

Potential Energy Surface of the C₃H₉⁺ Cations. Protonated PropanePierre M. Esteves,[†] Claudio J. A. Mota,^{*,†} A. Ramírez-Solís,[‡] and R. Hernández-Lamonedá[‡]*Contribution from the Instituto de Química, Departamento de Química Orgânica, Universidade Federal do Rio de Janeiro, Cidade Universitária, CT/Bloco A, 21949-900, Rio de Janeiro, Brazil, and Facultad de Ciencias, Universidad Autónoma del Estado de Morelos, Cuernavaca, Morelos 62210, México*

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Abstract: The potential energy surface of the C₃H₉⁺ cations was calculated. At the MP4(SDTQ)/6-311++G**/MP2(full)/6-31G** level of calculation, structure **4**, representing the C-proponium cation, was the lowest in energy, but the van der Waals complex between the isopropyl cation plus hydrogen lies only 0.3 kcal/mol above **4**. The results of the calculations are in good agreement with the experimental gas-phase energetic for the reactions involving the C₃H₉⁺ species. It was also calculated that the interconversion of the 1-H-proponium cation to the C-proponium cation involves no energy barrier and might be on a pathway explaining the formation of products ascribed to the direct C–C bond protonation in liquid and solid superacids.

Introduction

Protonation of alkanes in superacid systems was independently studied by Olah¹ and Hogeveen² during the late 1960s. These pioneering studies provided evidence for the formation of pentacoordinated carbonium ions,³ following proton attack on a C–C or C–H bond. The concept of σ basicity, introduced by Olah,⁴ has been extended to solid superacids, especially zeolites.⁵ Nevertheless, recent H–D exchange studies have questioned the involvement of carbonium ions as intermediates in alkane reactions over solid acids.⁶ Due to the high reactivity of the carbonium ions, most of the evidence supporting their existences relies on indirect observations, such as product selectivities and isotopic exchange, rather than on direct spectroscopic measurements. Except for the CH₅⁺ and C₂H₇⁺ cations, which have been widely studied in the gas phase,^{7,8} there are still few articles reporting spectroscopic observation of the higher alkonium ions. Hiraoka and Kebarle have studied the C₃H₉⁺ and *i*-C₄H₁₁⁺ cations in the gas phase,⁹ protonated propane and isobutane, respectively. They found that there exist at least two isomeric ions, the C-carbonium ion and the

H-carbonium ion,¹⁰ hypothetically formed by protonation in the C–C and in the C–H bonds, respectively. Initially, they described the C-proponium cation as the most stable C₃H₉⁺ species. However, additional experiments led them to conclude that the 2-H-proponium cation was of lower energy. For *i*-C₄H₁₁⁺, the gas-phase results pointed to the 2-H-isobutonium cation as the lowest energy species. Notwithstanding, they indicated that these ions could be better represented as a complex between hydrogen and the respective carbenium ion rather than as true carbonium ions. For the protonated propane, they were able to infer an energy difference of 5.2 kcal/mol between the ions and an activation energy of 9 kcal/mol for the interconversion of the C-proponium cation (**4**) in the 2-H-proponium cation (**3**), showing the first experimental evidence for a carbonium ion rearrangement.

Due to the shortage of direct experimental observation, the structure and energy of carbonium ions have been mostly studied by theoretical methods. The use of ab initio methods, particularly those including electron correlation effects, has been proven to provide excellent prediction of the energy and geometry of the methonium¹¹ and ethonium¹² cations. The predicted geometry for the methonium ion, with C_s symmetry, can explain the isotopic H–D exchange in superacid solutions, but recent calculations point to a structure with C_{2v} symmetry as having essentially the same energy. These results indicate that the interconversion among different isomeric structures of carbonium ions, or the bond-to-bond rearrangement as referred to

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by Olah,^{10,11j,13} is a facile process and should involve a low-energy barrier. Moreover, for the higher alkonium ions there are still few theoretical studies. Collins and O'Malley have used density functional (DFT) methods as well as second-order Møller–Plesset (MP2) level of calculation to study the proponium^{14,15} and isobutonium¹⁵ cations. For the C₃H₉⁺ system, they calculated the energy and structure of the 2-H-proponium (**3**) and the C-proponium (**4**) cations. They found that **4** is the most stable isomer at all levels of calculation, in contrast to the gas-phase experiments of Hiraoka and Kebarle, which indicated **3** as the lowest energy structure.^{9c} The calculated 2-H-proponium cation is better described as a van der Waals complex between a hydrogen molecule and the isopropyl cation. At MP2/6-311G** level and after zero-point energy correction (ZPE), the energy difference between the isomers **3** and **4** is 7 kcal/mol, favoring **4** as the lowest calculated energy structure. The activation energy for the interconversion of **4** to **3** was calculated to be 8.7 kcal/mol. Therefore, the transition state lies 1.7 kcal/mol above **3**. Since the calculated results are presumed for 0 K, they have corrected the experimental values of Hiraoka and Kebarle to the same temperature for comparison and they found an extrapolated experimental energy difference of 4.4 kcal/mol at 0 K and an activation energy of 10.2 kcal/mol for the interconversion of **4** to **3**.

Our interest in the mechanism of alkane activation on zeolites and other solid acids^{5c,f,6e} led us to begin a theoretical investigation on the structure, energy, and reactivity of carbonium ions. Although there is evidence for the involvement of these ions as intermediates or transition states in alkane activation in liquid superacids, there still exists some doubt⁶ about their formation on the zeolite surface. A theoretical study¹⁶ at the MP4(SDTQ)/6-31G**/MP2/6-31G** level of the *i*-C₄H₁₁⁺ species, protonated isobutane, indicated that the most stable structures are the van der Waals complexes formed by the interaction of *tert*-butyl cation with hydrogen and isopropyl cation with methane. Among the carbonium ions, the C-isobutonium cation is the lowest in energy, followed by the 2-H-isobutonium and 1-H-isobutonium cations. The theoretical study of Collins and O'Malley¹⁵ on the *i*-C₄H₁₁⁺ cations was independently carried out and focalized the C-isobutonium and 2-H-isobutonium cations. An interesting point in their study was that neither the MP2/6-31G** nor the DFT(BLYP)/6-31G** level of calculation

was able to find the 2-H-isobutonium cation as a minimum in the potential energy surface. The minimum found was best described as a van der Waals complex between hydrogen and the *tert*-butyl cation. We found the same with DFT calculation of the 2-H-isobutonium and the C-isobutonium, but at MP2/6-31G** level of calculation, we were able to characterize the respective carbonium ions as minima on the potential energy surface. Nevertheless, additional calculations¹⁷ indicated that the conversion of the 2-H-isobutonium cation in the van der Waals complex is a barrierless process. The calculated¹⁶ relative stabilities among the three isobutonium cations correlated very well with the experimental gas-phase protonation of isobutane,¹⁸ while the energetics of the van der Waals complexes¹⁶ showed good agreement with the measured gas-phase proton affinity of isobutane.¹⁹ In this work, we report the potential energy surface for C₃H₉⁺ cations, protonated propane, to further advance our knowledge on the mechanism of electrophilic alkane activation.

Computational Methods

Geometry optimizations were performed at second-order single reference Møller–Plesset perturbational theory on the restricted Hartree–Fock–Roothaan wave function where all electrons were submitted to the perturbational treatment MP2(full) using the 6-31G** basis set. The optimized geometries were characterized as minima on the potential energy surface by the absence of imaginary vibrational frequencies, whereas the transition states were characterized by the presence of one imaginary frequency. To obtain the thermodynamic properties, the vibrational frequencies were scaled by 0.93. The final MP2 (full) optimized geometries were subjected to a single-point energy calculation at the MP4(SDTQ)/6-311++G** level using the frozen core approximation. Calculations were carried out with the GAMESS US²⁰ and GAUSSIAN 94²¹ packages of molecular orbital programs.

Results

In addition to the three proponium cations, hypothetically formed by protonation in the primary C–H bond (**1** and **2**), secondary C–H bond (**3**), and C–C bond (**4**) of propane, two van der Waals complexes were also characterized as minima in the potential energy surface. Structure **5** represents the complex between the ethyl cation and methane and structure **6** the complex between the isopropyl cation and hydrogen. Table 1 shows the total absolute energies, zero-point energy (ZPE) and temperature corrections (298.15 K), and the entropy for structures **1**–**6** and other neutral molecules. The relative enthalpy between the charged structures is presented in Table 2. Unless otherwise stated, all of the discussion concerning the energy difference and the energy barrier refers to the enthalpy term, corrected for ZPE and 298.15 K. At MP2(full)/

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Table 1. Absolute Energies (–a.u.), Zero-Point Energies (ZPE), Enthalpy Changes, and Absolute Entropies of C₃H₉⁺ Isomers and Other Species (Geometry at MP2(full)/6-31G**)

species	MP2(full)/6-31G**	MP4SDTQ(fc)/6-311++G**	zero-point energy (kcal/mol) ^a	H ₂₉₈ ^o – H ₀ ^o (kcal/mol) ^a	S ₂₉₈ ^o (cal/mol K) ^a
1	118.964 61	119.054 92	66.4	4.0	69.3
2	118.966 42	119.055 65	66.4	3.9	68.7
3	118.972 00	119.060 93	66.6	3.9	68.7
4	118.975 56	119.073 65	67.4	4.2	71.5
5	118.974 52	119.063 45	64.8	5.4	85.2
6	118.973 55	119.063 30	60.0	5.4	83.8
7	118.966 87	119.054 56	66.2	3.8	68.2
8	118.966 35	119.054 12	66.2	3.8	67.8
9	118.968 79	119.056 50	66.8	3.7	67.4
10	118.964 69	119.052 52	65.7	3.7	67.2
11	118.971 12	119.061 69	64.6	4.7	76.5
12	118.964 11	119.056 23	63.5	4.1	69.4
13	118.971 12	119.039 77	62.5	4.3	71.3
14	118.948 02	119.040 18	63.5	4.3	71.5
15	117.808 31	117.885 36	55.1	3.4	64.5
16	117.806 45	117.882 78	55.1	3.1	61.1
H₂	1.157 66	1.167 73	6.1	2.1	31.1
CH₄	40.369 86	40.405 27	27.2	2.4	44.5
C₂H₄	78.327 23	78.384 31	30.6	2.5	52.5
C₂H₆	79.553 71	79.615 09	45.3	2.8	54.4
C₃H₈	118.740 88	118.828 40	49.3	2.7	56.8
c-C₃H₆	117.512 50	117.590 47	62.6	3.4	64.2
H⁺				1.5 ^b	26.0
H₃⁺	1.324 28	1.336 24	12.7	2.4	35.0
CH₃⁺	39.351 20	39.379 92	19.0	2.4	44.6
CH₅⁺	40.580 28	40.617 08	31.2	2.7	52.1
C₂H₅⁺	78.601 18	78.654 07	36.9	2.6	54.6
s-C₃H₇⁺	117.814 91	117.893 98	53.1	3.7	65.4

^a Data obtained were calculated using MP2(full)/6-31G** (scaled by 0.93) vibrational frequencies. ^b E_{trans} + Δ(pV) = ³/₂RT + RT = ⁵/₂RT.

Table 2. Relative Enthalpies (kcal/mol) of C₃H₉⁺ Isomers, Corrected to ZPE and 298.15 K (ΔH₂₉₈^o)^a (Geometry at MP2(full)/6-31G**)

species	MP2(full)/6-31G**	MP4SDTQ(fc)/6-311++G**	exptl
1	10.6	10.6	
2	9.4	10.1	
3	6.1	6.9	
4	4.9	0.0	
5	4.2	5.0	
6	0.0	0.3	
7	8.8	10.4	
8	9.1	10.6	
9	7.8	9.3	
10	9.5	11.0	
11	5.5	5.2	
12	8.1	6.9	
13	3.0	16.5	
15	18.4	17.2	
16	6.0	8.0	
14	6.9	9.3	
C₃H₈ + H⁺	148.1	149.8	150 ^b
H₂ + C₃H₇⁺	0.2	0.9	
CH₄ + C₂H₅⁺	5.2	6.4	6.6 ^c
C₂H₆ + CH₃⁺	47.2	47.2	
c-C₃H₆ + H₃⁺	88.7	87.6	
C₂H₄ + CH₅⁺	43.1	40.8	

^a Zero-point energy scaled by 0.93 in MP2(full)/6-31G** level.

^b Reference 29. ^c Reference 9.

6-31G**/MP2(full)/6-31G** level, structure **6**, representing the van der Waals complex between the isopropyl cation and hydrogen, is the most stable calculated structure with structure **5**, the van der Waals complex between the ethyl cation plus methane, lying 4.2 kcal/mol above. The protonium cations are all higher in energy. The C-proponium (**4**) and the 2-H-proponium (**3**) cations are about 5 and 6 kcal/mol higher in energy than **6**, respectively. The two 1-H-proponium cations structures are considerably higher in energy. Structure **2**, with the methyl group and the hydrogens of the three-center bond in a synclinal conformation, is 9.4 kcal/mol higher in energy

than **6** while structure **1**, with the methyl group and the hydrogens in the three-center bond in an anti-periplanar oriented conformation, is the highest calculated structure, lying 10.6 kcal/mol above **6**. A single-point energy calculation, using the larger MP4(SDTQ)/6-311++G** basis set, significantly alters this order, ranking structure **4** as the lowest energy species, followed by **6** and **5**. The H-proponium ions remain higher in energy, with structure **1** lying about 10 kcal/mol above **4**. At the MP4-(SDTQ)/6-311++G**//MP2(full)/6-31G** level, **6** is only 0.3 kcal/mol higher than **4**, which virtually indicates the same energy for both species.

Figure 1 shows the main calculated geometrical parameters for the carbonium ions and the van der Waals complexes. The geometries of **1** and **2** are very similar. The H–H bond distance in the three-center bond is 0.909 Å, significantly longer than the value of 0.741 Å in the H₂ molecule,²² and the C–H bond in the three-center bond is about 1.20 Å. On the other hand, the H–H bond length of 0.867 Å and the C–H bonds around 1.24 Å in **3** indicate a weaker bonding between the atoms of the three-center bond compared with **1** or **2**. The C-proponium cation (**4**) has an asymmetry in the three-center bond. The C–H bonding with the methyl moiety is stronger (1.118 Å) than with the ethyl moiety (1.272 Å). The C–C bond length in the three-center bond is about 2.1 Å, leading to a C–H–C angle of 117.1°. All of the calculated carbonium ions show a trigonal shaped three-center bond, but the H–C–H angle in the H-proponium ions is considerably smaller than in **4**. As expected, the parameters of the van der Waals complexes are very similar to the parameters of the respective carbenium ions methane and hydrogen. The C–H bond distance of 1.086 Å is in good agreement with the value in an isolated methane molecule²² (1.087 Å), while the H–H bond length in **6** is similar to that found in an hydrogen molecule. The geometry of the

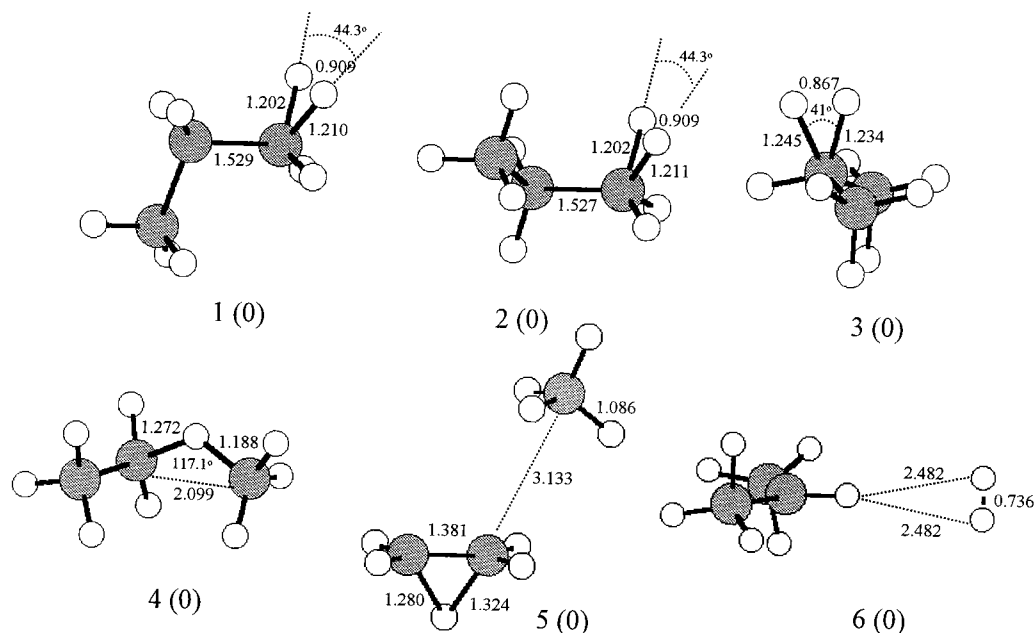


Figure 1. Calculated geometry, MP2(full)/6-31G**, of the $C_3H_9^+$ species. Brackets indicate the number of imaginary frequencies.

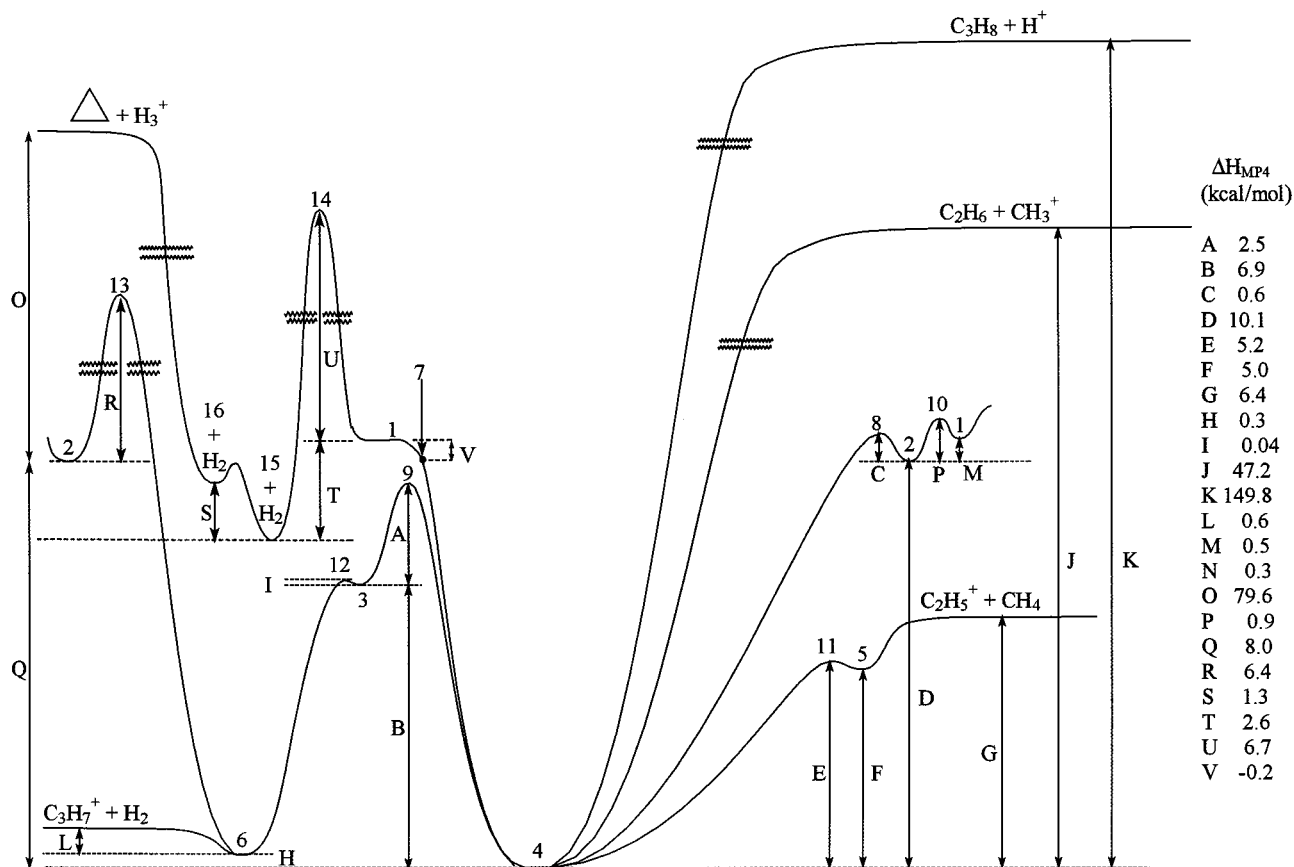


Figure 2. Pictorial representation of the calculated potential energy surface, MP4(SDTQ)/6-311++G**//MP2(full)/6-31G** (ZPE and temperature corrected) of $C_3H_9^+$.

ethyl cation in **5** is very similar to the calculated^{12c,f,23} structure for an independent ethyl cation, at similar level and basis set, showing a H-bridge between the two carbons. The presence of the methane at about 3.1 Å causes an asymmetry in the structure of the ethyl cation, augmenting the C–H bond length for the carbon near the methane molecule. The structure of

the isopropyl cation in **6** is also similar to previous calculations, which indicates that a structure with C_2 symmetry is the lowest in energy.²⁴

Figure 2 shows a pictorial representation of the calculated potential energy surface, at the MP4(SDTQ)/6-311++G**//MP2(full)/6-31G** level, for some possible reactions of the

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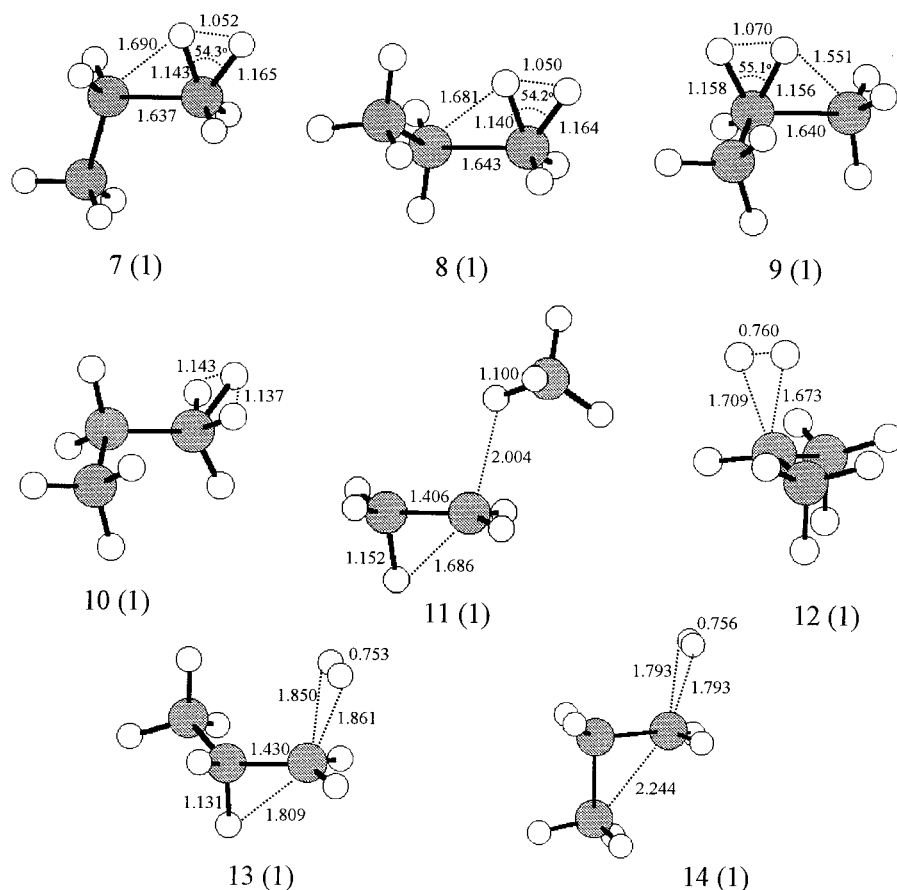


Figure 3. Calculated geometry, MP2(full)/6-31G**, of the $C_3H_9^+$ transition states. Brackets indicate the number of imaginary frequencies.

$C_3H_9^+$ species. Structure **4**, the C-proponium cation, has the lowest energy, at this level of calculation, followed by structure **6**, the van der Waals complex between methane and isopropyl cation, which lies only 0.3 kcal/mol above. Nevertheless, the energy barrier for the interconversion of **4** in **6** is 9.1 kcal/mol (A + B). For the isomerization of **3** to **4**, there is an activation energy of 2.5 kcal/mol (A). However, the interconversion of **3** in the respective van der Waals complex **6** is a barrierless process, requiring only 0.04 kcal/mol (I). The 1-H-proponium cation **1** is the highest calculated energy species. The isomerization of **1** to **2**, which is an internal migration of the hydrogen in the three-center bond, requires only 0.4 kcal/mol (P - M). The bond to bond rearrangement of **2** to **4** has an activation energy of 0.6 kcal/mol (C), while the conversion of **2** to **6** gives a calculated barrier of 6.4 kcal/mol (R). The isomerization of **1** to **4**, through transition state **7**, occurs without activation energy. After ZPE and temperature corrections, the transition state **7** is lower in energy than **1** (V). Another feasible pathway to **4** is the protonation of cyclopropane by H_3^+ to form the protonated cyclopropane and hydrogen. This reaction is exothermic by about 79 kcal/mol (O) to form structure **16** (not shown), representing the edge-protonated cyclopropane. Structure **15** (not shown) of the corner-protonated cyclopropane lies only 1.3 kcal/mol (S) below in energy than **16**. This value is comparable to the recent calculated²³ energy difference between these two species. However, the reaction of **15** with hydrogen to give **1** and then **4**, through formation of transition state **14**, requires 9.3 kcal/mol to proceed (U + T).

The conversion of **4** in the respective van der Waals complex **5** is an endothermic process and involves a barrier of 5.2 kcal/mol (E). The decomposition of **4** to the isolated ethyl cation plus methane requires an energy of 6.4 kcal/mol (G). On the

other hand, the decomposition of **4** to ethane plus the methyl cation is a highly endothermic process, requiring 47.2 kcal/mol (J). The van der Waals complex **6** and the C-proponium cation **4** lie, respectively, 0.6 (L) and 0.9 kcal/mol (L + H) below the energy of an isolated isopropyl cation plus a hydrogen molecule. The proton affinity of propane to form the C-proponium cation was calculated to be 149.8 kcal/mol (K) at the MP4(SDTQ)/6-311++G**//MP2(full)/6-31G** level.

Figure 3 shows the main geometric parameters of the transition states for the reactions indicated in Figure 2. The transition states for the decomposition of **3** and **4** to the respective van der Waals complexes have distinct geometries. While **11** has a geometry closer to that of **5**, with significant degree of H-bridge in the ethyl moiety, the geometry of **12** is closer to that of the carbonium ion **3**.

Discussion

The calculated potential energy surface of the $C_3H_9^+$, protonated propane, showed that, at the MP4(SDTQ)/6-311++G**//MP2(full)/6-31G** level, structure **4**, the C-proponium cation, has the lowest energy. However, structure **6**, representing the van der Waals complex between the isopropyl cation and hydrogen, lies only 0.3 kcal/mol above. This order is, however, dependent on the basis set used, and for practical aspects, both structures have similar energy. The van der Waals complex between methane and the ethyl cation is about 5 kcal/mol above **4**. These results are in contrast with the calculations^{15,16} of the $i-C_4H_{11}^+$ species, where the two van der Waals complexes are lower in energy than the respective carbonium ions. The main reason for the different behavior is that in the $i-C_4H_{11}^+$, the van der Waals complexes involve

tertiary and secondary carbenium ions, while for the $C_3H_9^+$ cations, the van der Waals complex **5** involves the ethyl cation. These calculations indicate that the stability of the carbonium ions, relative to the respective van der Waals complexes, is dependent on the nature of the C–C or C–H bond being protonated. Thus, carbonium ions formed by the protonation of a primary C–H and of a C–C bond of a linear alkane tend to be lower in energy than the respective van der Waals complexes, formed by the rupture of the three-center bond.

The stability of the carbonium ions followed the same trend previously observed for the isobutonium cations, showing that the C-carbonium ions are generally more stable than the H-carbonium ions. For the propanium cations, the order of stability of the carbonium ions is in agreement with solution²⁶ and gas-phase^{18a,27} protonation, which favored products arising from C–C protonation. Gas-phase protonation of the 2,2-deuteriopropane with H_3^+ yielded $C_2H_2D_2^+$ as the main ionic product,^{18a} accounting for 57% of the total ionic products. This product can be explained by the protonation of the C–C bond followed by loss of CH_4 . The $C_3H_6D^+$ cation, which is formed by protonation in the secondary C–D bond, followed by HD loss, accounted for 16%. Protonation in the primary C–H bond, which after H_2 loss, affords the $C_3H_5D_2^+$ cation, accounted for 18% of the total ionic products. Considering the statistical distribution of primary and secondary C–H bonds in propane, one can conclude that protonation of the secondary C–H is significantly more favored than protonation of the primary C–H, in agreement with the relative order of stability among the C- and H-propanium cations.

Hiraoka and Kebarle have studied⁹ the gas-phase reaction between $C_2H_5^+$ and CH_4 . At temperatures below $-60^\circ C$, the reaction was exothermic by 6.6 kcal/mol and proceeded without activation energy to form a $C_3H_9^+$ cation. At temperatures above $-60^\circ C$, the reaction proceeded with an activation energy of 2.5 kcal/mol to form the $C_3H_7^+$ and H_2 . Hiraoka and Kebarle proposed that a C-propanium cation was initially formed. Above $-60^\circ C$, it rearranges to a 2-H-propanium cation, which then gives rise to the isopropyl cation and hydrogen. Considering the sum of the enthalpy for $C_3H_9^+$ formation (-6.6 kcal/mol) and the activation energy of 2.5 kcal/mol, one finds an experimental value of 9.1 kcal/mol for the energy barrier for the rearrangement of the C-propanium cation in the isopropyl cation plus hydrogen. The MP4(SDTQ)/6-311++G**//MP2(full)/6-31G** level calculations for the potential energy surface of $C_3H_9^+$ cations are in good agreement with the experimental values, indicating that this level of calculation describes well the energetic processes of the propanium ions. Figure 2 shows that the reaction of $C_2H_5^+$ and CH_4 to form **4** is exothermic by 6.4 kcal/mol (G) and that there is a barrier of 9.3 kcal/mol (A + B) for the transformation of **4** in the isopropyl cation plus hydrogen. These results are in close agreement with the experimental values.⁹ Hiraoka and Kebarle also inferred⁹ an energy difference of 5.2 kcal/mol between the $C_3H_9^+$ species, based on the calculated exothermicity of the reaction $C_2H_5^+ + CH_4 \rightarrow i-C_3H_7^+ + H_2$. Using a reported²⁸ experimental heat of formation of 219 kcal/mol for the $C_2H_5^+$ ion, they calculated

the exothermicity of the reaction as 9 kcal/mol. Our calculated value for the exothermicity is 5.5 kcal/mol ($G - H - L$), which is significantly different from the value reported by Hiraoka and Kebarle. Notwithstanding, using new tabulated²⁹ value of 215.6 kcal/mol for the heat of formation of the $C_2H_5^+$ cation, one can infer an exothermicity of 5.9 kcal/mol for the same reaction, which is close to the calculated value at the MP4(SDTQ)/6-311++G**//MP2(full)/6-31G** level. Attempts to measure the experimental heat of formation of the 2-H-propanium cation through the gas-phase reaction between H_2 and isopropyl cation failed,^{9c} even at $-170^\circ C$. This is in agreement with the calculated potential energy surface for the $C_3H_9^+$ cations, which indicates a barrierless exothermic process for the decomposition of **3** in the isopropyl cation and hydrogen. Recently, Hiraoka and collaborators investigated²³ the energetics of clustering methane to the ethyl, isopropyl, and *tert*-butyl cations. The results with $C_2H_5^+$ showed that the enthalpy of clustering the first methane molecule to form a $C_3H_9^+$ species is -5.5 kcal/mol. For additional clustering of two or more methane molecules to the ethyl cation the enthalpy of clustering is constant and around -2 kcal/mol. For the methane clustering with the isopropyl and *tert*-butyl cation the enthalpy of clustering is about 2 kcal/mol and independent of the number of methane molecules. These results indicate that the species formed by clustering of two or more methane molecules is essentially the core $C_2H_5^+ \cdots CH_4$ surrounded by shells of methane molecule. They also carried out²³ ab initio calculations to describe the structure of the species formed by the first methane clustering with the ethyl cation. Calculations at the MP2/6-31G** level pointed to a structure with the geometry of the C-propanium ion, although they found an energy difference of -4.3 kcal/mol relative to the isolated ethyl cation and methane. Our data at the MP4(SDTQ)/6-311++G**//MP2/6-31G** level on the potential energy surface of the $C_3H_9^+$ indicate that **4** is 6.4 kcal/mol below the energy of an isolated ethyl cation plus methane. This value is close to the experimental clustering enthalpy of -5.5 kcal/mol found for Hiraoka and collaborators, giving additional support for their conclusions regarding the nature of the $C_3H_9^+$ species formed. The geometry of the C-propanium cation calculated by Hiraoka and collaborators is essentially the same as calculated in this work. The calculated proton affinity (PA) to form **4** was 149.8 kcal/mol. This value is in good agreement with the experimental reported²⁹ propane proton affinity of 150 kcal/mol.

The calculations indicated a low barrier for the interconversion of H-propanium in C-propanium cations. The isomerization of structure **2**, representing the 1-H-propanium cation, to **4**, the C-propanium cation, involves only 0.6 kcal/mol, and the interconversion of **1**, which represents another possible conformation for the 1-H-propanium cation, to **4** is a barrierless process. Calculation of the electronic energy shows that transition state **7** lies 0.2 kcal/mol above **1**. However, after zero-point energy and temperature corrections, **7** is 0.2 kcal/mol lower in energy than **1**, indicating a spontaneous isomerization of structure **1**, the 1-H-propanium cation, to **4**, the thermodynamically more stable C-propanium cation. The presence of a methyl group anti-periplanar to the three-center bond in **1** may facilitate the interconversion, increasing the electron density near the migrating proton of the three-center bond. On the other hand, the interconversion of **2** to the van der Waals complex **6** requires 6.4 kcal/mol and is a less favorable process. Hence, an alternative pathway which explains the products arisen from C–C bond protonation in liquid and solid superacid systems

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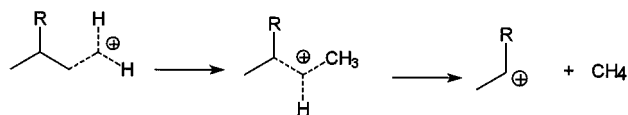
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Scheme 1. Interconversion, or Bond-to-Bond Rearrangement, of H-Carbonium to C-Carbonium Ion As a Possible Pathway To Explain Products of C-C Protonation



might be the initial protonation on the outer and more accessible C-H bonds with formation of a primary H-carbonium ion, which can easily rearrange to the thermodynamically more stable C-carbonium ion (Scheme 1). This pathway might explain the results³⁰ of isobutane protonation on zeolites at 450 °C, where formation of methane was similar or even higher than hydrogen, indicating a preferential C-C rather than tertiary C-H protonation, in contrast to the results^{26a,31} in liquid superacid, near room temperature, where hydrogen formation predominated over methane formation. On the other hand, recent theoretical³² and experimental³³ results of hydrocarbon reaction and carbocation formation on zeolites suggest that steric effects play an important role, probably making difficult the proton attack in the inner and more sterically crowded C-C bonds. Therefore, the pathway shown in Scheme 1, involving the interconversion of 1-H-carbonium ion to the C-carbonium ion can explain the results of isobutane cracking on zeolites at high temperatures. Indeed, calculations for the interconversion of the 1-H-isobutonium to the C-isobutonium cation indicate a similar barrier to that found for the interconversion of 1-H-proponium to the C-proponium cation and will be reported separately.¹⁷ It should be mentioned that although free carbocations are not observed as long-lived species on the zeolite surface,³⁴ the concept of σ -bond reactivity, as a consequence of carbonium ion relative stability, can still be applied. Other bond-to-bond rearrangements have already been reported in the literature for calculations^{12f,35} using the proton and NO^+ as the electrophilic attacking species.

The calculated geometries of the proponium cations followed the same trend observed for other carbonium ions. The geometries of the H-proponium cations show some interesting points with respect of the three-center bond. The C-H bond distance is slightly longer in **3** than in **1** or **2** while the H-H bond length is shorter in **3** than in **1** or **2**. This difference in geometry reflects the degree of bonding between the atoms of the three-center bond and is in good agreement with previous calculated results for other 1-H-carbonium ions. Calculations at the same level and basis set indicate a H-H bond distance in the three-center bond of 0.906 Å in the ethonium^{12f} and 0.903 Å in the 1-H-isobutonium cations.¹⁶ These values are comparable to the 0.909 Å calculated for the 1-H-proponium cation.

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The value of 0.867 Å calculated for the H-H distance of the three-center bond in the 2-H-proponium cation is shorter than the value calculated for the 1-H-carbonium ions, but longer than 0.832 Å, calculated for the 2-H-isobutonium cation.¹⁶ The calculated^{11c} H-H distance of 0.957 Å for the methonium cation is the longest among the H-carbonium ions. Therefore, a qualitative trend for the geometry of the H-carbonium ions can be inferred from calculations. The H-H bond length increases in the order tertiary H-carbonium < secondary H-carbonium < primary H-carbonium < methonium. This also reflects the relative stability and the carbonium ion character of the species. As the H-H bond length becomes shorter, the energy and the carbonium ion character decrease, while the tendency for decomposition to the respective van der Waals complexes increases.

The calculation of the geometry of the C-proponium cation showed asymmetry in the C-H of the three-center bond. The hydrogen atom is stronger bonded to the methyl moiety (1.188 Å) than with the ethyl moiety (1.272 Å). As for the H-carbonium ions, the three-center bond H-CH₃ distance can give an idea of the carbonium ion character of the species. In the ethonium cation,^{12f} this distance is 1.225 Å, and in the C-isobutonium cation,¹⁶ it is 1.137 Å. Moreover, as the H-CH₃ distance shrinks, the carbonium ion character decreases and the tendency for the decomposition to the van der Waals complexes increases.

Conclusions

The potential energy surface of the $C_3H_9^+$ cation was calculated. At our highest level of calculation, MP4/6-311++G**//MP2/6-31G**, the C-proponium cation was the lowest energy species with the van der Waals complex between the isopropyl cation and hydrogen lying only 0.3 kcal/mol above. The H-proponium ions are significantly higher in energy. The 2-H-proponium is about 7 kcal/mol and the 1-H-proponium about 10 kcal/mol higher than **4**. The calculated energies for the reaction of $C_2H_5^+$ with CH_4 to form $C_3H_9^+$ and isopropyl cation plus hydrogen correlated well with the experimental results, supporting the interpretation of an initial formation of the C-proponium ion which rearranges to a 2-H-proponium ion and then to the isopropyl cation and hydrogen.

The calculations showed that the interconversion, or bond-to-bond rearrangement, of carbonium ions is a fast process. The rearrangement of **2** to **4** requires only 0.6 kcal/mol, while the rearrangement of **1** to **4** is a barrierless process. These results may explain the formation of products arisen from C-C protonation of alkanes in liquid and solid superacid systems. Hence, protonation might occur at the outer, and more accessible, primary C-H bonds followed by an internal proton migration to form the thermodynamically more stable C-carbonium ion.

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