Ab Initio Study of the Adamantonium Cations: the Protonated Adamantane

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Received: September 22, 2000; In Final Form: January 18, 2001

The molecular structure and energetics of the adamantonium ions were computed at the MP2(full)/6-31G** level. Three structures were found to represent the adamantonium cations, respectively: the 1-H-adamantonium (**1**), 2-H-adamantonium (**2**), and C-adamantonium ions (**3**). This study revealed that, upon protonation, adamantane can also produce two van der Waals complexes: one formed by the weak interaction of the 1-adamantyl cation and H_2 (**4**) and the other formed by the interaction of the 2-adamantyl cation and H_2 (**5**). The stability order is predicted to be **5** > **3** > **4** > **1** > **2**. Given the size and complexity of this molecule, the quantum zero point energy (ZPE) and finite temperature (298 K) corrections were estimated from previously calculated values for the isobutonium (for protonation of tertiary C−H and C−C bonds) and the proponium cations (for protonation of the secondary C−H bond). The calculated proton affinity of adamantane was estimated as 175.7 kcal/mol.

Introduction

Superacid media have been used to conduct electrophilic activation and functionalization of alkanes.[1] For instance, protonation of isobutane occurs with formation of H_2 and *tert*-butyl carbenium ion as main products.[2] This result was explained in terms of protonation of the σ bonds, forming pentacoordinated carbonium ions. We have previously shown[3] that the most stable $i\text{-}C_4H_{11}^+$ species is the van der Waals complex between *tert*-butyl carbenium ion and H_2. This species is formed, with low or no activation energy upon decomposition of the 2-H-isobutonium cation.[4] Calculations also showed that other carbonium ions show similar behavior, decomposing into carbenium ions and a neutral molecule without activation energy. This means that tertiary and secondary H-carbonium ions are not well stabilized relative to the tertiary or secondary carbenium ion and H_2.

Adamantane has been used as a model molecule for electrophilic functionalization. Its symmetric structure provides a model for σ bond reactivity, while preventing reactions at the backside of the C−H bond. Nevertheless, the 1-adamantyl cation cannot assume a total planar conformation,[5] which could favor the 1-H-adamantonium, formed upon the protonation of the tertiary C−H bond (Scheme 1). Moreover, adamantane is a good molecule to compare the equilibrium reaction of H-carbonium ions with carbenium ion plus H_2. We wish to report theoretical results of the structure and energetics of the adamantonium ion, the protonated adamantane.

Computational Details

Calculations were performed at the MP2(full)/6-31G** level using the GAUSSIAN 94 package.[6] Full geometry optimizations were performed, and the presence of stationary points in the potential energy surface was ascertained by a gradient whose norm was smaller than 3×10^{-4} hartree/Å^2 (root-mean-square force). This level of theory has been proven to give good correlations with experiments for the protonated isobutane,[3,4] propane,[7] and butane[8] molecules.

For adamantonium, a molecule with 76 electrons and with a basis set consisting of 235 contracted Gaussian functions, frequency calculations to obtain zero-point energies (ZPE) and thermal corrections at MP2(full)/6-31G** level are extremely costly from the computational point of view and were not performed. Hence, these corrections were estimated from the values calculated for the isobutonium (for protonation of tertiary C−H and C−C bonds) and the proponium cations (for protonation of the secondary C−H bond). For the 1-H-adamonium ion (**1**) it is reasonable to expect that the ZPE difference (ΔZPE), in relation to structure **5**, is quite similar to the ZPE difference between the 2-H-isobutonium and the van der Waals complex involving the *tert*-butyl cation and H_2. Then, one could estimate the ΔZPE for the 1-H-adamantonium ion in relation to structure **5**, as the ΔZPE for the structures 2-H-isobutonium and $t\text{-}C_4H_9^+\cdot H_2$ (a van der Waals complex), computed at the same level of theory.[3,4] With this value one can estimate the enthalpy at 0 K. The same methodology can be applied for the thermal corrections to obtain the estimated enthalpy for all calculated structures at 298 K. Similarly, the relative ΔZPE and thermal corrections for the C-adamantonium species (**3**) relative to **5** was obtained from the C-isobutonium/$t\text{-}C_4H_9^+\cdot H_2$ (van der Waals complex). The ΔZPE and thermal corrections for the 2-H-adamantonium ion (**2**) relative to (**5**) were obtained by comparison with the 2-H-proponium ion/$t\text{-}C_4H_9^+\cdot H_2$ (also a van der Waals complex) system. The same approach was applied for structure **4**, taking the differences for $i\text{-}C_3H_7^+\cdot H_2$ (van der Waals complex)/$t\text{-}C_4H_9^+\cdot H_2$ (van der Waals complex). The estimated quantities are reported in Table 1 and the detailed computations were included as Supporting Information.

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10.1021/jp003431c CCC: $20.00

SCHEME 1: Carbonium Ions Formed upon the Various Protonation Pathways of Adamantane

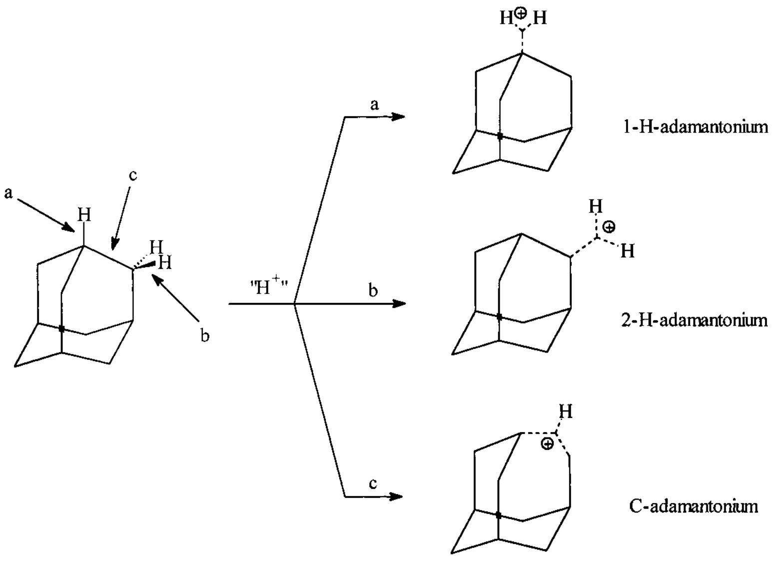


TABLE 1: Total Energies and Estimated Enthalpies for the Adamantonium Cations

species	MP2 (full)/6-31G* * U (a.u.)	MP2 (full)/6-31G* * ΔU (kcal/mol)[a]	ΔZPE estimated (kcal/mol)[b]	$\Delta[H^0(298) - H^0(0)]$ estimated (kcal/mol)	$[\Delta H^0(298)]$ estimated (kcal/mol)
1	**−389.76888**	17.1	6.3	−2.2	21.2
2	**−389.76343**	20.5	6.5	−2.2	24.8
3	**−389.78784**	5.2	5.5	−1.4	9.3
4	**−389.77890**	10.8	0.1	−0.7	11.6
5	**−389.79613**	0	0	0	0
AdH + H$^+$	**−389.51823**	174.4	2.6	−1.3	175.7

[a] 1 hartree = 1 a.u. = 627.5095 kcal/mol [b] Estimated from the values calculated for the isobutonium (for tertiary C−H and C−C bond protonation) and the proponium systems (for the secondary C−H bond protonation). (See Supporting Information for details.)

Results and Discussion

Five stable structures were found with the optimization algorithm: three adamantonium ions and two van der Waals complexes (Figure 1). Table 1 shows the internal energy for the adamantonium ions at MP2(full)/6-31G** level, and the estimated ZPE and thermal corrections for 298.15 K.

Structures **1** and **2** represent the 1-H-adamantonium and the 2-H-adamantonium ions, respectively. The three-center, two-electron bond (3c-2e) presents C−H bond lengths of 1.276 Å and 1.266 Å for structure **1**, whereas the H−H distance is 0.849 Å. The H−C−H bond angle was 39.0°. The values found for the 3c-2e bond in the 2-H-isobutonium cation, at the same level of calculation, were 1.290 Å and 1.283 Å for the C−H bond lengths, 0.832 Å for the H−H bond length, and 37.7° for the H−C−H bond angle.[3] The values of the geometrical parameters found for the 1-H-adamantonium cation are similar to the values found for the 2-H-isobutonium cation. Nevertheless, the data show that the 3c-2e bond in the 1-H-adamantonium cation is slightly stronger than in the 2-H-isobutonium, as reflected by the shorter C−H bond lengths, longer H−H bond length, and larger H−C−H bond angle in the 1-H-adamantonium. Structure **2**, the 2-H-adamantonium cation, presents bond lengths similar to the 1-H-adamantonium ion. The C−H bond lengths found for this structure were 1.266 Å and 1.280 Å, whereas the H−H bond length is 0.848 Å, and the H−C−H bond angle is 38.9°. These values in the 2-H-proponium ion, at the same level of theory, were 1.234 Å and 1.245 Å for C−H bond lengths, 0.867 Å for H−H bond length, and 41° for H−C−H bond angle.[7] This means that the 2-H-adamantonium cation presents a looser 3c-2e bond than the 2-H-proponium ion, as demonstrated by the larger C−H bond lengths, shorter H−H bond distances, and smaller H−C−H bond angle in the 2-H-adamantonium cation. Nevertheless, these structures are closely related, with basically the same configuration. Structure **3**, the C-adamantonium ion, presents two nonequivalent C−H bond distances at the 3c-2e bond, resembling the structure of the C-isobutonium ion. The C−H bond lengths are 1.191 Å and 1.294 Å, whereas the C−C distance is 2.348 Å and the bond angle is 142.1°. The values found for the C-isobutonium, at the same level, were 1.137 Å, 1.470 Å for the related C−H bond lengths, 2.470 Å for the C−C bond distance, and a C−H−C bond angle of 142.3°. The values of the related geometric parameters show similar trends, but with some significant changes, especially the longer C−H bond length of the 3c-2e bond, which is shorter in the C-adamantonium cation than in the C-isobutonium cation. This is possibly associated with geometric constraints imposed by the tricyclic adamantyl system, because the electronic factors are similar in both cases. Hence, the bond is shrunk to alleviate conformational pressure of the six-member ring system below the 3c-2e bond (cyclohexane ring at bottom of structure **3** in Figure 1).

Structures **4** and **5** are the van der Waals complexes between 2-adamantyl cation and H_2 and the 1-adamantyl cation and H_2, respectively. Structure **4** shows an intriguing issue related to the bonding nature in the carbenium ion. It can be observed (see Figure 1) that this species presents a nonclassical bonding, as in the 2-norbornyl cation.[9] ^{13}C NMR studies of the 1,3,5,7-tetramethyl-2-adamantyl cation (Scheme 2) have shown that the chemical shift of the cationic carbon atom (C2) appears at 92.3 ppm.[10] This value is at a significantly higher field than the position expected for a static classical carbenium ion (ca. 320 ppm).[11] Based on this experimental finding, a bridged structure

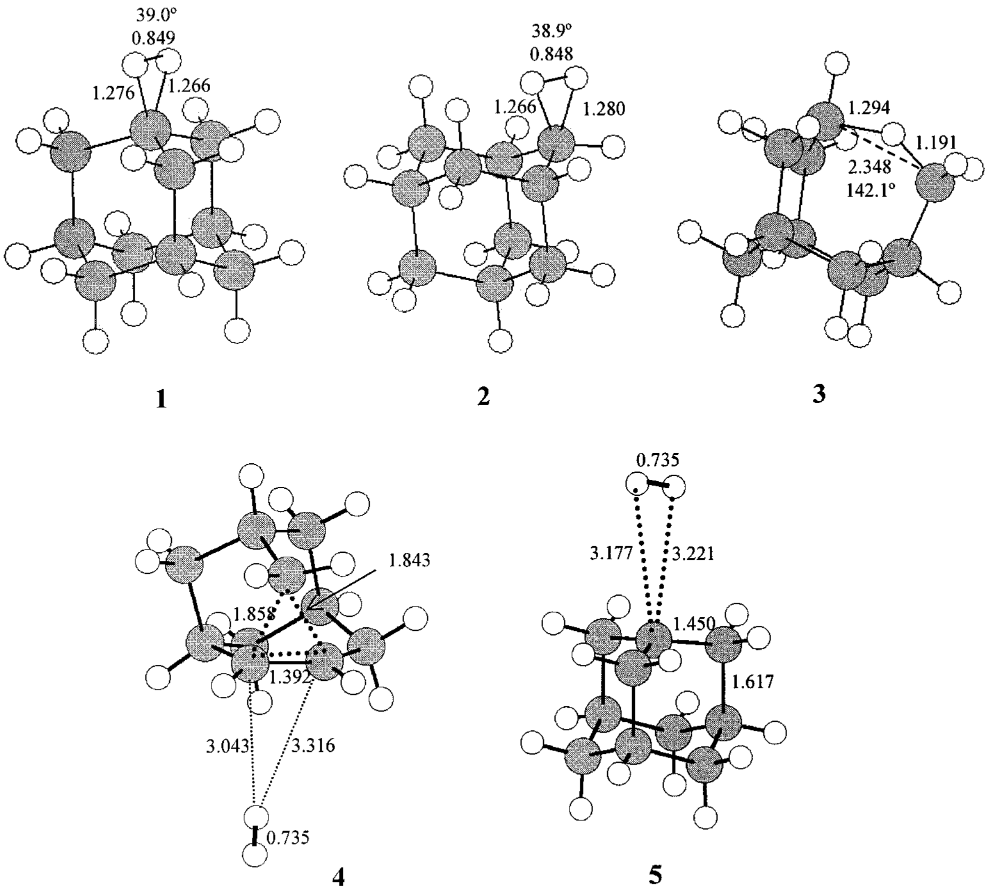
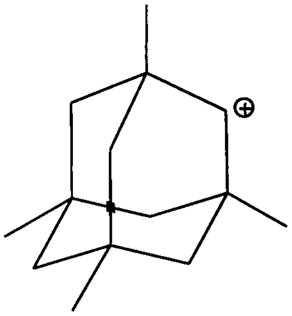


Figure 1. Geometry of the adamantonium ions, obtained at the MP2(full)/6-31G** level.

SCHEME 2: Structure of the Secondary 1,3,5,7-Tetramethyl-2-adamantyl Cation



has been proposed, similar to the carbenium ion calculated in the van der Waals complex **4**. This leads to important insights about the structure of the 2-adamantyl cation, which would show some resemblance with the structure of the 2-norbornyl system. The C−C bond length between the bridging CH_2 group and the two carbon atoms are 1.858 Å and 1.843 Å, respectively. The ring C−C bond that participates in the 3c-2e bond has a length of 1.392 Å, shorter than the one found for the adamantane (1.532 Å). The hydrogen molecule is about 3 Å away from the ion. We are currently working to obtain a more detailed description of the structure of this cation.

Structure **5** shows the typical structure of the 1-adamantyl cation interacting with the H_2 molecule. The hydrogen molecule is about 3.2 Å away from the cationic center. The calculated bond distance of 0.735 Å in the H_2 molecule, in **4** and **5**, is close to the experimental value (0.741 Å) for the isolated hydrogen molecule.[12] The C−C bonds adjacent to the cationic center in the 1-adamantyl cation showed bond distances of 1.450 Å and 1.617 Å. The $C^{\gamma}-C^{\delta}$ bond distances were calculated as 1.524 Å. These values are in agreement with reported values for the 1-adamantyl cation,[13] and indicate hyperconjugation with the C−C bond.

These ab initio calculations showed that the most stable structure is the van der Waals complex **5**. The next stable species is structure **3**, the C-adamantonium ion, being 9.30 kcal/mol less stable than **5**. Following the stability order, the van der Waals complex **4**, was computed to be 11.6 kcal/mol higher in energy than **5**. The 1-H-adamantonium and 2-H-adamantonium ions were the most energetic structures among all, being 21.2 and 24.8 kcal/mol higher in energy than structure **5**. The stability order of the true carbonium ions (structures **1**, **2,** and **3**) is in agreement with the σ basicity scale,[14] which predicts the C−C bond to be more basic than the tertiary and the secondary C−H bond, respectively. The calculated proton affinity of adamantane was 175.7 kcal/mol to form structure **5**.

The greater stability of van der Waals complex **5** agrees well with experimental[15] and theoretical[3,4] observations of isobutane protonation, which predicts the van der Waals complex involving the *tert*-butyl carbenium ion and H_2 to be the most stable $i\text{-}C_4H_{11}^+$ structure. This can be understood if we observe the hyperconjugation effect in the 1-adamantyl cation. In this cation the $C^{\gamma}-C^{\delta}$ bonds are aligned with the empty p orbital of the C^{α}, stabilizing this species. Thus, despite having a bent trivalent carbon atom, this orbital-stabilizing effect favors the formation of the tertiary 1-adamantyl cation plus hydrogen (structure **5**) relative to the 1-H-adamantonium cation. On the other hand, structure **3**, the C-adamantonium cation, is the next more stable species as compared with the van der Waals complex involving the 2-adamantyl cation plus hydrogen (**4**). This situation was also found for the proponium[7] and *n*-butonium cations.[8] Among the H-carbonium ions, one observes that the 1-H-adamantonium

(**1**) is more stable than the 2-H-adamantonium (**2**) by 3.6 kcal/mol, in agreement with the preferable electrophilic attack in the tertiary C−H bond of adamantane,[2,16,17] thereby confirming the σ bond reactivity proposed by Olah.[2,18] Nevertheless, we must stress again that the σ bond reactivity scale proposed for electrophilic activation of alkanes is a kinetic quantity, related with transition states, rather than related with the intrinsic basicity of the bonds (a thermodynamic property).[13,19]

Conclusions

Five stable structures were found at the MP2(full)/6-31G** level representing the products of adamantane protonation. The most stable structure was the van der Waals complex between hydrogen and the 1-adamantyl cation (**5**), followed by the C-adamantonium (**3**) and the complex between the 2-adamantyl cation and hydrogen (**4**). The H-adamantonium cations were significantly higher in energy. The 1-H-adamantonium lies 21.2 kcal/mol and the 2-H-adamantonium 24.8 kcal/mol above **5**. The calculated structure of the 2-adamantyl cation in complex **4** indicated that this cation has a bridged structure, in agreement with experimental NMR results of similar 2-adamantyl cation systems. The results for the protonated adamantane followed the same trend as previously found in the calculations of protonated isobutane, propane, and *n*-butane, indicating that van der Waals complexes of hydrogen and tertiary or secondary carbenium ions are more stable than the respective tertiary or secondary H-carbonium ions.

Acknowledgment. C.J.A.M. thanks support from FAPERJ, CNPq and FINEP/PRONEX. Authors also thank the Ibero-American Program of Science and Technology for the Development − CYTED (V-B). P.M.E. thanks FAPERJ for a fellowship.

Supporting Information Available: Detailed information on estimations of enthalpy corrections at 298.15K and 1 atm. This material is available free of charge via the Internet at http://pubs.acs.org.

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