents a planar conformation of C_s symmetry in which the cyclopropyl ring has opened and the distance between the phenylic bare carbon atom and the closest ethylenic carbon atom is 1.690 Å. The phenonium ion rearrangement can take place in two different ways. On one hand, **1** can evolve through a TS, **TS1-2**, with an energy barrier of 26.7 kcal/mol to give the α-methylbenzyl cation, **2**, which is 13.9 kcal/mol more stable than **1**. **TS1-2** of C_1 symmetry corresponds to the opening of the cyclopropyl ring with simultaneous migration of a hydrogen atom from one of the ethylenic carbon atoms to the other one. In **TS1-2** the distance between the migrating H atom and the ethylenic carbon atom to which it was originally bonded is 1.132 Å, and the distances between the phenylic and the ethylenic carbon atoms are 1.504 and 2.472 Å, respectively. In **2**, which displays a C_s symmetry, the transfer of the H atom is completed and the C−C distance between the phenylic and the CH−CH_3 fragments is 1.389 Å. According to our results the **1**−**2** interconversion is a one-step process. No intermediate **I** was located on the potential energy surface in agreement with previous computational evidence.[17] On the other hand, **1** can give the protonated benzocyclobutene of C_1 symmetry, **3**, which is 16.2 kcal/mol less stable than that through a TS for ring expansion, **TS1-3**, with an energy barrier of 16.9 kcal/mol. **TS1-3** presents a C_1 symmetry with a distance between the phenylic bare carbon atom and the closest ethylenic carbon atom of 1.492 Å while the other ethylenic carbon atom is starting to form a new bond with one of the *ortho* carbon atoms situated at 1.880 Å (see Figure 1). In **3** the four-membered ring presents C−C bond lengths between the two fragments of 1.494 and 1.668 Å, respectively. Direct connection between **2** and **3** was extensively explored but the search for the corresponding TS failed. **3** can undertake an important electronic rearrangement to give an open-chain minimum structure of C_1 symmetry, **4**, 46.7 kcal/mol higher in energy than **1** through the TS, **TS3-4**, 72.6 kcal/mol above **1**. At **TS3-4** of C_1 symmetry a hydrogen atom has migrated from the ethylenic carbon atom linked to the bare carbon atom of the phenylic fragment to the other ethylenic carbon atom, and the rupture of the ethylenic C−C bond has started.

A statistical thermodynamic analysis of our theoretical results was carried out at 298.15 K and 1 atm both in the gas phase and in solution (see Table 1). In the gas phase, ΔH values indicate that the relative thermal corrections are not very important with values in the range −0.1 to +0.4 kcal/mol except for **4** (+1.5 kcal/mol). The most important $-T\Delta S$ contribution corresponds to **4** (−3.6 kcal/mol), the remaining structures having positive values ≤1.0 kcal/mol. As a consequence, the Gibbs energy profile is quite similar to the electronic one including the ZPVE, except for **4**, which becomes stabilized by 2.1 kcal/mol.

When the electrostatic solute−solvent interaction is considered in the computations by means of the PCM-UAHF

Table 2. Electronic Energy Difference, ΔE, between **TS1-2** and **1** Evaluated at Different Theory Levels without the ZPVE Correction (in kcal/mol)

theory level	ΔE
MP2-FC/6-31G(d)	39.5
MP2-FC/6-31G(d,p)	39.4
MP2-FC/6-311G(d,p)	38.2
B3LYP/6-31G(d)	31.3
B3LYP/6-31G(d,p)	30.9
B3LYP/6-311G(d,p)	29.7
QCISD(T)/6-311G(d,p)//B3LYP/6-311G(d,p)	34.7
B3LYP/6-311++G(3df,3pd)//B3LYP/6-311G(d,p)	29.6
B3LYP/6-311G(2df,2pd)	29.7

continuum model **2**, **3**, **4**, and **TS1-3** become 1.4−2.2 kcal/mol less stabilized than **1** whereas **TS3-4** and **TS1-1** become more stabilized than **1** by 1.0 and 4.2 kcal/mol, respectively. Remarkably, the TS **TS1-2** is the most favored structure by solvent interaction, becoming 7.9 kcal/mol more stabilized than **1** in solution. Consequently, the major change in the Gibbs energy profile when passing from the gas phase to solution corresponds to the rearrangement of **1** into **2**, **TS1-2** presenting a Gibbs energy barrier of 18.7 kcal/mol while the rest of the energy profile in solution is similar to that in the gas phase.

Discussion and Comparison with Experiment. As mentioned in the Introduction, the energy barrier experimentally determined for the rearrangement of **1** to **2** is 13 kcal/mol.[7c] Our theoretical calculations at the B3LYP/6-311G(d,p) level render for this barrier a value of 29.7 kcal/mol in electronic energy without including the ZPVE correction (26.7 kcal/mol including the ZPVE). This figure is lower than that reported in a previous theoretical study at the HF/STO-3G level[17] but still far from the experimental value. We investigated the effect of using different correlated methods of calculation and more flexible basis sets on this energy barrier. Table 2 presents the results obtained in this investigation. MP2 and single-point QCISD(T) calculations give for this barrier values 5−9 kcal/mol greater than the B3LYP/6-311G(d,p) ones, the QCISD(T) value being the closest to the B3LYP ones. On the other hand, it seems clear that the value of the energy barrier diminishes when using a more flexible basis set with both B3LYP and MP2 methods. However, this energy barrier reduction is only 1.3 kcal/mol when going from MP2/6-31G(d) to MP2/6-311G(d,p) and 1.6 kcal/mol when going from B3LYP/6-31G(d) to B3LYP/6-311G(d,p) (the barrier obtained in the present work at the B3LYP/6-311G(d,p) level is identical to that rendered by B3LYP/6-311G(2df,2pd)), insufficient to obtain a reasonable agreement with the experimental value in superacid medium. These results clearly show that at the theory level used in the present work the effect of solvent appears to play a decisive role in approaching experimental data, thus allowing a rationalization of the experimental facts.

In effect, when the phenonium ion is obtained in the gas phase by the strongly exothermic addition of the phenylium ion to ethylene (−56.4 kcal/mol), it can readily undergo the rearrangement to **2** by surmounting the Gibbs energy barrier of 26.6 kcal/mol. This barrier, however, would constitute a difficult obstacle for phenonium ions formed by acid-induced AX elimination from β-phenylethyl substrates (see Scheme 1) and **1−2** isomerization would proceed in that case quite slowly, if at all. In superacid medium, on the other hand, the phenonium ion formed by ionization of β-phenylethyl chloride can isomerize into **2** through a Gibbs energy barrier of 18.7 kcal/mol. Protonation of benzocyclobutene under superacid conditions would yield **3** which evolves very rapidly via a Gibbs energy barrier of 1.7 kcal/mol to **1**, as expected by experimentalists.[9] According to our theoretical results, **3** is a minimum energy structure with a lifetime τ of about 1.0×10^{-12} s in the gas phase and 2.8×10^{-12} s in solution.[31]

In summary, the present theoretical results provide a better understanding of the experimental facts reported so far concerning the rearrangements of the phenonium ion. The keys to this rationalization are the location of the minimum energy structure of protonated benzocyclobutene, and particularly the important preferential stabilization by solvent interaction of the TS for the isomerization **1−2**, which transforms the Gibbs energy barrier of 26.6 kcal/mol for this process in the gas phase into a more accessible one of 18.7 kcal/mol in solution.

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Supporting Information Available: Table 1S, B3LYP/6-311G(d,p) absolute energies (hartree) and zero-point vibrational energies (kcal/mol) corresponding to the chemically important structures located along the electronic energy profile for the reaction of the phenylium ion with ethylene and its further rearrangements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[31] The mean lives of **3** were estimated as $\tau = 1/k_{\mathrm{iso}}$ where k_{iso} is the kinetic constant for the isomerization of **3** through **TS1-3** to **1**. K_{iso} was computed by using the conventional Transition State Theory $k = (k_B T/h) \exp(-\Delta G^{\#}/RT)$, where $\Delta G^{\#}$ is the energy barrier.