Triprotonated Methane, CH_7^{3+}: The Parent Heptacoordinate Carbonium Ion[1]

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Received April 2, 1996
Revised Manuscript Received July 5, 1996

CH_5^+ is considered the parent of nonclassical carbocations as it contains a five-coordinate carbon atom.[2] Recent extensive high-level *ab initio* calculations (Car-Perrrinello *ab initio* simulation)[3] reconfirmed the preferred C_s symmetrical structure[4] (Scheme 1) for the CH_5^+ cation with a three-center two-electron (3c-2e) bond as originally suggested by Olah et al. in 1969.[5] The parent six-coordinate carbocation, diprotonated methane (CH_6^{2+}), has two 3c-2e bonding interactions in its minimum-energy structure (C_{2v}) (Scheme 1) calculated[6] at the HF/6-31G** level which further indicates the importance of 3c-2e interactions in protonated alkanes. Using gold(I) organometallic ligand (LAu^+) as isolobal substitute for H^+, Schmidbaur et al. have prepared monopositively charged trigonal bipyramidal[7] and dipositively charged octahedral[8] gold complexes of five- and six-coordinate carbon and determined their X-ray structures (Scheme 2). These represent isolobal analogues of CH_5^+ and CH_6^{2+}, respectively. The significant metal−metal bonding that occurs in these gold complexes renders them remarkably stable, even isolable as crystalline salts. Nonetheless they greatly contribute to our knowledge of higher coordinate carbocations.

In continuation of our study of protonated alkanes, we have now extended our investigations to triprotonated methane, the parent heptacoordinate carbocation, CH_7^{3+}, by *ab initio* calculations using the correlated MP2/6-31G** level of calculations for geometry optimizations and frequency calculations.[9a] From calculated frequencies,[9b] the optimized structures were characterized as minima, saddle point, or transition structure, respectively. For the MP2/6-31G** optimized structures, further geometry optimizations and frequency calculations were carried out at the MP2/6-311++G(2df,2pd) and QCISD(T)/6-311G** levels. For improved energy, single-point energies at MP4-(SDTQ)/6-31G**, QCISD(T)/cc-pVTZ and CCSD(T)/cc-pVTZ levels as well as with the Gaussian-2 (G2) method[10] were computed on optimized geometries. Energies at the MP4-(SDTQ)/6-31G** level were calculated on MP2/6-31G** optimized geometries. The (G2) theory is a composite method based on MP2(FU)/6-31G* geometry which is treated in single-point calculations with a variety of basis sets at the post-SCF level. The correlation-consistent polarized valence triple-ζ basis set (cc-pVTZ)[11] was used for QCISD(T) and CCSD(T) calculations on MP2/6-311++G(2df,2pd) optimized geometries. Atomic charges were obtained using the natural bond orbital analysis[12] (NBO) method.

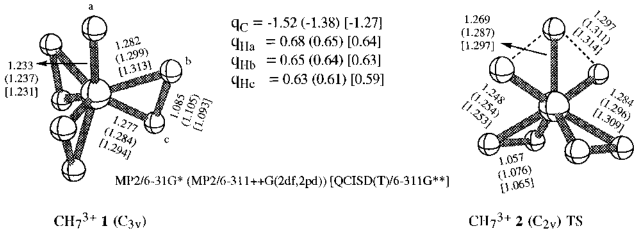
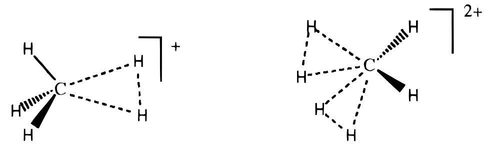


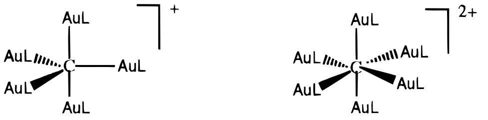
Figure 1. Calculated structures of **1** and **2** and calculated NBO charges of **1**.

Scheme 1



CH_5^+ C_s CH_6^{2+} C_{2v}

Scheme 2



$\{[(C_6H_5)_3PAu]_5C\}^+$ $\{[(C_6H_5)_3PAu]_6C\}^{2+}$

$L=(C_6H_5)_3P$

At the MP2/6-31G** level the C_{3v} symmetric form **1** is found to be a stable minimum for triprotonated methane, CH_7^{3+}. No other singlet minima were found. Structure **1** is a propeller-shaped molecule resembling a complex between CH^{3+} and three hydrogen molecules resulting in the formation of three 3c-2e bonds (Figure 1). In such a small first-row trication, the charge−charge repulsion must be substantial. However, the bonding interactions of trication **1** are strong enough to counter this charge−charge repulsion. The NBO charge calculations (Figure 1) show that the hydrogen atoms of **1** bear the positive charges. The C−H bond distances of 3c-2e interections ($C-H_b$ and $C-H_c$) are 1.282 and 1.277 Å. These are slightly longer than those found in the 3c-2e C−H bonds (1.181 Å) of the C_s structure of CH_5^+ at the same theoretical level. The non-3c-2e interacting C−H bond distance of **1** ($C-H_a$) is 1.233 Å. There is no bonding interaction between H_a and H_b which are separated by 1.555 Å. The calculated H_b-H_c distance in the 3c-2e interections is 1.085 Å. This is 0.351 Å longer than that found

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S0002-7863(96)01081-5 CCC: $12.00 © 1996 American Chemical Society

Table 1. Total Energies (−au) and Relative Energies (kcal/mol)

	energies (ZPE)[a]		relative energies	
	1	**2**	**1**	**2**
MP2/6-31G**//MP2/6-31G**	40.089 05 (32.9)	40.088 11 (32.3)	0.0	0.6
MP4(SDTQ)/6-31G**//MP2/6-31G**	40.113 46	40.112 33	0.0	0.7
MP2/6-311++G(2df,2pd)// MP2/6-311++G(2df,2pd)	40.139 13	40.138 42	0.0	0.5
QCISD(T)/6-311G**// QCISD(T)/6-311G**	40.136 74	40.135 82	0.0	0.6
G2	40.128 75	40.128 68	0.0	0.1
QCISD(T)/cc-pVTZ// MP2/6-311++G(2df,2pd)	40.168 12	40.167 25	0.0	0.6
CCSD(T)/cc-pVTZ// MP2/6-311++G(2df,2pd)	40.168 06	40.167 19	0.0	0.6
final relative energies[b]			0.0	0.0

[a] Zero-point vibrational energies (ZPE) at MP2/6-31G**//MP2/6-31G** scaled by a factor of 0.93. [b] Final relative energies based on CCSD(T)/cc-pVTZ//MP2/6-311++G(2df,2pd)+ZPE.

Scheme 3

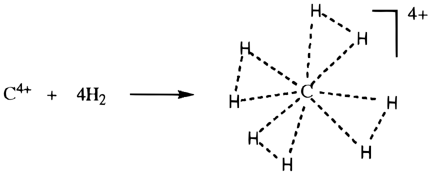
		ΔH (kcal/mol)[a]	ΔH (kcal/mol)[b]
CH_7^{3+} (**1**) -------> CH_6^{2+} + H^+	(1)	-243.2	-241.1
CH_7^{3+} (**1**) -------> CH_4^{2+} + H_3^+	(2)	-253.7	-260.3

[a] *at MP4(SDTQ)/6-31G**//MP2/6-31G** + ZPE ;* [b]*with the G2 method*

in the free hydrogen molecule at the same level of theory, and it is also slightly longer than that in H_2^+ (1.031 Å). We have located a transition structure, **2** (Figure 1), at the MP2/6-31G** level for intramolecular hydrogen transfer in the trication. Optimizations of the structures **1** and **2** with the MP2/6-311++G(2df,2pd) and QCISD(T)/6-311G** changed the geometries very little. The C−H and H−H bonds become slightly longer. Structure **2** lies only 0.7 kcal/mol higher in energy than structure **1** at MP4(SDTQ)/6-31G**//MP2/6-31G**. At G2, this energy difference reduces to only 0.1 kcal/mol. At our highest level of theory (CCSD(T)/cc-pVTZ//MP2/6-311++G(2df,2pd)+ZPE), the energy difference between **1** and **2** has vanished. Hydrogen scrambling in CH_7^{3+} **1** therefore is very facile. This type of facile hydrogen scrambling is also calculated for CH_4^{2+},[13] CH_5^+,[3b] and CH_6^{2+} [6] carbocations.

We considered two possible dissociation paths for the ion **1,** both of expected high exothermicity. At G2 the dissociation into CH_6^{2+} and H^+ (eq 1) is calculated to be exothermic by 241.1 kcal/mol (Table 1 and Scheme 3), while dissociation into CH_4^{2+} and H_3^+ (eq 2) is even more exothermic by 19.2 kcal/mol. However, no transition state could be located for either reaction at the MP2/6-31G** level.

Scheme 4



We also searched for minimum-energy structures for tetraprotonated methane, CH_8^{4+}. One can visualize a CH_8^{4+} structure with four dihydrogen units complexed with a tetrapositively charged carbon atom, C^{4+} (Scheme 4). Such an octacoordinate carbocation complex can be compared with the CH^{3+} + $3H_2$, CH_2^{2+} + $2H_2$, and CH_3^+ + H_2 complexes in CH_7^{3+}, CH_6^{2+}, and CH_5^+ carbocations, respectively. However, at MP2/6-31G** all efforts proved futile.

The present study shows that triprotonated methane CH_7^{3+} **1** is a minimum on its potential energy surface, although its deprotonation is highly exothermic. The calculated structure of this trication has three 3c-2e bonds oriented in a propeller-shaped pattern. Hydrogen scrambling in CH_7^{3+} **1** should be very facile. While experimental verification of CH_7^{3+} will be extremely difficult, more stabilized analogues, including Schmidbaur type's gold complexes, e.g, $\{[(C_6H_5)_3PAu]_{7-n}CH_n\}^{3+}$, may be more feasible. CH_8^{4+} remains even computationally elusive as charge−charge repulsions appear to have reached their prohibitive limit.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

JA961081V

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