Protio-*tert*-butyl Dication ($(H_3C)_2C^+CH_4^+$): Hydrogen–Deuterium Exchange and Theoretical Study. The Role of Protosolvation on Alkyl Cation Reactivity in Superacidic Solution[1]

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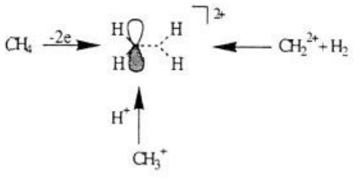
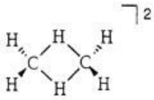
Alkane dications (RH^{2+}) of which the methane dication (CH_4^{2+}) is parent[2] were so far considered to be only of theoretical interest and were observed in gaseous ion mass spectrometric studies. The methane dication was calculated to be of C_{2v} symmetry, with an empty perpendicular p-orbital and involving 3c–2e bonding.[2] The parent methane dication, besides being obtained by 2e-oxidation of methane, can also be considered to be formed by protonation of the methyl cation and the reaction of CH_2^{2+} with H_2.

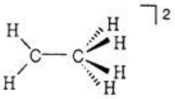


The boron analog of CH_4^{2+} is BH_4^+. Olah et al.[3] previously observed H/D exchange upon treatment of diborane with deuterated superacids, indicative of the intermediacy of BH_3D^+ or $B_2H_6D^+$.

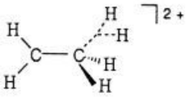
The ethane dication, $C_2H_6^{2+}$, was first studied theoretically by Olah and Simonetta[4] with a D_{2h} diborane-like structure (CH_3^+ dimer). Later Schleyer and Pople[5] showed that the C_{2v} symmetrical carbenium carbonium ion isomer is energetically favored by 9.0 kcal/mol at the MP4SDQ/6-31G**//HF/6-31G* level. Subsequently, Olah et al.[6] showed that the global minimum of this ethane dication is a C_s symmetrical structure. This carbenium carbonium dication structure of the ethane dication can be considered either as a complex between H_2 and the ethylene dication, $C_2H_4^{2+}$, or as the protoethyl dication.



D2h



C2v



Cs

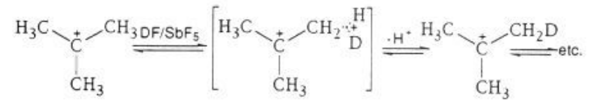
So far there has been no indication for protoalkane dications in solution (condensed state) nor has any experimental evidence been obtained to support such a possibility. We report now in the case of the *tert*-butyl cation such evidence both by experiment and by theory and call attention to its significance.

Alkyl cations, such as the *tert*-butyl cation, are stable in superacidic media and thus cannot be involved in any deprotonation equilibria. (Otherwise, isobutylene would react with excess

$$(H_3C)_3C^+ \not\rightleftharpoons (H_3C)_2C{=}CH_2 + H^+$$

tert-butyl cation, which is experimentally shown not to be the case.) This is the consequence of the high acidity of the system which prevents olefin formation. Extensive evidence was reported to establish this point, which is crucial for the ability to prepare stable long-lived alkyl cations.

We have now observed that the stable *tert*-butyl cation undergoes slow but well-characterized (^1H and ^2H NMR) hydrogen–deuterium exchange when 1:1 DF/SbF_5 (0.2 mL) is added to 1 mL of a solution of the *tert*-$C_4H_9^+$ in SbF_5/SO_2ClF (0.15 M). The hydrogen–deuterium exchange at −78 °C is about 2% over a period of 12 days.[7] The low temperature and high acidity of the system further assured complete absence of deprotonation, and no evidence of any oligomerization was observed. Sommer and co-workers have previously studied hydrogen–deuterium exchange of isobutane in DF/SbF_5 medium. Although the exchange is fast at both methyl and methine C–H bonds, hardly any exchange was observed once the isobutane was ionized to the *tert*-butyl cation.[8] To account for the isotopic exchange in the system, protonation (deuteration) of the *tert*-butyl cation to the protio-*tert*-butyl dication must occur.



To further comprehend the nature of the $C_4H_{10}^{2+}$ system, theoretical calculations were carried out. All structures were first optimized at the Hartree–Fock level with the SPARTAN[9] program using the standard 6-31G* basis set. Stationary points were characterized by calculation of the analytical frequencies at the HF/6-31G*//HF/6-31G* level. The minimum structures **1** and **2** (0 imaginary frequencies) were then further optimized at the MP2(FU)/6-31G* level. Single-point calculations were performed at the MP4SDTQ/6-31G*//MP2(FU)/6-31G* level with the GAUSSIAN92[10] program. The final geometries and energies are given in Figures 1 and Table I, respectively.

Two minimum structures were located for at the HF/6-31G* level. The carbenium carbonium structure **1** corresponds to a C–H protonated *tert*-butyl cation ($(H_3C)_2C^+CH_4^+$). This species is the global minimum at this level of theory (Table I), being even more stable than the *tert*-butyl cation (0.7 kcal/mol at MP2-(FU)/6-31G*//MP2(FU)/6-31G*). Two C–H bonds on the methyl substituents are aligned in plane with the empty p-orbital on the tertiary carbon atom (Figure 1). The corresponding HCC bond angles are significantly smaller (104°) compared to those of the other C–H bonds (111°). The corresponding bonds are elongated to 1.12 Å on these positions. Hyperconjugation from two σ-bonds is thus indicated. The distortion of the angles is very close to the value calculated for the *tert*-butyl cation.[11] However, none of the C–H bonds on the carbonium center is oriented such that efficient hyperconjugation is possible. The calculated

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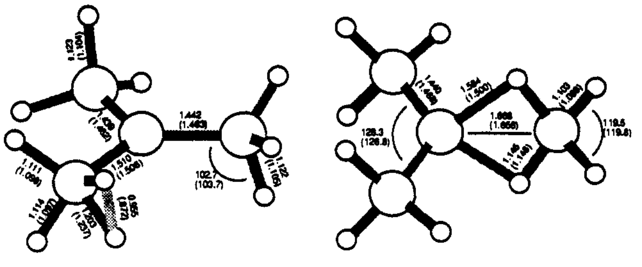
Table I. Total Energies (Hartrees) and Relative Energies (kcal/mol) of the Protonated *tert*-Butyl Cation Structures **1** and **2**

	HF/6-31G*// HF/6-31G* [a]	MP2(FU)/6-31G*// MP2(FU)/6-31G*	MP4SDTQ/6-31G*// MP2(FU)/6-31G*	relative energy MP4SDTQ/6-31G*// MP2(FU)/6-31G*+ZPE
1	−156.434 91(82.2)	−156.960 71	−157.011 67	0.0
2	−156.401 14(82.0)	−156.936 37	−156.987 77	14.8

[a] Zero-point vibrational energy in kcal/mol in parentheses.



1(C_1) **2**(C_{2v})

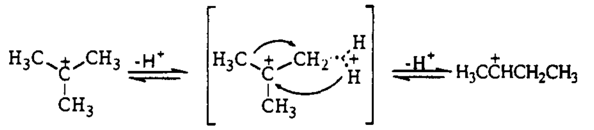
Figure 1. Selected MP2(FU)/6-31G* optimized parameters of **1** and **2**. HF/6-31G* values are given in parentheses (bond length in angstroms, angles in degrees).

geometry suggests that hyperconjugative stabilization can be partly turned off by further protonation since only two and not three bonds interact with the carbocation center.

The second dicationic structure **2** corresponds to a complex between $H_3CCH_3^{2+}$ and CH_4 and lies about 14.8 kcal/mol (MP4SDTQ/6-31G*//MP2(FU)/6-31G* + ZPE) above **1** (Table I).

The ^{13}C NMR chemical shifts of the *tert*-butyl cation were subject to a recent theoretical investigation using the high-level *ab initio*/IGLO method.[12] It was reported by Schleyer et al.[11] that the IGLO DZ//MP2(FU)/6-31G* calculated value for the most stable isomer (C_{3h}) of the *tert*-butyl cation (^{13}C δ 352.4) was 17.2 ppm more deshielded than the experimental result (335.2 ppm[13]). In order to explore the effect of further protonation on the gas-phase chemical shift of the *tert*-butyl cation, calculations were performed on the global minimum structure **1** at the IGLO DZ//MP2(FU)/6-31G* and IGLO II//MP2(FU)/6-31G* levels. Full protonation would result in a chemical shift of ^{13}C δ 323.2 (DZ//MP2(FU)/6-31G*) in the gas phase, which is 12.0 ppm even more shielded than the experimental value in the condensed phase. The corresponding value at the IGLO II//MP2(FU)/6-31G* level is ^{13}C δ 327.5. In superacidic solution there is obviously only a very limited equilibrium between the protio-*tert*-butyl dication and the *tert*-butyl cation. However, protosolvation of the methyl C–H bonds can contribute to an overall decrease of hyperconjugative stabilization.

The ability of strong superacids[14] to protosolvate (protonate) alkyl cations has significant implications on the reactivity of the ions in hydrocarbon transformations. Alkyl cations (except the methyl cation) are stabilized not only by weak external solvation but also intramoleculary by C–C or C–H hyperconjugation.[15] In the case of the *tert*-butyl cation, the β-C–H bonds can strongly interact with the carbocationic center, contributing to the overall stability of the ion. The more stable an alkyl cation, the lower its reactivity. If superacidic protosolvation is operating, on the other hand, C–H hyperconjugative stabilization would be decreased. This would lead to an enhanced electron deficiency and reactivity of the carbocationic center. Olah and Prakash reported[16] previously ^{13}C-scrambling of the long-lived *tert*-butyl cation in superacidic media. The suggested mechanism involved an initial 1,2-hydride shift in the *tert*-butyl cation to give the primary isobutyl cation, which then gives *via* a 1,3-methyl shift (through a protonated cyclopropane) the *sec*-butyl cation, etc. The difficulty with the mechanism is the unfavorable energetics going from a tertiary to a primary carbocation (an upper limit of 30 kcal/mol was estimated[16]). This was never satisfactorily explained, although the subsequent formation of a favorable protonated cyclopropane-like intermediate should partially compensate for the overall energetics. We suggest now that the ^{13}C-scrambling may indeed involve the protio-*tert*-butyl dication. Its intermediacy would allow interconversion of the *sec*- and *tert*-butyl cations *via* bond-to-bond migration of CH_3 and H, without involvement of a primary cation.



The same mechanism can be considered from the industrially significant isomerization of butane to isobutane studied by Olah et al.[17] in superacid media. The industrially important isobutylene–isobutane alkylation for high octane gasoline production proceeds readily in strong acid (HF, H_2SO_4) solutions. Besides providing good ionizing media, strong acids can also protosolvate the intermediate carbocations, enhancing their reactivity particularly in the crucial hydride abstraction step from isobutane.

tert-Alkyl cations, such as the *tert*-butyl cation, are more stable but therefore less reactive electrophiles than secondary or primary alkyl chains. Their electrophilic reactivity can be, however, substantially enhanced by protosolvation, which diminishes hyperconjugative C–H bond back-donation. Protosolvation can play a role not only in liquid but also in solid superacidic systems where the acid sites are clustered. Bi- or multidentate interactions can also be considered to contribute to enzymatic activations. We are continuing to explore these possibilities.

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Supplementary Material Available: Cartesian coordinates of the optimized structures of **1** and **2** (2 pages). Ordering information is given on any current masthead page.

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