

The Alkane σ -Bond Basicity Scale RevisitedPierre M. Esteves,[†] Gabriel G. P. Alberto,[†] Alejandro Ramírez-Solís,[‡] and Claudio J. A. Mota^{*,†}

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Abstract: The energy of the *n*-butonium and isobutonium cations was calculated. At the MP4/6-311++G**//MP2(fu)/6-31G** level, the C-carbonium ions were more stable than the H-carbonium ions. The results are in agreement with gas-phase data of *n*-butane and isobutane protonation but disagree with results in liquid superacid, where protonation of the tertiary C–H of isobutane is preferred over C–C protonation. Additional calculations, including the superacid moiety, revealed that the activation energy for C–C protonation is higher than the energy for attack at the tertiary C–H. This suggests that the σ bond reactivity in the liquid superacid system is controlled by the activation energy for proton transfer, rather than by the intrinsic basicity of the bond. The higher stability of the C-carbonium relative to the H-carbonium ions was ascribed to a better charge distribution among the atoms and groups of the three center bond.

Introduction

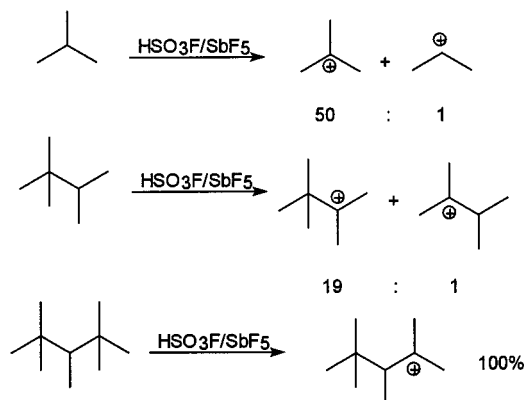
Pentacoordinated carbonium ions have been proposed as intermediates in electrophilic alkane activation. Based on the reactivity of different alkanes in liquid superacid solutions,¹ Olah² developed the concept of σ -bond reactivity with the following order: *t*-C–H > C–C > *s*-C–H > primary-C–H > CH₄. Olah pointed out that this order of σ -bond reactivity is qualitative and dependent on the steric hindrance of the superacid and the hydrocarbon structure. When isobutane is reacted^{2a} in HSO₃F/SbF₅ formation of *tert*-butyl cation and hydrogen is about 50-fold higher than formation of isopropyl cation plus methane, indicating the preferential protonation of the tertiary C–H over the C–C bond. Substituting a methyl group for a *tert*-butyl group in isobutane, to form the 2,2,3-trimethylbutane, reduces the selectivity to 19:1 for tertiary C–H protonation in relation to C–C. Another substitution of methyl to a *tert*-butyl group, to form the 2,2,3,4,4-pentamethylpentane, leads to a complete protonation in the C–C bond with formation of methane and the 2,3,4,4-tetramethyl-2-pentyl carbenium ion, indicating that the tertiary C–H is sterically hindered for proton attack by the superacid (Scheme 1).

An interesting reaction accompanying protonation in superacid is the H/D exchange. When reacted with DSO₃F/SbF₅ at –78 °C, isobutane exchanges almost exclusively at the tertiary C–H. At –10 °C, however, besides the preferential exchange at the methine position, it also exchanges the methyl hydrogens.^{1d}

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Scheme 1. Reactivity of *t*-C–H and C–C Bonds in Liquid Superacid

These results are consistent with the formation of the 2-H-isobutonium and 1-H-isobutonium cations as intermediates or transition states.

The smallest carbonium ions, CH₅⁺ and C₂H₇⁺, have been directly observed in the gas phase with the aid of high-pressure mass³ and infrared⁴ spectroscopy. Nevertheless, higher carbonium ions have a strong tendency to decompose into a neutral molecule (H₂ or an alkane) and a carbenium ion. Hence, protonation of propane and isobutane in the gas phase⁵ occurs with formation of the *s*-C₃H₇⁺ and *t*-C₄H₉⁺ cations and hydrogen

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or methane as byproducts. Recent ab initio calculations on the potential energy surface of the protonated propane⁶ and protonated isobutane⁷ indicated that some carbonium ions are not stable intermediates, spontaneously decomposing to secondary and tertiary carbenium ions. For the protonated propane it was found that the C-proponium is the lowest energy species followed by the 2-H-proponium and the 1-H-proponium cations. For the protonated isobutonium the most stable species is the van der Waals complex between the *tert*-butyl cation and hydrogen followed by the complex between the isopropyl cation and methane. Among the carbonium ions, the C-isobutonium is the lowest in energy followed by the 2-H-isobutonium and the 1-H-isobutonium cations. These calculations are in good agreement^{5a} with the product distribution observed for the gas-phase protonation of propane and isobutane, suggesting that the relative stability of the carbonium ions may be used to explain the results. Nevertheless, the calculations of the relative stability among the isobutonium cations show some discrepancy with the results of isobutane protonation in liquid superacid, where the preferential protonation in the tertiary C–H bond was observed. In addition, the energy difference between the 1-H-isobutonium and 2-H-isobutonium cannot account for the observed H/D exchange selectivity at $-10\text{ }^{\circ}\text{C}$, suggesting that a free carbonium ion might not be involved in these reactions.

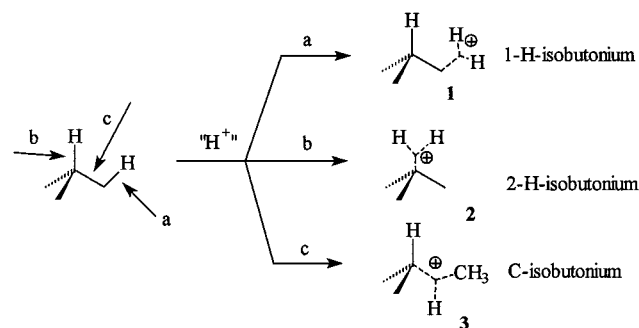
In the present work, we report a theoretical study comparing the relative stability of the butonium cations to derive a thermodynamic scale for the alkane σ -basicity. We also wish to report some preliminary calculations of the H/H exchange and C–C protonation of isobutane involving a cluster representing the liquid superacid system, to shed some light on the factors that control the σ -bond reactivity in superacid and in the gas phase.

Computational Methods

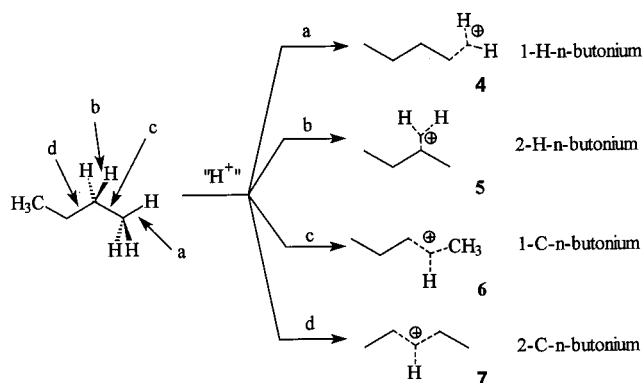
Geometry optimizations of the butonium ions were performed at the MP2(full)/6-31G** level. The optimized geometries were characterized as minima on the potential energy surface by the absence of imaginary vibrational frequencies. To obtain the thermodynamic properties, the vibrational frequencies were scaled⁸ by 0.93. The final MP2(full) optimized geometries were subjected to a single-point energy calculation at the MP4SDTQ(fc)/6-311++G** level. All the structures were corrected for thermal (289.15 K) and zero-point energy. Charges were calculated using the ChelpG scheme.⁹ Calculations were carried out with the GAMESS US¹⁰ and Gaussian 94¹¹ computational programs.

To study the H/H exchange and the C–C protonation of isobutane a cluster comprising a HF molecule and SbF₅ moiety was used. The transition states were obtained using the Bery and the eigenvector follower (EF) algorithms and characterized as having only one imaginary frequency, which corresponds to the reaction mode. A pseudopotential,¹² with relativistic corrections, was used to describe the antimony atom in the SbF₅ molecule. All the calculations involving the H/H exchange and the C–C protonation of isobutane were performed at the B3LYP/6-31++G**//B3LYP/6-31++G** level.

Scheme 2. Schematic View of Isobutane Protonation



Scheme 3. Schematic View of *n*-Butane Protonation



Results and Discussion

Protonation of isobutane can occur at three positions, as shown in Scheme 2. Structures **1** and **2** represent protonation of the primary and tertiary C–H, respectively. Structure **3** is formed upon protonation in the C–C bond. The *n*-butane has a more complicated reaction scheme, and protonation can occur in four different positions (Scheme 3), each one leading to different conformational isomers of the respective carbonium ion. Structures **4** and **5** refer to protonation in the primary and secondary C–H, respectively. Structures **6** and **7** represent the carbonium ions formed upon protonation of the C–C bonds of *n*-butane. For comparison purposes among the butonium ions, all the discussion will be based on the energy of the most stable conformer for each carbonium ion. A complete study of the potential energy surface of the *n*-C₄H₁₁⁺ species will be reported separately, as already done with the *iso*-C₄H₁₁⁺ species.^{7b}

Table 1 and Figure 1 present the relative enthalpies, corrected for zero-point energy and to 298.15 K, for all the butonium ion structures at the MP4SDTQ(fc)/6-311++G**//MP2(full)/6-31G** level. The electrostatic potential derived charges (ChelpG) on the atoms of the 3c–2e bond were also shown in Table 1 for the butonium cations. The C-carbonium ions were calculated to be more stable than the respective H-carbonium ions. Among

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Table 1. Relative Calculated (MP4SDTQ(fc)/6-311++G**//MP2(full)/6-31G**) Enthalpies (kcal/mol) of $C_4H_{11}^+$ Isomers (corrected to zero-point energy and to 298.15 K (ΔH_{298}^0)^a) and ChelpG Charges Calculated for the Atoms Involved in the 3c-2e Bonds (see Scheme 4)

species	rel enthalpy (kcal/mol)	ChelpG charges		
		C ^b	Rb	H
1	17.3	-0.43	+0.30 (H)	+0.30
2	11.2	+0.28	+0.25 (H)	+0.25
3	0.0	-0.38 (C _{methyl})	+0.37 (C _{isopropyl})	+0.10
4	19.0	-0.37	+0.24 (H)	+0.32
5	15.5	+0.01	+0.22 (H)	+0.30
6	8.7	-0.20 (C _{methyl})	+0.01 (C _{n-propyl})	+0.14
7	4.2	+0.06	+0.05 (C)	+0.15

^a Calculated using MP2(full)/6-31G** vibrational frequencies (scaled by 0.93). ^b Parentheses refer to the type of the atom in the 3c-2e bond.

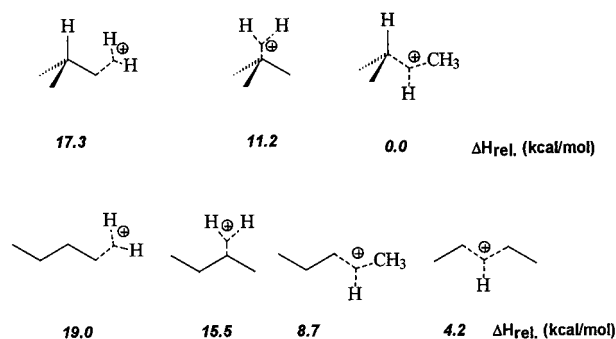
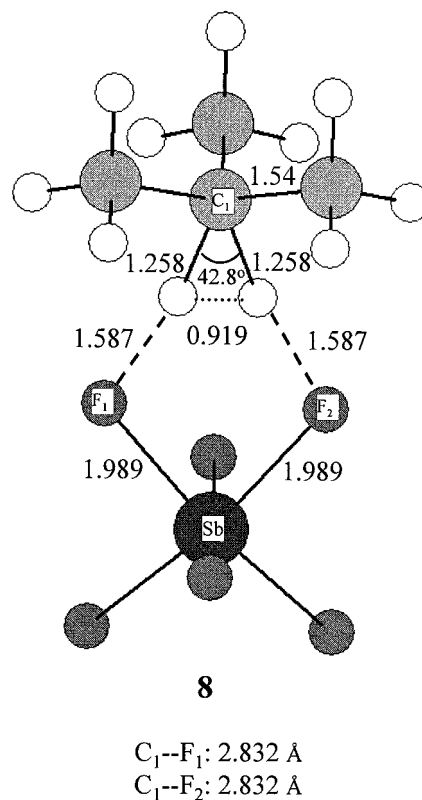


Figure 1. Relative enthalpy (ΔH) for the butonium cations.

the H-butyonium ions, the stability decreases in the following order: *tert*-H-carbonium > *sec*-H-carbonium > primary-H-carbonium. This order is only in partial agreement with the experimental scale of σ -bond reactivity developed by Olah, based on the protonation of alkanes in liquid superacid, where tertiary C-H bonds are normally more reactive than the C-C bonds. This inversion can be understood if we consider that the experimental scale is based on kinetic considerations. Therefore, it should be related to the activation energies for the protonation of the σ bonds. To test this hypothesis we decided to investigate the barriers for the protonation of the tertiary C-H and C-C bonds of isobutane with a cluster representing the superacid system. Figures 2 and 3 show the enthalpy of activation and the main geometric parameters of the transition state for the H/H exchange, structure **8**, and C-C protonation of isobutane, structure **9**. It can be seen that the TS for exchange is 8.6 kcal/mol lower in energy than the TS for C-C protonation, in agreement with the experimental findings of σ -bond reactivity in liquid superacid. Although there is no definite proof that exchange and ionization, to form the *tert*-butyl carbenium ion, in superacids occurs through similar transition states, it is reasonable to suppose that they are related reactions. For instance, as the strength of the superacid system increases, by increasing the amount of SbF_5 , the ratio of exchange to ionization to *tert*-butyl carbenium ion decreases.¹³ Calculations^{7b} of the potential energy surface of the *iso*- $C_4H_{11}^+$ species showed that the 2-H-isobutyonium spontaneously decomposes to the *tert*-butyl carbenium ion and hydrogen. Hence, as the nucleophilicity of the superacid conjugated anion decreases, by increasing the SbF_5 content, the hydrogen atoms of the three center bond of the TS for exchange become less coordinated with the anion. This gives the TS a more carbonium ion character and, by

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$$\Delta H^\ddagger = 16.4 \text{ kcal/mol}$$

Figure 2. Enthalpy of activation and main geometric parameters of the TS for protonation in the tertiary C-H of isobutane (H/H exchange).

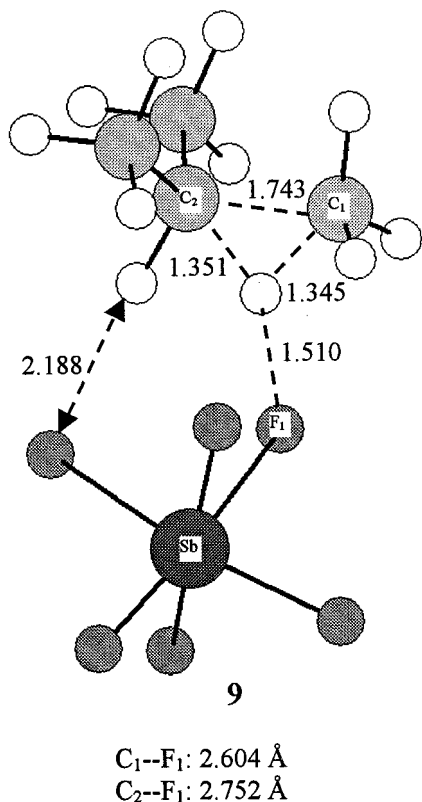
consequence, favors ionization to the *tert*-butyl carbenium ion. Additional evidence supporting this view comes from a recent kinetic isotopic effect study of isobutane ionization in liquid superacid,¹⁴ where a k_H/k_D of 1.5 was observed at -10°C , compatible with the geometry for the TS resembling a 2-H-isobutyonium cation. It should be stressed that calculations indicated that the H/H exchange is a concerted reaction without forming a carbonium ion as the intermediate, although the TS has, clearly, a carbonium ion nature.

The calculations indicate the energy differences among the carbonium ions and can be considered as a thermodynamics-based scale that reflects the intrinsic basicity of the σ bonds (equilibrium-derived quantities). On the other hand, the scale derived by Olah, based on product distribution of alkane protonation in liquid superacid, reflects the energy barrier for proton transfer and is associated with the reactivity of the σ bond (kinetics-derived quantities). These results confirm the previous hypothesis that the scale in superacid reflects the reactivity of the σ bonds, rather than their intrinsic basicity.

The higher enthalpy of activation for protonation of the C-C bond of isobutane by superacids may arise from steric reasons. In structure **9** the proton is more distant from the carbon atom than in **8**. This is a consequence of the repulsion associated with the fluorine atoms in the $HSbF_6$ moiety, which are closer to the carbon atoms of isobutane in **9** (2.604 and 2.752 Å) than in **8** (2.832 Å). Indeed, it has been proposed^{2a,15} that relatively bulky electrophilic species are responsible for proton transfer

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$$\Delta H^\ddagger = 25.0 \text{ kcal/mol}$$

Figure 3. Enthalpy of activation and main geometric parameters of the TS for protonation in the C–C of isobutane.

reactions in liquid superacids and the product distribution is strongly affected by the steric hindrance of the σ bonds. Thus, the direct attack of the inner C–C bonds can be sterically demanding, specially in tertiary alkanes, and involves a significant higher energy than attack in the outer and more accessible tertiary C–H. It should be also pointed out that the bond-to-bond rearrangement of the H-carbonium to the C-carbonium ions is an easy process, involving small or no energy barrier.^{6,7b} Then, protonation in the primary C–H bonds of propane⁶ and isobutane⁷ can directly form the respective C-carbonium ion and, consequently, the products ascribed to its decomposition. On the other hand, the gas-phase results of protonation of propane and isobutane by H_3^+ are in good agreement with calculations,^{6,7} suggesting that in the absence of strong steric effects the order of basicity of the σ bonds prevails. Indeed, Field has reported¹⁶ that in the chemical ionization mass spectra of alkanes, the reactivity of C–C bonds is about 4-fold higher than the reactivity of the C–H bonds, in agreement with the calculated relative basicity of σ bonds.

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Scheme 4. Canonical Structures Representing the Charge Distribution in the Carbonium Ions



The fact that the C-carbonium ions are more stable than the respective H-carbonium ions can be rationalized on the basis of canonical structures for the three center two electron bond (3c–2e), as shown in Scheme 4. One can visualize the groups in the three center bond spreading the positive charge. In the case of H-carbonium ions (R = H), there is only one resonance structure where the positive charge lies over the carbon atom of the alkyl group, while in C-carbonium there are two structures. Hence, less charge is concentrated on the hydrogens of the three center bond in C-carbonium ions, resulting in a better stabilization. Table 1 shows that for the C-butionium ions **3**, **6**, and **7** the charge on the hydrogen of the three center bond is within +0.10 to +0.15, while for the H-butionium ions **1**, **2**, **4**, and **5** the charges are within +0.24 to +0.32. The alkyl group participating in the three center bond also has a great influence on the stability of the carbonium ion. The C-isobutionium (**2**) is lower in energy than the C-*n*-butionium ions (**6** and **7**). This can be associated with the stabilization of the positive charge by the carbon atoms involved in the 3c–2e bond. In the C-isobutionium ion, one of the carbons has the character of a secondary carbonium ion, while in the isomeric 2-C- and 1-C-*n*-butionium ions the carbons have the character of a primary and a methyl carbonium ion, respectively.

Conclusions

A theoretical study on the relative stability of butonium cations was carried out. The results, at the MP4/6-311++G**//MP2(fu)/6-31G** level, showed that the C-butionium cations are more stable than the respective H-butionium cations. This order may be explained by a better charge distribution among the atoms and groups of the three center bond in the C-carbonium ions.

The results are in good agreement with gas-phase data of isobutane and *n*-butane protonation, which points to a preferential attack in the C–C bond. Nevertheless, in liquid superacid isobutane shows a preferential protonation in the tertiary C–H bond. This disagreement may be explained by the fact that the reactivity of the σ bonds in superacid is related to the activation barrier for proton transfer, rather than the intrinsic basicity of the σ bond.

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