Protonated Isobutane. A Theoretical ab Initio Study of the Isobutonium Cations

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Abstract: The structure and energy of the isobutonium cations, protonated isobutane, were studied by *ab initio* methods. At MP2(full)/6-31G** level, besides the C-isobutonium cation (**5**), the 2-H-isobutonium cation (**6**), and the 1-H-isobutonium cation (**7**), two additional structures, representing the van der Waals complex between methane and isopropyl cation (**8**) and hydrogen plus *tert*-butyl cation (**9**), could also be characterized. The energy increases in the order **9** < **8** < **5** < **6** < **7**, indicating the lower energy of the van der Waals complexes. The experimental proton affinity of isobutane is in good agreement with the calculated values for the van der Waals complexes **8** and **9**, indicating the facility of rupture of the three center bond in **5** and **6**. On the other hand, the relative order of stability of the isobutonium cations can explain the experimental gas phase protonation of isobutane by small electrophiles, such as H_3^+ and H_3O^+, as well as the H−D exchange in liquid superacid.

Introduction

Protonation of a π bond of an alkene or an aromatic molecule gives a carbenium ion, where a carbon atom has an empty p orbital and an electronic sextet. On the other hand, protonation of an alkane molecule conceptually gives a carbonium ion,[1] where a three center two electron bond[2] is formed, preserving the electronic octet of the carbon atom. Gas phase[3] and liquid superacid media[4] have shown evidence for the formation of CH_5^+, the simplest carbonium ion. Several theoretical studies[5] also support its existence and generally point to a structure with C_s symmetry. Gas phase decomposition of CH_5^+ into CH_3^+ and H_2 is endothermic by about 40 kcal/mol,[6] suggesting that methonium ion might be an intermediate in methane reactions in superacid systems.
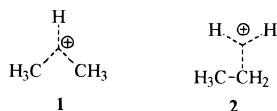
Protonated ethane can exist in, at least, two isomeric structures: the C-ethonium cation (**1**) and the H-ethonium cation

(**2**). In his pioneering studies of alkane reactions in superacid media, Olah recognized the possibility of different sites of protonation in ethane and higher alkanes, stressing that the ability to protonate either the C−C or the C−H bonds of alkanes in solution is strongly related to steric effects associated with the electrophile and the hydrocarbon.[4b,7] Gas phase studies[6,8] of Hiraoka and Kebarle on the $C_2H_7^+$ cation indicated that two isomeric structures could be formed. They proposed that a H-protonated $C_2H_7^+$ cation (**2**) was initially formed in the reaction of $C_2H_5^+$ with H_2 and rearranged to a thermodynamically more stable C-protonated $C_2H_7^+$ cation (**1**). Hiraoka and Kebarle also studied the reaction of $C_2H_5^+$ with CH_4 to form the $C_3H_9^+$ cation, the protonated propane. They initially ascribed[8] the C-protonated $C_3H_9^+$ cation (**3**) as the more stable structure. However, additional experiments led them to conclude that the H-protonated $C_3H_9^+$ cation (**4**), which they described as resembling a complex between the isopropyl cation and hydrogen, was lower in energy than **3**.
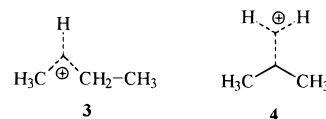
The gas phase experimental studies of Hiraoka and Kebarle with small alkane molecules and of Field and co-workers on the chemical ionization of higher linear alkane molecules[9] showed a preferential protonation in the C−C bond. Theoretical calculations on the $C_2H_7^+$ cation[10] support these data, but the geometry and energy difference between H and C-protonated ethane is very much dependent on the calculation and basis set used. A similar trend was found in the calculation[11] of the protonated propane, where inclusion of electron correlation effects showed to be important.

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Isobutane is the simplest representative of tertiary alkanes. It is also a commercially important hydrocarbon, as it is used in alkylation plants to produce high octane gasolines.[12] Based on a study of the protonation of several linear and branched alkanes,[7,13] Olah established an empirical order of σ bond reactivity in superacid solutions: tertiary C—H > C—C > secondary C—H > primary C—H > CH_4. This order is mostly qualitative and very much dependent on the steric hindrance of the hydrocarbon structure. He found that for the protonation of isobutane in liquid superacid solutions[13a] the *tert*-butyl carbenium ion and hydrogen were the main products, but a significant amount of methane was also observed. These results are consistent with protonation in the tertiary C—H and in the C—C bonds of isobutane. An interesting observation arises from H—D exchange studies. At −78 °C there is an almost exclusive exchange of the tertiary hydrogen,[13] which is compatible with the formation of an intermediate or a transition state resembling a tertiary H-isobutonium cation (Scheme 1). On the other hand, at −10 °C, besides exchange at the tertiary position, exchange at the primary position was also observed and ascribed to the formation of a primary H-isobutonium cation.[14] Small amounts of methane were also observed, indicating that protonation in the C—C bond is a minor pathway compared with protonation in tertiary and primary C—H bonds in liquid superacids.

The search for solid acid catalysts, capable of activating alkanes, is a major goal in petroleum chemistry. The transformation of isobutane on zeolite catalysts at 400 °C and higher temperatures is consistent with the protonation in the C—H and C—C bonds.[15] Nevertheless, the ratio of C—C to C—H protonation, determined by the ratio of formation of methane and hydrogen at lower conversion ranges, is higher or equal to 1.

There are few studies concerning the $C_4H_{11}^+$ cation, especially the isobutonium cation, in the gas phase. Hiraoka and Kebarle studied[6] the reaction between sec-$C_3H_7^+$ and CH_4. According to them, the reaction is exothermic by 3.4 kcal/mol, and a C-isobutonium cation (**5**) is initially formed. They were not able to measure the equilibrium between the 2-H-isobutonium cation (**6**) and hydrogen plus $C_4H_9^+$ but estimated that dissociation should be endothermic by 1 kcal/mol. Therefore, they concluded that **6** is thermodynamically more stable than **5** by 2.7 kcal/mol.

Aquilanti and collaborators[16] studied the protonation of 2-deuterio-2-methylpropane by H_3^+ and D_3^+. They found that deuterated isopropyl cation accounted for about 56% of the product ions, indicating that C—C protonation was the main process occurring. Protonation in the tertiary C—H bond (C—D in this case), to form the *tert*-butyl cation, accounted for 16%, while protonation in the primary C—H bond, to form a primary cation, accounted for 26% of the total ionic products. Since

there are nine primary C—H bonds and only one tertiary C—H bond in the isobutane, the results show that protonation in the tertiary C—H is energetically more favored than protonation in the primary C—H bond. However, protonation in the C—C bond is slightly more favored than protonation in the tertiary C—H. Gas phase protonation of isobutane by H_3O^+ and H_3S^+ has also been studied.[17] With H_3O^+, protonation in the C—C bond to form the s-$C_3H_7^+$ cation, is preferred by a factor of 10 over protonation in the C—H bond, reflecting the higher nucleophilicity of the C—C bonds. On the other hand, protonation with H_3S^+ gives only the t-$C_4H_9^+$ cation. The author did not offer any explanation for the different behaviors but suggested the formation of a more weaker complex between H_3S^+ and isobutane.

The different results observed in gas, liquid, and solid phases for the protonation of isobutane indicate the somewhat complex scheme for tertiary alkanes, where steric effects might play an important role and influence the selectivity pattern. On the other hand, a theoretical description of protonated isobutane would help to understand the protonation of tertiary alkanes. The apparent absence of theoretical studies on the energy and geometry of protonated isobutane led us to carry out a quantum chemistry *ab initio* investigation of the relative energy and geometry of the ions **5**, **6**, and **7**, aiming to acquire a better understanding of the chemistry of isobutane protonation in solid, liquid, and gas phase.

Computational Methods

Calculations at Hartree—Fock, single reference second order Möller—Plesset pertubation theory (MP2), and Density Functional Theory (DFT) levels were performed for cations **5**, **6**, and **7** and the van der Waals complexes **8** and **9**. Optimized geometries were obtained for the five structures, and the harmonic frequency analysis was obtained using analytical second derivatives. Calculations were carried out with the GAMESS US,[18] HONDO 8.5,[19] and Gaussian 94[20] packages of molecular orbital programs. All the MP2 and DFT calculations were performed using the corresponding 6-31G** basis set. For all the optimized geometry structures at MP2 level, a single point MP4 energy calculation, using the same basis set, was also done considering the frozen core approximation. The DFT algorithm chosen combined the Becke's three parameter hybrid method, using the LYP correlation functional (B3LYP). The optimized structures were characterized as minima in the potential energy surface by the absence of imaginary vibrational frequencies. The zero-point energies (ZPE), derived from MP2-(full)/6-31G**, were scaled by 0.93[21] and used to correct the final relative energies. The DFT frequencies were scaled by a factor of 0.96, which was obtained using the DFT(B3LYP) vibrational frequencies of methane and the experimentally known frequencies.

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Table 1. Absolute Energies (−au) of i-$C_4H_{11}^+$ Isomers and Related Species

| species | MP2(full)/6-31G**// MP2(full)/6-31G** | -/6-31G**// MP2/6-31G** | | | DFT(B3LYP)/6-31G**// DFT(B3LYP)/6-31G** |
		MP3(fc)	MP4SDQ(fc)	MP4SDTQ(fc)	
5	158.18585	158.21936	158.22699	158.24430	
6	158.16992	158.20017	158.20657	158.22431	
7	158.16043	158.19026	158.19627	158.21405	158.70758
8	158.18888	158.22393	158.23185	158.24730	158.74930
9	158.18883	158.22175	158.22962	158.24655	158.74653
CH_4	40.36986	40.38285	40.38549	40.38862	40.52402
i-C_4H_{10}	157.93088	157.95989	157.96620	157.98337	158.47225
H_2	1.15766	1.16316	1.16456	1.16456	1.17854
i-$C_3H_7^+$	117.81491	117.83736	117.84274	117.85475	118.22252
t-$C_4H_9^+$	157.03031	157.05771	157.06417	157.08105	157.56770

Table 2. Relative Energies (kcal/mol) of i-$C_4H_{11}^+$ Isomers Corrected to Zero Point Energy and 298.15 K[a]

| species | MP2(full)/6-31G**// MP2(full)/6-31G** | -/6-31G**// MP2(fc)/6-31G** | | | DFT(B3LYP)/6-31G**// DFT(B3LYP)/6-31G** |
		MP3(fc)	MP4SDQ(fc)	MP4SDTQ(fc)	
5	5.96	5.60	5.75	5.51	
6	15.98	17.66	18.58	18.07	
7	22.04	23.98	25.15	24.61	28.60
8	3.78	2.44	2.41	3.34	2.39
9	0.00	0.00	0.00	0.00	0.00

[a] Zero point energy and temperature correction shown in Table 3.

Table 3. Zero Point Energies (ZPE), Enthalpy Changes ($H_{298}^0 - H_0^0$), and Absolute Entropies (S_{298}^0) of i-$C_4H_{11}^+$ Isomers[a]

| species | zero point energy (kcal/mol) | | $H_{298}^0 - H_0^0$ (kcal/mol) | | S_{298}^0 (cal/mol·K) | |
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP[c]
5	82.40		5.61		84.44	
6	83.25		4.78		75.84	
7	83.39	82.86	4.74	4.79	75.68	76.52
8	81.24	80.98	6.48	6.64	93.19	97.49
9	76.91	77.07	7.00	6.42	96.95	94.27
CH_4	27.15	27.16	2.40	2.39	44.45	44.47
i-C_4H_{10}	79.47	79.37	4.27	4.19	70.49	72.21
H_2	6.14	6.14	2.07	2.07	31.08	31.13
s-$C_3H_7^+$	53.12	52.30	3.68	3.76	65.35	67.85
t-$C_4H_9^+$	70.31	70.29	4.59	4.66	76.42	79.27
H^+			1.48[b]	1.48[b]	26.01	26.01

[a] Data obtained using MP2(full)/6-31G** (scaled by 0.93) and DFT(B3LYP)/6-31G** (scaled by 0.96) vibrational frequencies. [b] $E_{trans} + \Delta(pV) = {}^3/_2RT + RT = {}^5/_2$ RT. [c] Using not scaled frequencies

Results

The calculations showed that five stable different structures could be characterized. Besides the carbonium ions **5**, **6**, and **7**, two additional structures were also obtained. Structure **8** can be visualized as a van der Waals complex between methane and the isopropyl cation and structure **9**, as the van der Waals complex between H_2 and the *tert*-butyl cation. Table 1 shows the absolute energies and Table 2 shows the relative energies, after ZPE and temperature (298.15 K) corrections (Table 3), for the structures at all levels of calculation used in this study. Structures **8** and **9** are lower in energy than the carbonium ions. Structure **9** is the most stable one, lying about 3 kcal/mol below structure **8**. Among the carbonium ions, the C-isobutonium cation (**5**) is the most stable structure, about 6 kcal/mol above **9**. The H-isobutonium cations are significantly higher in energy. The 2-H-isobutonium cation (**6**) and the 1-H-isobutonium cation (**7**) are 16−18 and 22−24 kcal/mol higher in energy than structure **9**, respectively. It is important to notice that structures **5** and **6** could only be characterized as minima in the potential energy surface at the MP2/6-31G** level. At the DFT (B3LYP)/6-31G** level, these structures could not be characterized, and the van der Waals complexes **8** and **9** were always

the resulting stable structures using the DFT algorithm. Therefore, all the subsequent geometric results are referred to MP2 calculations.

Figure 1 shows some selected geometrical data for all the structures. For the van der Waals complex **8**, the C−H bond lengths in the CH_4 moiety (1.086 Å) are very close to the experimental distance in an isolated methane molecule (1.087 Å).[22] The isopropyl cation shows a planar conformation, as expressed by the angles between the carbon atoms, near 120°. The complex has a C_s symmetry, and the eletrostatic potential-derived charge[23] (CHelpG) on the central carbon atom is +0.545. The distance between the methane moiety and the isopropyl moiety is 2.89 Å. In structure **9**, the situation is similar to **8**. The H−H bond distance (0.735 Å) is close to the experimental value (0.741 Å)[22] in a hydrogen molecule. The *tert*-butyl moiety also shows a planar conformation, with the angles between the carbon atoms near 120°. The CHelpG charge on the central carbon is +0.609 and about +0.17 on the hydrogens of the methyl groups. The distance between the hydrogen and the central carbon atom of the *tert*-butyl group is 3.34 Å. For the carbonium ions the geometries show significant differences with respect to the van der Waals complex. The C−H bond distances of the three center bond in **5** are not the same. The hydrogen shows a stronger bonding with the methyl carbon (1.137 Å) than with the isopropyl carbon (1.470 Å). The C−C bond length in the three center bond is significantly longer (2.470 Å) than in a normal isobutane molecule (1.535 Å).[22] The C−H−C angle in the three center bond is 142.3°, indicating a nonlinear geometry. The CHelpG charge on the central carbon atom of the isopropyl moiety is +0.39, significantly lower than the charge in structure **8**, indicating the interaction with the hydrogen in the three center bond. The CHelpG charge on the carbon of the methyl group is −0.21, stressing the stronger bonding with the hydrogen of the three center bond. The C−H bond length of the three center bond in **6** is about 1.29 Å, significantly longer than the experimental tertiary C−H bond distance in isobutane (1.122 Å).[22] The distance between the hydrogens in the three center bond is 0.832 Å, which is longer than the experimental distance of 0.741 Å in the H_2 molecule.[22] The H−C−H angle in the three center bond is 37.7°, stressing

(22) *CRC Handbook of Chemistry and Physics*, 75th ed., Lide, D. R., Ed.; CRC Press: 1994.
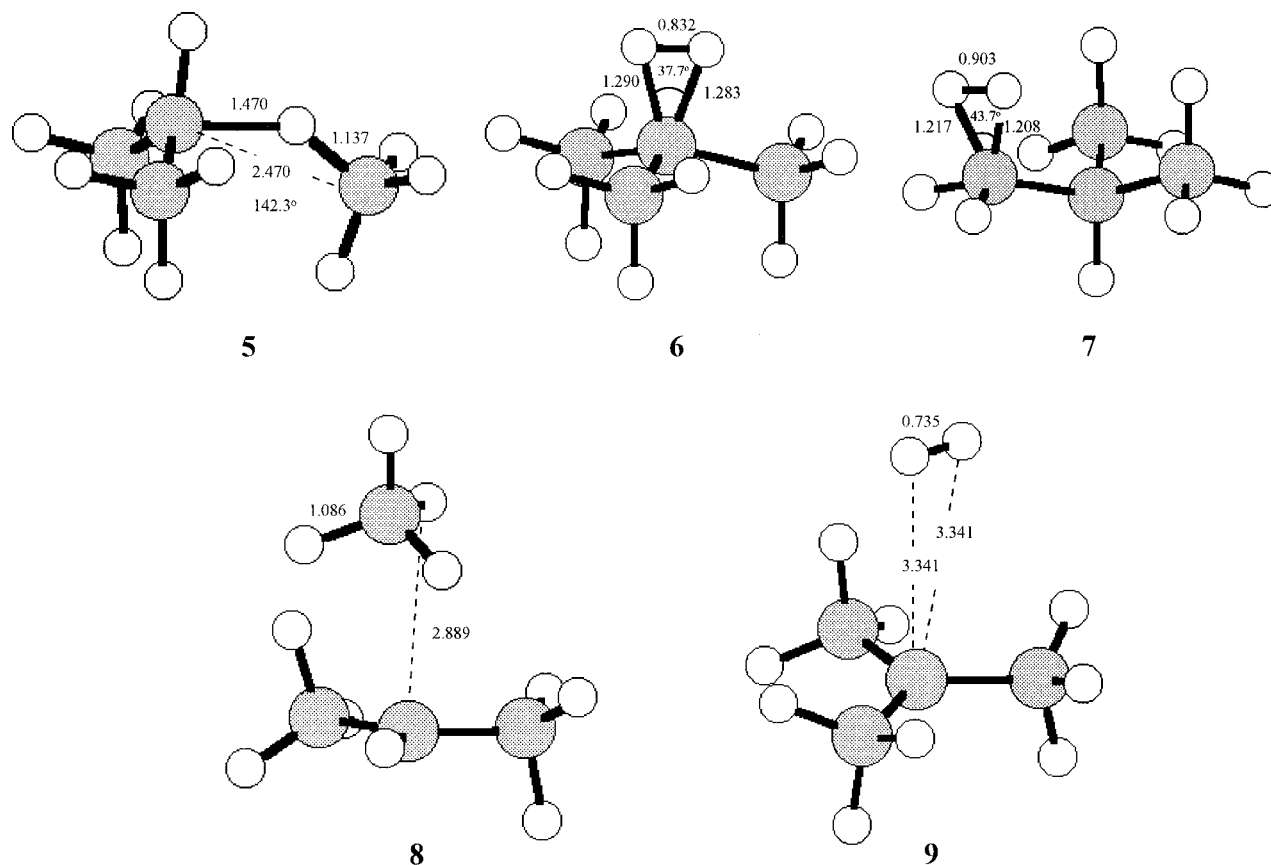
Figure 1. MP2 (full)/6-31G** geometries of i-$C_4H_{11}^+$ isomers.

Table 4. Thermochemical Data for Selected Reactions at 298.15 K[d]

| | MP2(full)/6-31G** | | -/6-31G**//MP2(fc)/6-31G** | | | DFT(B3LYP)/6-31G** | | |
| | | | MP3(fc) | MP4SDQ(fc) | MP4SDTQ(fc) | | | |
reaction	ΔH	ΔS	ΔH	ΔH	ΔH	ΔH	ΔS	exptl ΔH
$C_4H_{11}^+$ (**5**) → i-C_4H_{10} + H⁺	157.20	12.06	160.02	160.85	160.94			
$C_4H_{11}^+$ (**6**) → i-C_4H_{10} + H⁺	147.19	20.66	147.96	148.02	148.38			
$C_4H_{11}^+$ (**7**) → i-C_4H_{10} + H⁺	141.13	20.82	141.64	141.45	141.84	145.05	21.70	
$C_4H_{11}^+$ (**8**) → i-C_4H_{10} + H⁺	159.39	3.31	163.18	164.19[a]	163.11[b]	171.26	0.73	164.0[c]
$C_4H_{11}^+$ (**9**) → i-C_4H_{10} + H⁺	163.17	-0.45	165.62	166.60[a]	166.45[b]	173.65	3.95	166.8[c]

[a] Considered as the theoretical proton affinity [PA(MP4SDQ/6-31G**//MP2/6-31G**)]. [b] Considered as the theoretical proton affinity [PA(MP4SDTQ/6-31G**//MP2/6-31G**)]. [c] Experimental proton affinity (PA). [d] ΔH (kcal/mol) and ΔS (cal/mol·K).

the nonlinearity of this type of bonding. The CHelpG charge on the central carbon atom is +0.284, which is significantly lower than the charge in structure **9** (+0.609) and about +0.22 on the hydrogens of the three center bond. The CHelpG charge on the hydrogens of the methyl groups is about +0.14. The geometry of structure **7** shows a C—H bond distance in the three center bond around 1.21 Å, slightly higher than the experimental primary C—H bond length in isobutane (1.113 Å).[22] The H—C—H angle in the three center bond is 43.7°, slightly higher than in **6**, reflecting the longer H—H bonding in **7** (0.903 Å) compared to **6**. The CHelpG charges on the atoms of the three center bond are −0.306 on the carbon and +0.28 on the hydrogens.

Table 4 shows some selected thermochemistry reactions involving the i-$C_4H_{11}^+$ isomers and related cations at MP2, MP4, and DFT levels. Comparison with experimental data of isobutane proton affinity[6,24] showed a very good agreement with MP4 calculations. Table 5 shows some selected calculated

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Table 5. Selected Calculated Vibrational Frequencies of the i-$C_4H_{11}^+$ Isomers

structure	frequency (cm⁻¹)	intensity (D²/amu·Å²)	approximate description of normal mode
5	2488.64	1273.49	sym stretch of 3c-2e bond
	92.48	308.46	stretch of C−C 3c-2e bond
6	3172.36	0.98	stretch H−H (sym stretch of C−H 3c-2e bond)
	1815.78	3.36	asym stretch of C−H
7	3014.21	100.85	asym stretch of CH_4
	2899.92	488.08	sym stretch of C−H of CH_4
	2706.60	0.18	stretch H−H of CH_4 (sym stretch of C−H 3c-2e bond)
	2175.91	87.93	asym stretch of C−H of CH_4
8	3074.72	0.28	sym stretch of CH_4
9	4266.11	0.02	stretch of H_2

vibrational frequencies of the carbonium ions **5**, **6**, and **7** at MP2(full) level, together with the assigned vibrational mode. Calculation of the vibrational modes of the H_2 molecule, at the same level and basis set used, indicated a symmetric vibration at 4296 cm⁻¹, which is higher than the experimental value[22] of 4160 cm⁻¹. The calculated H−H symmetric vibration for the van der Waals complex **9** (4266 cm⁻¹), as could be anticipated,

is close to the calculated value for an isolated H_2 molecule. On the other hand, the frequency of H−H vibration for the H-isobutonium ions **6** and **7** is 3172 and 2706 cm^{-1}, respectively, characterizing the three center bonding in these ions.

Discussion

Energy and Geometry. The calculations pointed out that among the i-$C_4H_{11}^+$ species, the protonated isobutane, the most stable structure is the one representing the van der Waals complex between hydrogen and *tert*-butyl cation (**9**). The complex between methane and isopropyl cation (**8**) is 2.4, 3.8, and 3.3 kcal/mol higher in energy at the DFT, MP2 (full) and MP4 levels, respectively. All the isobutonium cations are higher in energy compared with the van der Waals complexes **8** and **9**. The C-isobutonium cation (**5**) is 6 and 5.5 kcal/mol higher in energy than **9** at the MP2 (full) and MP4 levels, respectively, while the 2-H-isobutonium cation (**6**) is 16 and 18.1 kcal/mol higher than **9** at the MP2 (full) and MP4 levels, respectively. The 1-H-isobutonium cation is the highest calculated energy structure, lying 22 and 26.6 kcal/mol higher in energy than **9** at MP2 (full) and MP4 levels, respectively. At the DFT (B3LYP)/ 6-31G** level, structures **5** and **6** could not be characterized, and calculations always converge to the respective van der Waals complexes. On the other hand, structure **7** could be characterized as a minimum in the potential energy surface at DFT level, lying 28.6 kcal/mol higher in energy than **9**. These findings indicate that DFT level of theory does not represent correctly weak interactions like three center two electron bondings in carbonium ions. Indeed, literature data[25] have already showed that DFT is not good for describing weak interactions.

The results of the MP2 and MP4 calculations on the relative stabilities of the carbonium ions stressed the preference for the C-isobutonium cation relative to the H-isobutonium cations. This result is in agreement with previous calculations[10,11] on ethonium and proponium cations, which pointed out that the C-carbonium ions are more stable than H-carbonium ions, even in tertiary alkanes. This fact may be explained by the electron distribution in the three center bond. In the C-carbonium ions, the positive charge on the hydrogen of the three center bond is significantly lower than in isomeric H-carbonium ions, which means that the charge is better distributed and delocalized among the atoms, lowering the energy of the ion.

The calculated geometries of the carbonium ions show some significant differences. In **6**, the H−H bond length in the three center bond is shorter than in **7**, reflecting the stronger interaction between the hydrogens in the former ion. Compared with calculations of methonium and ethonium cations, at the same level and basis set, the H−H bond distance in **7** (0.903 Å) is equivalent to the distance in the ethonium cation (0.906 Å)[10f] and shorter than in methonium cation (0.957 Å).[5c] These results indicate that the degree of interaction between the hydrogens of the three center bond in H-carbonium ions is dependent on the type of carbon atom participating in the bond. In tertiary H-carbonium ions, the H−H bonding is shorter than in primary H-carbonium ions, which, in turn, show a stronger H−H bonding than in the methonium cation. The calculations of vibrational frequencies also stress this point. The H−H stretching vibration in **6** is observed at 3172 cm^{-1}, while in **7** it is observed at 2706 cm^{-1}. The values calculated[10f] for H-ethonium and methonium cations are 2716 and 2619 cm^{-1}, respectively. These results reinforce the previous discussion on the degree of H−H bonding in H-carbonium ions, showing that in tertiary H-carbonium ions, there is a stronger bonding

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between the hydrogens of the three center bond, while in methonium and primary H-carbonium ions the H−H bonding is weaker. By consequence, the C−H bond distance in the three center bond follows an opposite trend, being longer for tertiary H-carbonium ions and shorter for the methonium cation. As the strength of an H−H bond is usually higher than the strength of a primary or tertiary C−H bond, it would be reasonable to associate the relative stabilities of H-carbonium ions to the degree of H−H bonding in the three center bond. This assumption can explain the relative stabilities of the H-isobutonium cations **6** and **7**.

The geometry of the C-isobutonium cation shows some peculiarities. The C−H bond lengths in the three center bond are not identical, indicating asymmetry. The bonding with the methyl carbon is significantly shorter than with the isopropyl carbon. In the C-ethonium cation, where a hydrogen is bonded to two methyl groups, the C−H distances are equal (1.225 Å).[10f] The C−H−C bond angle of 142.3° in **5** is significantly higher than the 105.6 ° calculated[10f] for the C-ethonium cation. This finding reflects the nature of the three center bond in higher alkanes. Since in **5** the C−H bond lengths are not equal, the C−C bond becomes more stretched, leading to a higher C−H−C angle, compared with the C-ethonium cation.

Thermochemical Calculations. The data in Table 4 show that the experimental proton affinity of isobutane,[6] determined by Hiraoka and Kebarle, to form two isomeric i-$C_4H_{11}^+$, correlates very well with the calculated MP4(SDQ) and MP4-(SDTQ) proton affinity of isobutane to form the van der Waals complexes **8** and **9**, rather than with the carbonium ions, **5** and **6**. This finding indicates that in the experimental gas phase measurements of Hiraoka and Kebarle, the two protonated isobutane formed are not the real carbonium ions but the van der Waals complexes. The experimental[6] $\Delta H_f°$ of 170.7 kcal/ mol for the C-isobutonium and 168.0 kcal/mol for the 2-H-isobutonium were also very close to the values calculated for the van der Waals complexes **8** (170.93 kcal/mol at MP4(SDQ)/ 6-31G** and 172.01 kcal/mol at MP4(SDTQ)/6-31G**) and **9** (168.52 kcal/mol at MP4(SDQ)/6-31G** and 168.67 kcal/mol at MP4(SDTQ)/6-31G**). The experimental energy difference of 2.7 kcal/mol between the two i-$C_4H_{11}^+$ ions, observed by Hiraoka and Kebarle,[6] is close to the energy difference between the van der Waals complexes **8** and **9**, which is 3.3 kcal/mol at the MP4(SDTQ)/6-31G**//MP2/6-31G** level of calculation and 2.41 kcal/mol at the MP4(SDQ)/6-31G** level. The energy difference between the carbonium ions **5** and **6** is considerably higher, favoring structure **5** by approximately 12.6 and 12.83 kcal/mol, at the same level of calculation, respectively. It is interesting to note that the experimental PA and $\Delta H_f°$ of the $C_4H_{11}^+$ species are better correlated with the MP4(SDQ)/6-31G** results rather than with the MP4(SDTQ)/6-31G** ones.

As mentioned by Hiraoka and Kebarle, the i-$C_4H_{11}^+$ ion, resembling the 2-H-isobutonium cation, is not a real carbonium ion but a loosely bound complex between hydrogen and *tert*-butyl cation. The calculations not only supported this point but also indicated that the i-$C_4H_{11}^+$ ion, resembling the C-isobutonium cation in the work of Hiraoka and Kebarle, is not a real carbonium ion either but a weakly bound complex between methane and isopropyl cation. Hence, it could be inferred that the C-isobutonium and the 2-H-isobutonium ions are very unstable intermediates (very shallow minima in the potential energy surface), which tend to decompose to the corresponding van der Waals complexes **8** and **9**.

Comparison with Experimental Results. One of the major goals in studying the structure and energetics of carbonium ions is to correlate these subjects with the chemistry of electrophilic

Scheme 1. H−D Exchange of Isobutane in Liquid Superacid at −78 °C
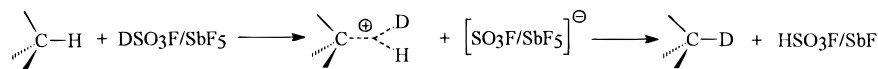
alkane activation, especially in superacid solutions and zeolite surfaces. In liquid superacid solutions isobutane preferentially reacts to form the *tert*-butyl cation and hydrogen,[7,26] suggesting the formation and decomposition of the 2-H-isobutonium cation rather than the C-isobutonium cation. On the other hand, gas phase results[16] of isobutane protonation with H_3^+, obtained by Aquilanti and collaborators, clearly indicated the preferred electrophilic attack in the C−C bond, with formation of methane and isopropyl cation. Protonation in the tertiary C−H, to form hydrogen and *tert*-butyl cation, is the second major process, followed by protonation in the primary C−H bond to form hydrogen and the primary isobutyl cation. These gas phase results are in good agreement with the calculated relative stabilities of the isobutonium cations, **5**, **6**, and **7**, suggesting that these carbonium ions might be involved in the gas phase protonation of isobutane. The different regioselectivity for isobutane protonation in gas phase and superacid solution may be attributed to steric reasons associated with the electrophile. In the work of Aquilanti, the protonation is carried out by H_3^+, which is small enough to reach the inner C−C bonds of isobutane. On the other hand, in liquid superacid solution, protonation is carried out by H_2F^+, $H_2SO_3F^+$, and more associated cations,[7] which are significantly more space demanding to attack the inner C−C bonds of isobutane. Indeed, Olah has already used[7] this concept in explaining the different regioselectivity observed for alkane protonation in HF/SbF5 and HSO3F/SbF5. Another evidence for the importance of steric effects for the C−C protonation in isobutane arises from the gas phase work of Hiraoka.[17] When using H_3O^+ as the protonating agent, he observed C−C protonation as the preferred pathway. However, when the bulkier H_3S^+ was used as electrophile, C−H protonation was favored.

An interesting reaction accompanying protonation and ionization of alkanes in liquid superacid systems is the H−D exchange. At −78 °C, isobutane exchanges the tertiary hydrogen almost exclusively.[7] This result is in contrast with H−D exchange in D_2SO_4, where only the methyl hydrogens are exchanged.[27] The different regioselectivity for exchange in superacids and sulfuric acid is due to different mechanisms. In the latter, there occurs an initial oxireduction reaction[28] to give the *tert*-butyl cation, which can undergoes consecutives elimination−protonation reactions. In superacids, the exchange in the tertiary position suggests the formation of the 2-H-isobutonium cation, as shown in scheme 1. At −10 °C, besides the preferred exchange in the methine, exchange of the hydrogens in the methyl position is also significant[14] and associated with formation of the 1-H-isobutonium cation. This latter result is in agreement with the calculated relative stabilities of the H-isobutonium cations **6** and **7**.

Recent studies on the role of acid strength in the ionization (formation of *tert*-butyl cation) and H−D exchange of isobutane in DF/SbF5 superacid systems carried out by Sommer and collaborators[29] indicated that as the acid strength increases, by

Scheme 2. Possible Transition State for H−D Exchange in Liquid Superacid Systems
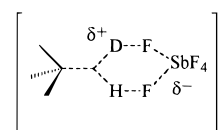
increasing the amount of SbF5, the ratio of ionization to H−D exchange increases. On the basis of our present calculations and from the gas phase experimental data of Hiraoka and Kebarle,[6] one would expect that protonation in the tertiary C−H bond of isobutane, with formation of a free 2-H-isobutonium cation, should straightforwardly give the *tert*-butyl cation and hydrogen. Therefore, the observed H−D exchange in the methine position of isobutane should not involve a free carbonium ion as intermediate, as pictured in Scheme 1. We suggest that exchange occurs by a transition state, resembling the 2-H-isobutonium cation (**6**), where the proton and the deuteron, in the three center bond, are interacting with the anion (Scheme 2). As the acid strength increases, by the addition of more SbF5, the nucleophilicity of the anion decreases, due to a better delocalization of the negative charge. Hence, the interaction with the atoms in the three center bond becomes weaker, leading to a transition state with more carbonium ion character, thus favoring ionization to *tert*-butyl cation and hydrogen rather than exchange. A similar transition state has already been proposed by Olah,[7,30] to account for the formation of SbF3 in hydrocarbon reactions in HF/SbF5 superacid solution.

It seems that, in zeolites, protonation in the C−C and in the tertiary C−H bond of isobutane are equally probable.[15] This result is somewhat surprising, since recent calculations[31] on the structure of carbocations adsorbed on a cluster, representing a real part of the zeolite Y structure, suggested that steric factors play an important role in hydrocarbon reaction over zeolites. Therefore, one would expect a preferential protonation in the more accessible C−H bonds of isobutane. On the other hand, the energy barrier for the interconversion of H-isobutonium and C-isobutonium ions, isotopal rearrangement as referred by Olah, could be small and account for the observed results in zeolites. Gas phase experimental results for ethonium[6,8] and proponium cations[8] suggest that the barrier is around 2−5 kcal/mol, and could be even lower for higher alkanes. We are presently studying the energy barrier for the interconversion of H and C-isobutonium cations and the reaction pathway involved in C−H and C−C bond protonation.

Conclusions

Theoretical studies at the MP4/6-31G**//MP2/6-31G** level of the protonated isobutane revealed that the van der Waals complexes **8** and **9** are lower in energy than the isobutonium cations **5**, **6**, and **7**. After ZPE and temperature corrections, structure **9** was found to be the lowest energy species. Among the carbonium ions, the energy increases in the order **5** < **6** < **7**, stressing the lower energy of C-carbonium ions. The relative

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stabilities of the H-carbonium ions may be explained by the extent of H−H bonding in the three center bond, being stronger in **6** than in **7**, while the lower energy of **5** compared with the H-isobutonium cations is probably due to the better charge distribution among the atoms of the three center bond.

The experimental data of proton affinity for isobutane and the heat of formation of the $C_4H_{11}^+$ cations obtained by Hiraoka and Kebarle are better correlated with the calculated value obtained for the van der Waals complexes, **8** and **9** rather than for the carbonium ions **5** and **6**, indicating that once the C-isobutonium and 2-H-isobutonium cations are formed, there is a fast and favorable conversion to form the van der Waals complexes between the carbenium ions and hydrogen or methane. On the other hand, the experimental gas phase results of isobutane protonation by H_3^+ are in good agreement with the calculated relative stabilities of the isobutonium cations, stressing the role of carbonium ions in alkane protonation.

Supporting Information Available: Complete geometric data, charge distribution and vibrational frequencies for all the $i\text{-}C_4H_{11}^+$ isomers (15 Tables) (10 pages). See any current masthead page for ordering and Internet access instructions.

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