J. Phys. Chem. A **2000,** *104,* 6233−6240

The *n*-Butonium Cation (n-$C_4H_{11}^+$): The Potential Energy Surface of Protonated *n*-Butane

Pierre M. Esteves,[†] Gabriel G. P. Alberto,[†] Alejandro Ramírez-Solís,[‡] and Claudio J. A. Mota*,[†]

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

Received: March 28, 2000

The structure and energetics of the *n*-butonium ion, the protonated form of *n*-butane, were computed at the MP4SDTQ(fc)/6-311++G**//MP2(full)/6-31G** level. Eleven stable structures were found for the *n*-butonium ion, following the stability order 2-C-*n*-butonium > 1-C-*n*-butonium > 2-H-*n*-butonium > 1-H-*n*-butonium. The transition states for intramolecular bond-to-bond rearrangement and for decomposition of the carbonium ions into the van der Waals complexes were also calculated. The H-*n*-butonium and the 1-C-*n*-butonium ions are higher in energy than the van der Waals complexes **13**, **14**, and **15**. The van der Waals complexes between the isopropyl cation plus CH_4 and the *tert*-butyl cation plus H_2 are the most stable $C_4H_{11}^+$ species. It was concluded that the 1-H-*n*-butonium ion prefers to undergo intramolecular rearrangement to the 1-C-*n*-butonium ion, whereas the 2-H-*n*-butonium ion prefers to decompose into the van der Waals complex of the *sec*-butyl cation plus H_2. The calculated proton affinity of *n*-butane (156.7 kcal/mol) agrees well with the experimental value of 153.7 kcal/mol. The $C_4H_{11}^+$ (b) species, formed upon the gas-phase reaction between $C_2H_5^+$ and ethane, was confirmed to be the 2-C-*n*-butonium cation, and the $C_4H_{11}^+$ (a) species was confirmed to be the 2-H-*n*-butonium cation, as proposed by Hiraoka and Kebarle (*Can. J. Chem.* **1980**, *58*, 2262−2270). The experimental activation energy of 9.6 kcal/mol was compared with the value of 12.8 kcal/mol, computed for the reaction **11** → **5** through the transition state **21**.

Introduction

Carbonium ions are important species involved in acid-catalyzed alkane transformations. The methonium[1] (CH_5^+) and ethonium[2] ($C_2H_7^+$) ions are the smallest members of this family and have already been observed in the gas phase by spectroscopic methods.[3,4] Theoretical ab initio calculations[5,6] predict a structure with C_s symmetry for CH_5^+, although the interconversion among different configurations involves low activation barriers, making the hydrogen atoms very mobile in the structure.[7−9] For the $C_2H_7^+$ cation, theoretical calculations[10] reveal the C-ethonium ion, hypothetically formed through the protonation in the C−C bond of ethane, as the lowest energy species. Nevertheless, the higher carbonium ions have almost not been studied by theoretical methods. Our group has recently performed ab initio calculations for the proponium[11] and the isobutonium[12,13] cations, at the perturbational second- and fourth-order Møller−Plesset levels of theory. For i-$C_4H_{11}^+$, protonated isobutane, the calculations indicated that the van der Waals complexes between *tert*-butyl carbenium ion and hydrogen and isopropyl carbenium ion and methane are lower in energy than the carbonium ions themselves. Indeed, additional calculations[13] revealed that decomposition of 2-H-isobutonium, hypothetically formed through the protonation of the tertiary C−H bond of isobutane, and of C-isobutonium, formed upon protonation of the C−C bond of isobutane, to the respective van der Waals complexes occurs with low or no activation energy. A similar conclusion was found by Collins and O'Malley using DFT calculations.[14]

The good correlation of the theoretical results for propane and isobutane with the available experimental results led us to investigate the structure and energetics of the *n*-butonium cations (n-$C_4H_{11}^+$). These species are isomeric with the isobutonium cations, and this fact allows direct comparisons among the different $C_4H_{11}^+$ structures. In a recent study,[15] we compared the relative energies of the $C_4H_{11}^+$ carbonium ions. The calculations confirmed that the C-butonium ions are lower in energy than the H-butonium ions. The results were interpreted in terms of charge delocalization in the atoms and groups of the three-center−two-electron (3c−2e) bonds. Thus, on H-carbonium ions, the hydrogen atoms bear a higher positive charge compared with those on C-carbonium, where the carbon atoms and alkyl groups can better accommodate the charge. This study also indicated that protonation of alkanes in liquid superacids are governed by kinetic factors associated with the barrier for proton transfer to the σ bond, rather than by the thermodynamic factors associated with the basicity of the C−C and C−H bonds.

Protonation of *n*-butane can take place at the primary C−H bonds (six overall), at the secondary C−H bonds (four overall), and at two distinct types of C−C bonds (two external and one internal) to form different isomeric structures of the n-$C_4H_{11}^+$ cation, as shown in Scheme 1. Experimental data indicate that *n*-butonium ions are intermediates in some gas-phase reactions. Hiraoka and Kebarle[16] studied the gas-phase reaction of $C_2H_5^+$ with ethane and observed the formation of a $C_4H_{11}^+$ (b) intermediate, which they suggested was the 2-C-butonium ion. They estimated the exothermicity of the reaction as 13 kcal/mol (Scheme 2). The $C_4H_{11}^+$ (b) species interconverts to the isomeric $C_4H_{11}^+$ (a) species, which can easily decompose into $C_4H_9^+$ and H_2. This reaction has an activation energy of 9.3

---

* Author to whom correspondence should be addressed.

[†] Universidade Federal do Rio de Janeiro.

[‡] Universidad Autónoma del Estado de Morelos.

10.1021/jp001152j CCC: $19.00

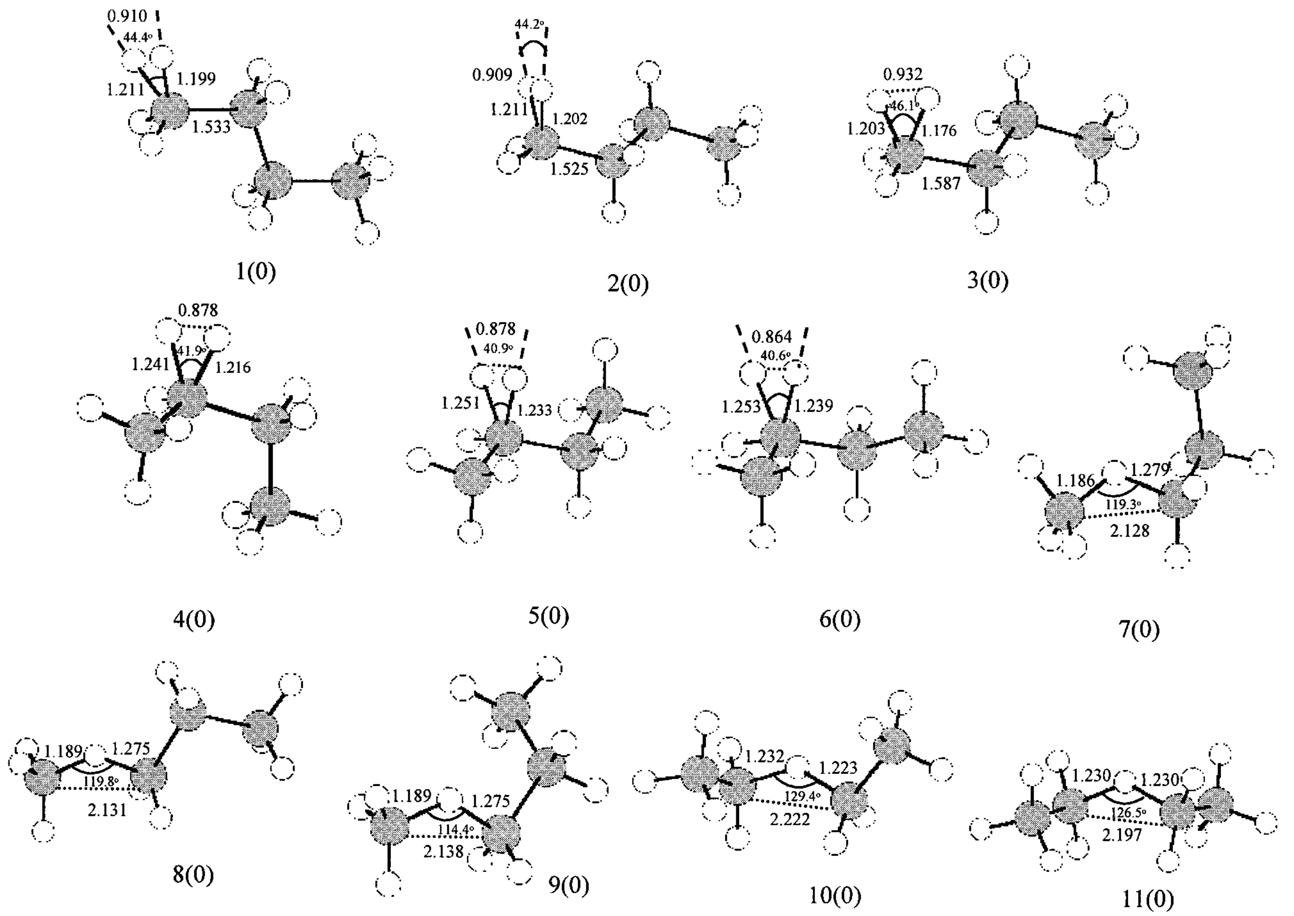
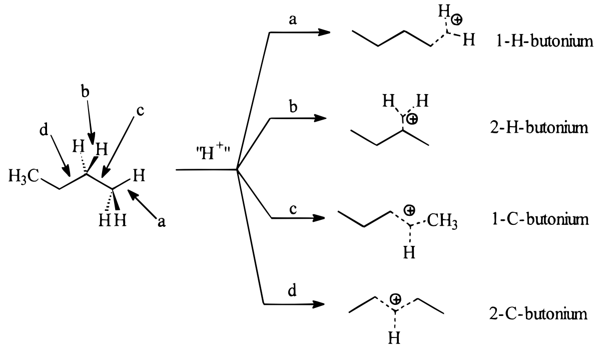


Figure 1. Minima computed for the *n*-$C_4H_{11}^+$ species.

SCHEME 1 : Schematic View of the Protonation of *n*-Butane



SCHEME 2 : Energetics of $C_2H_5^+ + C_2H_6$ Gas-Phase Reactions (data from ref 16)

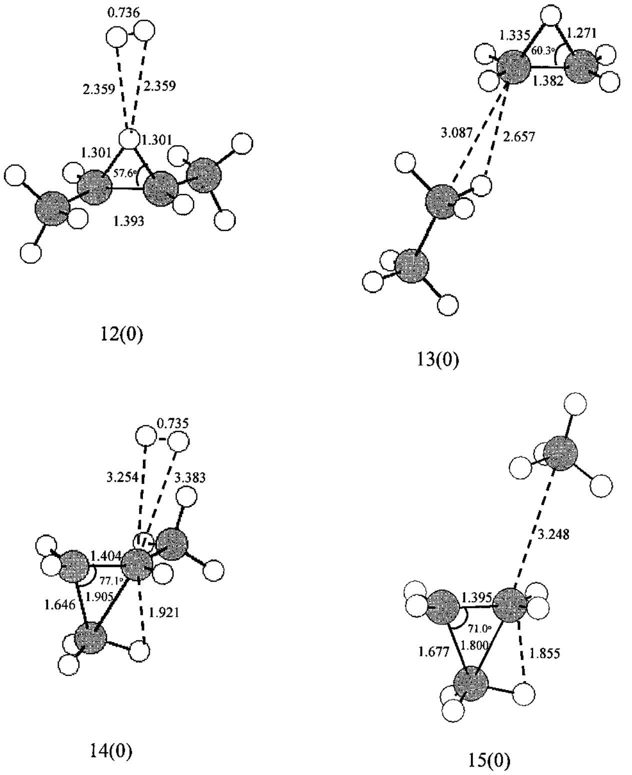
$C_2H_5^+ + C_2H_6 \rightarrow C_4H_{11}^+(b)$	$\Delta H = -13$ kcal/mol
$C_4H_{11}^+(b) \rightarrow [C_4H_{11}^+(a)] \rightarrow C_4H_9^+ + H_2$	$\Delta H = -7.8$ kcal/mol; $\Delta H^{\neq} = 9.6$ kcal/mol
$C_2H_5^+ + C_2H_6 \rightarrow C_4H_9^+ + H_2$	$\Delta H = -20.8$ kcal/mol

kcal/mol and is exothermic by 7.8 kcal/mol. Hiraoka and Kebarle proposed that the 2-H-butonium cation corresponds to the structure of the $C_4H_{11}^+$ (a) species. Hence, it decomposes to the *sec*-butyl cation plus hydrogen. The $C_2H_5^+ + C_2H_6 = C_4H_9^+ + H_2$ equilibrium showed a value of $\Delta H = -20.8$ kcal/mol. The proton affinity (PA) of *n*-butane was estimated to be 155 kcal/mol, forming the 2-C-butonium ion. Updated data, obtained from the NIST database[17] (see Supporting Information), indicate an exothermicity of 13.6 ± 3 kcal/mol for the reaction $C_2H_5^+ + C_2H_6 \rightarrow C_4H_{11}^+(b)$ and estimate the proton affinity of *n*-butane as 153.7 kcal/mol. These new values still hold with the data previously reported. Nevertheless, the enthalpy change for the $C_2H_5^+ + C_2H_6 = C_4H_9^+ + H_2$ equilibrium is much smaller than previously reported by Hiraoka and Kebarle. Using the new experimental literature from NIST, one predicts the ΔH value as -12.3 kcal/mol. As a consequence, the enthalpy change for the interconversion of $C_4H_{11}^+(b) \rightarrow [C_4H_{11}^+(a)] \rightarrow C_4H_9^+ + H_2$ was recomputed to be 1.3 kcal/mol.

Experiments in liquid superacid media[18] showed that *n*-butane is formed when a mixture of ethylene and ethane is bubbled through such media. The reaction was explained in terms of the formation of the 2-C-*n*-butonium ion as an intermediate. In this work, we report a detailed ab initio computational study of the *n*-butonium ion, protonated *n*-butane, showing the potential energy surface and comparing the energetic and interconversion results with available solution and gas-phase data.

1.1 Computational Details

All calculations were performed at the MP4SDTQ(fc)/6-311++G**//MP2(full)/6-31G** level, as previously used for isobutonium and proponium cations. This level of theory proved to give good correlation with published experimental data. Nevertheless, for hypercoordinated ions such as carbonium, it is possible that these species may present large, fairly flat regions, which would mean that small changes in the relative energies could represent large displacements in the nuclear positions. Thus, the use of this level of calculation, despite being accurate enough for predicting the energetics of chemical processes (within a few kcal/mol of the true values), serves as an initial exploratory study of the main processes in the highly complex potential energy surface (PES) of the hypercoordinated



12(0) 13(0) 14(0) 15(0)

Figure 2. van der Waals complexes computed as minima for the *n*-$C_4H_{11}^+$ species.

n-butonium ions. The vibrational frequencies were obtained at the MP2(full)/6-31G** level, and the number of imaginary frequencies, computed for these stationary points in the PES, characterizes the structure as a minimum (no imaginary frequencies) or as a transition state (one imaginary frequency). All energy differences were corrected for zero-point energy (ZPE) and for a finite temperature of 298.15 K, considering the vibrational frequencies to be scaled by 0.93.[19] If not otherwise stated, all discussion refers to enthalpy differences at 1 atm and 298.15 K. The calculations were performed using the Gaussian 94[20] and GAMESS US[21] packages.

1.2 Results

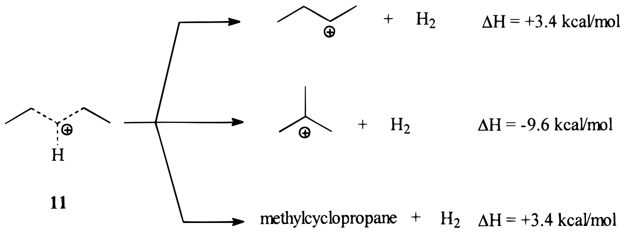
Eleven structures were located as minima in the potential energy surface of protonated *n*-butane. Figure 1 shows the structures corresponding to these minima. Protonation at the primary C−H bond produces structures **1**−**3**, corresponding to conformational isomers of the 1-H-*n*-butonium cation. Protonation at secondary C−H bonds leads to structures **4**−**6**, the conformers of the 2-H-*n*-butonium cation. Protonation at primary C−C bonds (external) forms the conformers **7**−**9**, corresponding to the 1-C-*n*-butonium ion, and protonation at the secondary C−C bond (internal) leads to the conformers **10**−**11** of the 2-C-*n*-butonium cation. Other minima in the PES were also found, and they correspond to van der Waals complexes (Figure 2). Structure **12** corresponds to the complex between the *sec*-butyl cation and H_2. Structure **13** represents the $C_2H_5^+$ cation plus ethane. The complex between protonated methylcyclopropane plus hydrogen corresponds to structure **14**, while protonated cyclopropane plus methane is shown as structure **15**. Table 1 reports the relative enthalpies, computed at the MP4SDTQ(fc)/6-311++G**//MP2(full)/6-31G** level (using the scaled vibrational frequencies at the MP2 level). See Scheme 3 for the thermochemistry of the formation of the van der Waals complexes from **11**.

TABLE 1: Relative Energies of *n*-$C_4H_{11}^+$ Isomers Corrected for Zero Point Energies and 298.15 K[a]

species	MP4SDTQ(fc)/6-311++G**// MP2(full)/6-31G**
1	16.6
2	15.7
3	16.4
4	12.5
5	11.3
6	11.8
7	4.5
8	5.1
9	4.7
10	0.1
11	0.0
12	2.3
13	13.4
14	2.2
15	1.4
16	15.7
17	16.1
18	14.8
19	15.1
20	13.3
21	12.8
22	13.4
23	21.5
24	22.3
25	12.1
26	11.0
27	11.3
28	6.6
29	6.3
30	12.2
s-$C_3H_7^+{\cdot}CH_4$ **(31)**	−5.8
t-$C_4H_9^+{\cdot}H_2$ **(32)**	−9.7
n-C_4H_{10} + H^+	156.7
$C_2H_5^+$+ C_2H_6	16.0
t-$C_4H_9^+$+ H_2	−9.6
s-$C_3H_7^+$+ CH_4	−4.5
s-$C_4H_9^+$ + H_2	3.4
s-$C_4H_9^+$[b] + H_2	3.5

[a] Values of ΔH^0_{298} in kcal/mol. [b] Protonated methylcyclopropane.

SCHEME 3 : Thermochemistry of the Formation of van der Waals Complexes from the 2-C-*n*-Butonium Ion (11)



The ab initio calculations at the MP4 level indicate that the most stable *n*-$C_4H_{11}^+$ species is the 2-C-*n*-butonium cation **11**. Nevertheless, its conformer **10** is only 0.1 kcal/mol higher in energy. The next more stable structure is the van der Waals complex of the *sec*-butyl cation and H_2 (**12**), illustrating the trend of the 2-H-*n*-butonium ions to decompose, as observed for the 2-H-proponium cation.[11] The 1-C-*n*-butonium cations (**7**−**9**) are next in stability, reinforcing the lower energy of C-carbonium ions compared to H-carbonium ions. Among the H-*n*-butonium ions, the 1-H-*n*-butonium cations were calculated to be more energetic than the 2-H-*n*-butonium ions. One observes that **2** is the most stable structure among the conformers corresponding to the 1-H-*n*-butonium ion, being 0.9 and 0.7 kcal/mol lower in energy than structures **1** and **3**, respectively. Among the 2-H-*n*-butonium ions, **5** was found to be the most

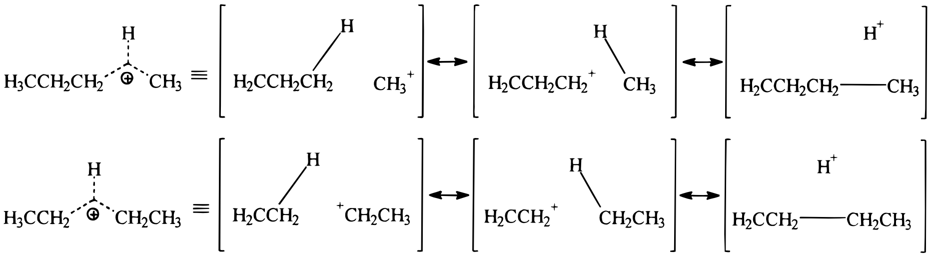


Figure 3. Resonance structures for the C-butonium cations.

stable structure, followed, respectively, by **6** and **4**. The van der Waals complexes **13**, **14**, and **15** show higher stability than the 1-H-*n*-butonium cations. These ab initio calculations indicate that the stability of the carbonium ions, formed by the protonation of different σ bonds of *n*-butane, decreases in the order secondary C−C > primary C−C > secondary C−H > primary C−H. We must stress here that this order of stability is in agreement with the concept of σ bond reactivity proposed by Olah[22] and is also consistent with the results obtained for the proponium[11] and isobutonium[12,13] ions.

The greater stability of the 2-C-*n*-butonium cations in relation to the 1-C-*n*-butonium cations can be rationalized in terms of resonance structures. One can conclude that the 2-C-*n*-butonium cation has a greater capability of stabilizing the positive charge, as it can delocalize the charge over two ethyl groups linked to the three-center−two-electron bond. For the 1-C-*n*-butonium cation, one of the resonance structures involves a methyl cation, explaining the difference in stability compared to the 2-C-*n*-butonium cation (Figure 3).

TABLE 2: Geometric Data for the Three-Center−Two-Electron Bond in Several Carbonium Ions[a]

cation	d_{H-H} (Å)	d_{C-H} (Å)	d_{C-C} (Å)	θ_{H-C-H} (degrees)
methonium	0.957	1.177/1.177	−	48.0
H-ethonium	0.905	1.207/1.206	−	44.0
1-H-proponium	0.909	1.210/1.202	−	44.3
1-H−*n*-butonium	0.909	1.211/1.202	−	44.2
1-H-isobutonium	0.903	1.217/1.208	−	43.7
2-H-proponium	0.867	1.245/1.234	−	41.0
2-H−*n*-butonium	0.878	1.251/1.233	−	40.9
2-H-isobutonium	0.832	1.290/1.283	−	37.7
C-ethonium	−	1.220/1.220	1.940	105.3
C-proponium	−	1.272/1.188	2.099	117.1
1-C-*n*-butonium	−	1.279/1.186	2.128	119.3
2-C-*n*-butonium	−	1.230/1.230	2.197	126.5
C-isobutonium	−	1.470/1.137	2.470	142.3

[a] Data involving the most stable conformer for each type of carbonium ion. Computed at the MP2(full)/6-31G** level.

Some selected geometrical parameters of the *n*-butonium ions and the van der Waals complexes are shown in Figures 1 and 2, respectively. It was found that the conformers have similar geometrical parameters. For the 1-H-*n*-butonium ions (**1**−**3**), the H−H distance in the three-center−two-electron bond ranges from 0.909 to 0.932 Å, substantially longer than the bond distance in the H_2 molecule (0.741 Å).[23] These values are similar to the H−H distance calculated for the 1-H-proponium (0.909 Å) and 1-H-isobutonium (0.903 Å) cations. The C−H distance is about 1.20 Å, indicating a high degree of involvement of the carbon atom in the 3c−2e bond, as observed for 1-H-proponium (1.202 and 1.210 Å) and 1-H-isobutonium (1.208 and 1.217 Å) cations. The H−C−H bond angle of the 3c−2e bond is in the range of 44°−46°. These results are comparable to the values obtained for the 1-H-proponium (44.3°) and 1-H-isobutonium (43.7°) ions. For the 2-H-*n*-butonium cations (structures **4**−**6**), one observes that the H−H distances range from 0.86 to 0.88 Å, while the C−H distances range from 1.21 to 1.25 Å. The H−C−H bond angles are within the range of 40°−42°. These values are similar to the calculated parameters for 2-H-proponium (0.867 Å for H−H bond distance, 1.234 and 1.245 Å for C−H bond distances, and 41° for the H−C−H bond angle of the 3c−2e bond). These results indicate that the 3c−2e bond in the 2-H-*n*-butonium cations is weaker than that in the 1-H-*n*-butonium, showing a greater character of H_2 and *sec*-butyl carbenium ion. This can be understood by analyzing the resonance structures for the 3c−2e bond. In the 2-H-*n*-butonium cation, one resonance structure has the positive charge on a secondary carbon atom, whereas in 1-H-*n*-butonium, the charge is localized over a primary carbon atom. In the case of the 1-C-*n*-butonium ions, an asymmetry is found in the 3c−2e bond, as reported for the C-proponium and C-isobutonium cations. The C−H bond distance, referring to the methyl group, was calculated to be 1.19 Å, whereas the C−H bond distance in the alkyl moiety is 1.28 Å, similar to that observed for C-proponium (1.188 and 1.272 Å for the methyl and ethyl moieties, respectively) and substantially different from that observed for the C-isobutonium cation (1.137 and 1.470 Å for methyl and isopropyl moieties, respectively). The C−C bond distance of the 3c−2e bond is about 2.13 Å in the 1-C-*n*-butonium cation, whereas it is 2.099 and 2.470 Å for the C-proponium and C-isobutonium cations, respectively. The geometrical parameters are slightly different for the 2-C-*n*-butonium cation, primarily because of the higher symmetry of the 3c−2e bond. The C−H bond distances are 1.23 Å, and the C−C bond length is 2.197 Å for structure **11** and 2.222 Å for **10**. The C−H bond distances for these cations are approximately equal to the average of the C−H bond distances in the 1-C-*n*-butonium cations. The C−H−C bond angle in the 2-C-*n*-butonium cations is 129.4° for structure **10** and 126.5° for structure **11**. These values are slightly larger than the values found for the equivalent bond angle in structures **7**−**9**. A value of 114° was found for **9** and an angle of 120° was calculated for structures **7** and **8**. The C−H−C bond angle was calculated to be 117.1° for the C-proponium ion and 142.3° for the C-isobutonium ion, probably associated with steric interaction between the alkyl moieties attached to the three-center−two-electron bond. Some selected geometrical parameters for the three-center−two-electron bond in carbonium ions are summarized in Table 2.

Structures **12**, **13**, **14**, and **15** represent van der Waals complexes of neutral molecules with carbenium ions (Figure 2). Structure **12** represents the van der Waals complex between H_2 and *sec*-butyl cation. Earlier studies showed[24] that the *sec*-butyl cation has a bridged hydrogen atom, with a C−H bond distance in the 3c−2e bond of 1.301 Å. The H_2 molecule is formed in the complex, as expressed by the H−H bond distance (0.736 Å). The C−H bond distance, involving the bridged hydrogen atom in the carbenium ion moiety, is 1.301 Å, equal to the calculated distance in the isolated *sec*-butyl cation. The H_2 molecule is about 2.36 Å away from the *sec*-butyl moiety.

TABLE 3: Activation ($\Delta H^{\ddagger}$) and Reaction ($\Delta H^{\text{reaction}}$) Enthalpies for Interconversion and Decomposition of *n*-Butonium Ions

reactant	transition state	product	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta H^{\text{reaction}}$ (kcal/mol)
1	**16**	**8**	−0.9	−11.5
1	**23**	**4**	5.0	−14.3
2	**17**	**8**	0.4	−10.6
2	**24**	**12**	6.6	−13.3
4	**19**	**7**	2.6	−8.0
4	–	**9**	–	−7.8
4	**20**	**10**	0.9	−12.4
4	**25**	**14**	−0.4	−10.2
4	**25**	**12**	−0.4	−10.2
5	–	**8**	–	−6.2
5	**21**	**11**	1.5	−11.3
5	**26**	**12**	−0.3	−9.0
6	–	**7**	–	−7.3
6	**22**	**10**	1.5	−11.7
6	**27**	**12**	−0.5	−9.5
7	**28**	**31**	2.2	−10.3
8	**29**	**15**	1.2	−3.6
9	**28**	**31**	1.9	−10.6
10	**30**	**13**	12.1	13.3
11	**30**	**13**	12.2	13.4

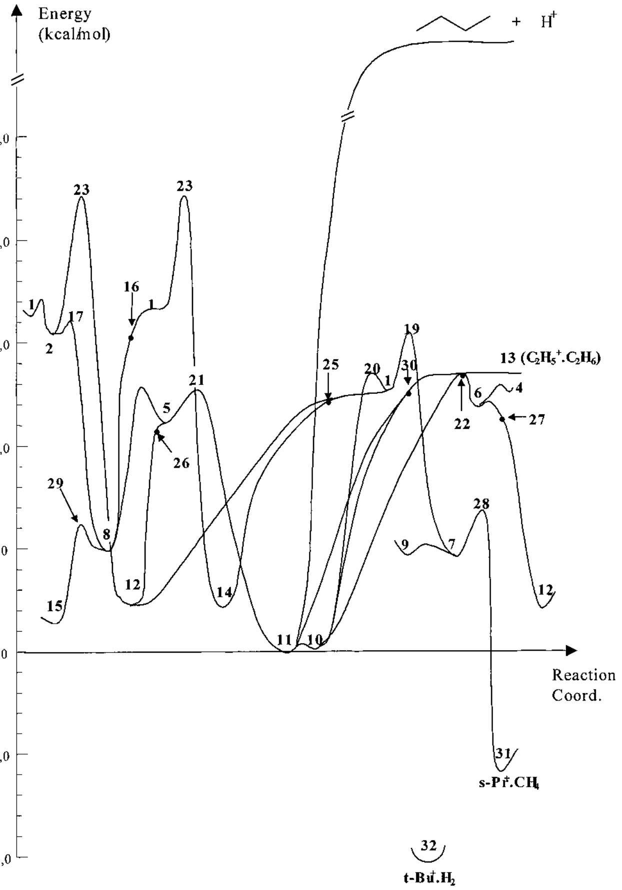


Figure 4. Pictorial representation of the potential energy surface of the *n*-butonium cation.

This structure can be produced by the decomposition of the 2-H-*n*-butonium cations. Structure **13** is the van der Waals complex between the ethyl cation ($C_2H_5^+$) and ethane, possibly formed from the decomposition of the 2-C-*n*-butonium cations. The ethyl cation has a bridged structure, in agreement with other ab initio calculations and experiments.[25] The distance between the nearest hydrogen atom of the ethane molecule and the nearest carbon atom in the ethyl cation is 2.657 Å. The bridged hydrogen atom in the ethyl cation is asymmetrically bonded to the carbon atoms because of the interaction with the ethane molecule. Structure **14** is the van der Waals complex between the protonated methylcyclopropane cation and H_2. It can be formed from the decomposition of 2-H-*n*-butonium cations with anchimeric assistance from the methyl group at the β position relative to the 3c−2e bond. In this complex, the hydrogen molecule is about 3.3 Å away from the carbenium ion. The structure of protonated methylcyclopropane is similar to that found for corner-protonated cyclopropane.[26] Structure **15** corresponds to the van der Waals complex of corner-protonated cyclopropane and CH_4, which could be formed by the decomposition of the 1-C-*n*-butonium ions. The methane molecule lies 3.248 Å from the carbenium ion. Protonated cyclopropane has a geometry slightly different from an isolated ion[26] because of the interaction with the methane molecule.

These minima in the potential energy surface are interconvertible by intramolecular rearrangements. Figure 4 shows a (reduced dimensional) pictorial representation of the potential energy surface of the *n*-butonium cations. Figures 5 and 6 show the structures of the transition states (TS) for the reactions presented in Figure 4. Structures **16**−**22** correspond to the transition states for these reactions and are shown in Figure 5. Structures **16**, **17**, and **18** represent the transition states for the interconversion of the 1-H-*n*-butonium cations (**1**, **2**, and **3**) into the 1-C-*n*-butonium ions (**7**, **8**, and **9**). It is observed (see Table 3) that this reaction is exothermic by 10.5 kcal/mol to 11.5 kcal/mol and involves no or low activation barriers (−0.8 to 0.4 kcal/mol). Transition state **19** was found for the interconversion of the 2-H-*n*-butonium cations (**4**−**6**) into the 1-C-*n*-butonium cations (**7** and **8**). This reaction was, again, exothermic by 8.0 kcal/mol, and involved an activation barrier of 2.6 kcal/mol, slightly higher than the barrier found for the same reaction from 1-H-*n*-butonium. The transition states **20**−**22** connect the 2-H-*n*-butonium cation with the 2-C-*n*-butonium cations (**10** and **11**). This reaction has an activation barrier of 0.9−1.5 kcal/mol and is exothermic by 12.4−11.3 kcal/mol.

The decomposition of the *n*-butonium cations into van der Waals complexes occurs through transition states **23**−**30** (Figure 6). Structure **23** refers to decomposition of cation **1** into the van der Waals complex **14**, with the anchimeric assistance of the ethyl group (C−C−C bond angle of 97.4°). This reaction is exothermic by 14.3 kcal/mol and presents an activation barrier of 5.0 kcal/mol. Transition state **24** is relative to the decomposition of cation **2** to complex **12**, with the anchimeric assistance of the C−H bond, as evidenced by the H−C−C bond angle of 89.8°. This reaction is exothermic by 13.3 kcal/mol and presents an activation barrier of 6.6 kcal/mol. The transition states **25**, **26**, and **27** refer to the decomposition of the 2-H-*n*-butonium cations (**4**−**6**) into H_2 and the *sec*-butyl cation (van der Waals complex **12**), with no or low anchimeric assistance. The decomposition reaction is exothermic by 9.0−10.2 kcal/mol and presents no activation barrier (−0.5 to −0.3 kcal/mol). Transition state **28** corresponds to the decomposition of the 1-C-*n*-butonium cations (**7**−**9**) directly to the van der Waals complex between methane and the isopropyl cation (structure **31**, Figure 7). This reaction is exothermic by about 10 kcal/mol and presents activation barriers ranging from 1.9 to 2.2 kcal/mol. Structure **29** is the transition state connecting the 1-C-*n*-butonium cation (**8**) and the van der Waals complex **15**. This reaction is exothermic by 3.6 kcal/mol with an activation energy of 1.2 kcal/mol. Structure **30** is the transition state connecting the 2-C-*n*-butonium ions (**10** and **11**) to the van der Waals complex **13**. This reaction is endothermic by 13.3 kcal/mol and

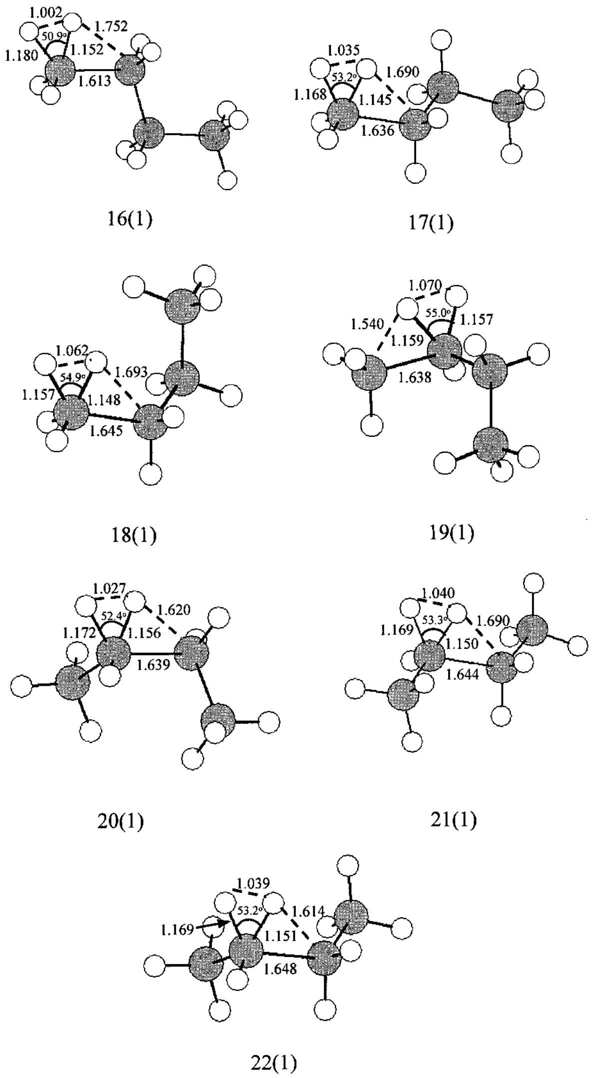


Figure 5. Optimized geometries and selected geometrical parameters for the transition states for intramolecular rearrangement of the n-$C_4H_{11}^+$ carbocations.

the transition state is about 12 kcal/mol above the carbonium ions themselves. The reverse reaction presents no activation energy. The energy barriers and heats of reaction for these reactions are summarized in Table 3.

1.3 Discussion

The potential energy surface of the n-$C_4H_{11}^+$ cations, computed at the MP4SDTQ(fc)/6-311++G**//MP2(full)/6-31G** level and considering corrections for ZPE and 298.15 K, showed that the most stable species is structure **11**, the 2-C-n-butonium cation. Structure **10** lies 0.1 kcal/mol higher in energy relative to structure **11**. Nevertheless, we found, as in our previous theoretical investigations of the isobutonium cations, that the most stable $C_4H_{11}^+$ species in the ground-state potential energy surface is the van der Waals complex between the *tert*-butyl cation and H_2 (**32**). The trend observed in the calculations for other alkanes (ethane, propane, and isobutane), indicating the stability order primary H-carbonium < secondary H-carbonium < tertiary H-carbonium < C-carbonium ions, was also observed for the n-butonium cation. Nevertheless, protonation in the central C−C bond of the n-butane is favored, which indicates a preference for proton attack at regions with greater electronic density.

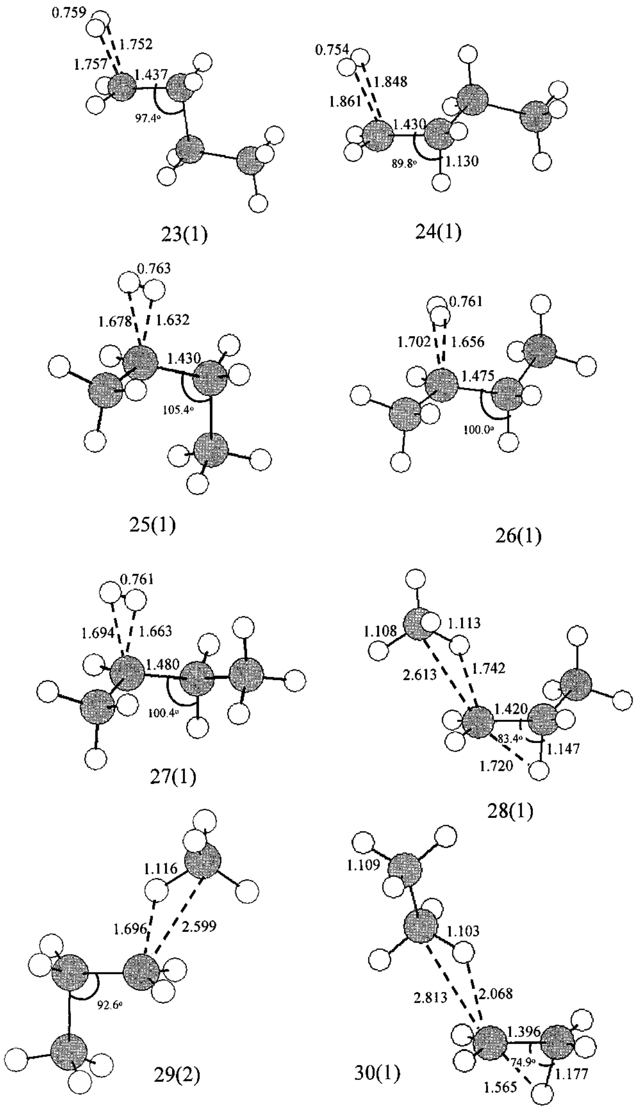
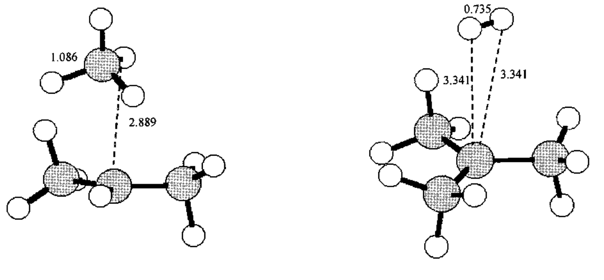


Figure 6. Optimized geometries and selected geometrical parameters for the transition states for decomposition of the n-$C_4H_{11}^+$ carbocations.



31 (0) **32 (0)**

Figure 7. MP2(full)/6-31G** optimized geometries and selected geometrical parameters for the van der Waals complexes of $C_3H_7^+\cdot CH_4$ and t-$C_4H_9^+\cdot H_2$.

Sommer and collaborators[27] showed the relative importance of protonation at different positions in the reaction of n-butane with HF/SbF$_5$. The relative rates of protonation at the central C−C bond, primary C−C, and secondary C−H bonds were measured as being 60:36:4, without considering statistical factors relative to the total number of bonds. This indicates the higher reactivity of the central C−C bond compared with the primary C−C and secondary C−H bonds. These results agree with the present ab initio calculation, which showed structure **11** to be the most stable among the *n*-butonium cations. Studies by Olah and Lin[28] on the electrophilic nitration of *n*-butane with $NO_2^+SbF_6^-$ also support the preferential attack in the secondary C−C bond followed by primary C−C, secondary C−H, and primary C−H (24:15:2.3:1, considering statistical factors). Cracking of *n*-butane on the H-ZSM-5 zeolite[29] at low conversion levels indicated the preferential attack on the central and primary C−C bonds relative to the secondary C−H bonds (38:31:5, considering statistical factors). We point out here that these results are in agreement with the σ bond basicity order predicted for *n*-butane.

Gas-phase protonation of *n*-butane with small electrophiles,[30] such as H_3^+ [31] and CHO^+,[32] show, in general, the following reactivity order: primary C−C > secondary C−C > secondary C−H > primary C−H. Calculations are in agreement with these results, predicting the preferred protonation of C−C bonds in comparison to C−H bonds. Nevertheless, the experimental data show a greater selectivity for protonation in the primary C−C bonds compared to the central C−C bond, in disagreement with the calculated stability order of the 2-C-*n*-butonium and 1-C-*n*-butonium cations. A possible explanation for this discrepancy is that the gas-phase reaction is kinetically controlled instead of thermodynamically driven. Another possibility to explain this fact would be the initial protonation in the more external and accessible C−H bonds to form the H-*n*-butonium cations followed by rearrangement of these species to the C-carbonium ions. The interconversion of the 1-H-carbonium ions into the 1-C-carbonium cations has low, or even no, activation barrier, as indicated by present and previous calculations.[13] On the other hand, the energy barrier for the interconversion of the 2-H-*n*-butonium cations to the C-*n*-butonium cations is higher than the barriers for the rearrangement of the 1-H-*n*-butonium cations to the C-*n*-butonium ions. The energy barriers computed for the decomposition of the 2-H-*n*-butonium cation to the van der Waals complexes were found to be negative, meaning a barrierless process. These data express the greater tendency of the 2-H-*n*-butonium cation to decompose into the van der Waals complexes, whereas the 1-H-*n*-butonium ions tend to undergo rearrangement to form the 1-C-*n*-butonium ions by insertion of the proton into a primary C−C bond. This explains the greater selectivity observed in the gas phase for the products arising from protonation of the primary C−C bond. Thus, the observed products could be generated not only from the direct protonation of the primary C−C bond, but also from the rearrangement of the 1-H-*n*-butonium into the 1-C-*n*-butonium, followed by decomposition, in a “two-channel” process.

The calculations predict a PA of 156.7 kcal/mol for *n*-butane to form the 2-C-butonium ion. This is in good agreement with the experimental value of 155 kcal/mol, reported by Hiraoka and Kebarle,[16] and the value of 153.7 kcal/mol, computed from updated data obtained from the NIST database.[17] The energy difference between isolated $C_2H_5^+$ and C_2H_6 and cation **11** has a predicted ΔH value of +16.0 kcal/mol. This is in good agreement with the estimated experimental ΔH value of +13.6 ± 3 kcal/mol, supporting the model proposed by Hiraoka and Kebarle that cation $C_4H_{11}^+$ (b) is the 2-C-*n*-butonium ion (structures **10** and/or **11**). Hiraoka and Kebarle reported the enthalpy change for the reaction $C_2H_5^+ + C_2H_6 \rightarrow s\text{-}C_4H_9^+ + H_2$ as −20.8 kcal/mol. Nevertheless, the new value predicted using the updated data of NIST database is much smaller, being computed as −12.3 kcal/mol. The enthalpy change predicted by the ab initio calculations for this reaction is −12.6 kcal/mol, thus in good agreement with present experimental result for the reaction. The new pictorial potential energy diagram supported by the updated experimental data and the ab initio calculations shows that species $C_4H_{11}^+$ (a) (supposed to be the 2-H-*n*-butonium cation) proposed by Hiraoka and Kebarle is now higher in energy than $C_4H_{11}^+$ (b) (the 2-C-*n*-butonium cation). The former, which corresponds to structure **5** in the present work, decomposes with a low barrier to the $s\text{-}C_4H_9^+$ cation and H_2. In fact, the ab initio calculations predict that the decomposition of **5** (2-H-*n*-butonium) to **12** (the van der Waals complex between $s\text{-}C_4H_9^+$ and H_2) through transition state **26** is a process with no barrier or with very low activation energy ($\Delta H^\ddagger = -0.3$ kcal/mol). The transition state to link **11**, $C_4H_{11}^+$ (b), to **5** has the structure **21** (Figure 4). Then, the predicted activation energy for the reaction is +12.8 kcal/mol. This is close to the experimental activation energy of 9.6 kcal/mol observed by Hiraoka and Kebarle, supporting the mechanism and species proposed in ref 16.

The most stable species on the potential energy surface of $C_4H_{11}^+$ is structure **32**, which corresponds to the van der Waals complex between the $t\text{-}C_4H_9^+$ cation and H_2. It was not possible to find a transition state connecting structure **11** and **32** in a single elementary step. The rearrangement of the 2-C-*n*-butonium cation to the 2-H-*n*-butonium cation occurs with an activation barrier of 12.8 kcal/mol. The 2-H-*n*-butonium cation (**5**) decomposes with no energy barrier into the van der Waals complex **12**. Hence, the pathway that would lead to the more stable *tert*-butyl cation plus H_2 would be the rearrangement of the *sec*-butyl cation into the van der Waals complex **12**. This reaction was calculated by Schleyer,[24] also at the MP4 level, and was predicted to have an energy barrier of 19.6 kcal/mol for the rearrangement of the *sec*-butyl cation into the *tert*-butyl cation, in good agreement with the experimental result of 18 kcal/mol in solution.[33] This reaction does not appear to occur at the experimental conditions of the Hiraoka and Kebarle experiment.

1.4 Conclusions

Ab initio calculations, at the MP4 level, were carried out to determine the structure and energetics linking the many stable isomers of the *n*-butonium ions. The transition states interconnecting these species, as well as the decomposition products, were also determined. The stability order of the *n*-butonium species was shown to be 2-C-*n*-butonium > 1-C-*n*-butonium > 2-H-*n*-butonium > 1-H-*n*-butonium. The van der Waals complexes **13**, **14**, and **15** are more stable than the H-*n*-butonium and 1-C-*n*-butonium ions. The van der Waals complexes of the isopropyl cation plus CH_4 and of the *tert*-butyl cation plus H_2 were found to be the most stable structures among all of the $C_4H_{11}^+$ isomers. It was concluded that the 1-H-*n*-butonium ions prefer to undergo intramolecular rearrangement to the 1-C-*n*-butonium ions, whereas the 2-H-*n*-butonium ions prefer to decompose into the van der Waals complex of the *sec*-butyl cation and H_2. The calculated proton affinity of *n*-butane (156.7 kcal/mol) agrees well with the experimental value of 155 kcal/mol, reported by Hiraoka and Kebarle. The $C_4H_{11}^+$ (b) species, formed upon the gas-phase reaction between $C_2H_5^+$ and ethane, was confirmed to be the 2-C-*n*-butonium cation, whereas the $C_4H_{11}^+$ (a) species was found to correspond to the 2-H-*n*-butonium cation, as proposed in ref 16. The activation energy of 9.6 kcal/mol found by Hiraoka and Kebarle is comparable to the value of 12.8 kcal/mol computed for the reaction **11** → **5** through transition state **21**.

Acknowledgment. The authors thank the NCE-UFRJ for the use of the IBM-SP2 computational facilities. C.J.A.M. thanks

FAPERJ (Grant E-26/170136/97), CNPq, and FINEP/PRONEX for support. The authors also thank the Ibero-American Program of Science and Technology for Development (CYTED, project V-4) for partial support. P.M.E. thanks CAPES (Brazil) for a scholarship. The authors also acknowledge one of the referees who provided updated experimental data for the $C_2H_5^+ + C_2H_6$ reaction that helped us to improve this work.

Supporting Information Available: Two tables containing absolute energies, zero point energies (ZPE), thermal corrections, and absolute entropies at 298.15 K. Table A1 lists the zero point energies (ZPE), thermal corrections ($H^0_{298} - H^0_0$), and absolute entropies, and Table A2 lists the absolute energies, for the *n*-butonium cations and related species. Data obtained from the NIST Database (http://webbook.nist.gov/chemistry), used for the computation of the actual values for experimental results, are also included.

References and Notes

(1) (a) Tal'roze, V. L.; Lyubimova, A. L. *Dokl. Akad. Nauk SSSR* **1952**, *86*, 909. (b) Field, F. H.; Munson, M. S. B. *J. Am. Chem. Soc.* **1965**, *87*, 3289.

(2) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119−6125.

(3) (a) Boo, D. W.; Lee, Y. T. *Chem. Phys. Lett.* **1993**, *211*, 358. (b) Boo, D. W.; Lee, Y. T. *J. Chem. Phys.* **1995**, *103*, 520. (c) Boo, D. W.; Liu, Z. F.; Suits, A. G.; Lee, Y. T. *Science* **1995**, *269*, 57. (d) Bunker, P. R. *J. Mol. Spectrosc.* **1996**, *176*, 297. (e) Boo, P. W.; Loe, Y. T. *Int. J. Mass. Spectrom. Ion Processes* **1996**, *159*, 209.

(4) (a) Yeh, L. I.; Price, J. M.; Lee, Y. T. *J. Am. Chem. Soc.* **1989**, *111*, 5597. (b) Obata, S.; Hirao, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3271.

(5) Schleyer, P. v. R.; Carneiro, J. W. M. *J. Comput. Chem.* **1992**, *13* (8), 997−1003.

(6) Olah, G. A.; Rasul, G. *Acc. Chem. Res.* **1997**, *30*, 245−250 and references therein.

(7) Schreiner, P. R.; Kim, S.-J.; Schaefer, H. F.; Schleyer, P. v. R. *J. Chem. Phys.* **1993**, *99*, 3716.

(8) Marx, D.; Parrinello, M. *Nature* **1995**, *375*, 216.

(9) Müller, H.; Kutzelnigg, W.; Noga, J.; Klopper, W. *J. Chem. Phys.* **1997**, *106*, 1863.

(10) Carneiro, J. W. M.; Schleyer, P. v. R.; Saunders, M.; Remington, R.; Schaefer, H. F., III; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 3483−3493.

(11) Esteves, P. M.; Mota, C. J. A.; Ramirez-Solis, A.; Hernandez-Lamoneda, R. *J. Am. Chem. Soc.* **1998**, *120*, 3213.

(12) Mota, C. J. A.; Esteves, P. M.; Ramírez-Solís, A.; Hernández-Lamoneda, R. *J. Am. Chem. Soc.* **1997**, *119*, 5193−5199.

(13) Esteves, P. M.; Mota, C. J. A.; Ramírez-Solís, A.; Hernández-Lamoneda, R. *Top. Catal.* **1998**, *6* (1−4), 163−168.

(14) (a) Collins, S. J.; O'Malley, P. J. *Top. Catal.* **1998**, *6*, 151−161. (b) Collins, S. J.; O'Malley, P. J. *Chem. Phys. Lett.* **1994**, *228*, 246. (c) Collins, S. J.; O'Malley, P. J. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4347.

(15) Esteves, P. M.; Alberto, G. G. P.; Ramírez-Solís, A.; Mota, C. J. A. *J. Am. Chem. Soc.* **1999**, *121*, 7345−7348.

(16) Hiraoka, K.; Kebarle, P. *Can. J. Chem.* **1980**, *58*, 2262−2270.

(17) The NIST database is available at the Internet address http://webbook.nist.gov/chemistry/. Original references for data can be obtained from this database.

(18) (a) Schlosberg, R. H.; Siskin, M.; Kosci, W. P.; Parker, F. J. *J. Am. Chem. Soc.* **1976**, *98*, 7723. (b) Siskin, M. *J. Am. Chem. Soc.* **1976**, *98*, 5413.

(19) Hout, R. F., Jr.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234−250.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, revision C.3*; Gaussian Inc., Pittsburgh, PA, 1995.

(21) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

(22) *CRC Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1994.

(23) (a) Olah, G. A. *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 171−212. (b) Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1973**, *95*, 4960−70.

(24) Sieber, S.; Buzek, P.; Schleyer, P. v. R.; Kock, W.; Carneiro, J. W. M. *J. Am. Chem. Soc.* **1993**, *115*, 259−270.

(25) (a) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649−5657. (b) Carneiro, J. W. M.; Schleyer, P. v. R.; Saunders, M.; Remington, R.; Schaefer, H. F., III.; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 3483−3493. (c) Hiraoka, K.; Mori, T.; Yamabe, S. *Chem. Phys. Lett.* **1993**, *207*, 178−184.

(26) Kock, W.; Liu, B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 3479−3480.

(27) Sommer, J.; Bukala, J.; Hachoumy, M. *Res. Chem. Intermed.* **1996**, *22* (8), 753−766

(28) Olah, G. A.; Lin, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 1259−1261.

(29) Ono, Y.; Kanae, K. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 663.

(30) (a) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1963**, *39*, 3341−3348. (b) Solka, B. H.; Lau, A. Y. K.; Harrison, A. G. *Can. J. Chem.* **1974**, *52*, 1798−1806.

(31) Aquilanti, V.; Galli, A.; Giardini-Guidoni, A.; Volpi, G. G. *J. Chem. Phys.* **1968**, *48*, 4310−4313.

(32) Futrell, J. H.; Abramson, F. P.; Bhattacharya, A. K.; Tiernan, T. O. *J. Chem. Phys.* **1970**, *52*, 3655−3664.

(33) Saunders, M.; Hagen, E. L.; Rosenfeld, J. *J. Am. Chem. Soc.* **1968**, *90*, 6882.