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Comparison of structures and energies of $CH_5^{2+\bullet}$ with $CH_4^{+\bullet}$ and their possible role in superacidic methane activation

GOLAM RASUL, G. K. SURYA PRAKASH, AND GEORGE A. OLAH

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, CA 90089-1661

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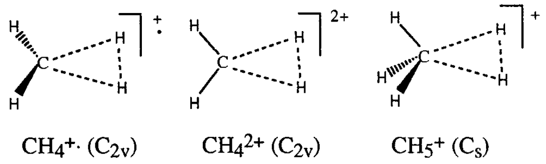
ABSTRACT Contrary to previous theoretical studies at the UHF/6-31G* level, the methonium radical dication CH_5^{2+} is not a C_s symmetrical structure with a 2e—3c bond but a C_{2v} symmetrical structure 1 with two 2e—3c bonds (at the UHF/6-31G, UMP2/6-31G**, and UQCISD(T)/6-311G** levels). The C_s symmetrical structure is not even a minimum at the higher level of calculations. The four hydrogen atoms in 1 are bonded to the carbon atom by two 2e—3c bonds and the fifth hydrogen atom by a 2e—2c bond. The unpaired electron of 1 is located in a formal p-orbital (of the sp^2-hybridized carbon atom) perpendicular to the plane of the molecule. Hydrogen scrambling in 1 is however extremely facile, as is in other C_1 cations. It is found that the protonation of methane to CH_5^+ decreases the energy for subsequent homolytic cleavage resulting in the exothermic (24.1 kcal/mol) formation of $CH_4^{+\bullet}$. Subsequent reaction with neutral methane while reforming CH_5^+ gives the methyl radical enabling reaction with excess methane to ethane and H_2. The overall reaction is endothermic by 11.4 kcal/mol, but offers under conditions of oxidative removal of H_2 an alternative to the more energetic carbocationic conversion of methane.**

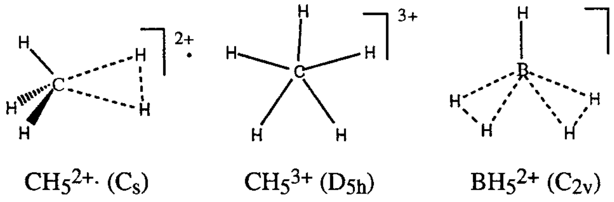
Activation of alkanes, main components of petroleum and natural gas, is an important area of chemistry. Consequently, knowledge of the parent methane cations and dications are of great significance. There have been many experimental and theoretical studies of methane cations and dications (1–3). The methane radical cation, $CH_4^{+\bullet}$ is the parent ion in mass spectrometry. In an early PNDO study by Olah and Klopman (4) the structure of $CH_4^{+\bullet}$ was found to have C_{2v} symmetry and can be considered as $CH_2^{+\bullet}$ radical cation complexed with a hydrogen molecule involving a three-center two-electron (2e—3c) bond. The 2e—3c unit is perpendicular to the plane of the molecule. High level *ab initio* calculations are in agreement with this conclusion (ref. 5 and references therein). Isoelectronic boron analog of $CH_4^{+\bullet}$ is neutral $BH_4^{\bullet}$, also has similar C_{2v} symmetrical structure (6). Methane dication CH_4^{2+} have also been observed in the gas phase (7–11). Planar C_{2v} symmetrical structure is preferred for the CH_4^{2+} as shown by Wong and Radom (12). Earlier calculations predicted (13, 14) a square planar D_{4h} symmetrical structure for the CH_4^{2+} dication. The sp^2-hybridized carbon atom of CH_4^{2+} contains a 2e—3c bond and an empty p-orbital perpendicular to the plane of the molecule.

CH_5^+ is considered the parent of nonclassical carbocations containing a five coordinate carbon atom. Recent extensive *ab initio* calculations by Marx and Parrinello (15) as well as by Müller and Kützelnigg (16) reconfirmed the preferred C_s symmetrical structure (17, 18) for the CH_5^+ cation with a 2e—3c bond as originally suggested by Olah and coworkers (19, 20). The structure can be viewed as a proton inserted into one of the C—H σ bonds of methane to form a 2e—3c bond between carbon and two hydrogen atoms. At the same time ready bond-to-bond (polytopal) proton migration makes it a rather fluxional molecule (19, 20), the process involving extremely low barriers (17, 18).



Structure **1**

The five-coordinate methonium radical dication, $CH_5^{2+\bullet}$, was first observed in the gas phase by charge-stripping mass spectrometry by Proctor *et al.* (9). Later the dication was also observed in the gas phase by Stahl *et al.* (10) and by Holmes and coworkers (11). Stahl *et al.* (10) calculated the structure of $CH_5^{2+\bullet}$ at the *ab initio* UHF/6-31G* level. They concluded (10) that the C_s symmetrical structure is the global minimum for the dication with a 2e—3c bonding interactions. We recently reported (21) that the planar D_{5h} symmetric structure **5** is an energy minimum for the CH_5^{3+} trication. On the other hand, our calculations showed that the energy-minimum structure of isoelectronic boron analog, the BH_5^{2+} dication has the planar C_{2v} symmetric structure **6**, with two 2e—3c bonds (21).



Structure **2**

We report now that at the higher levels of theory the methonium radical dication $CH_5^{2+\bullet}$ has not a C_s symmetrical structure with a 2e—3c bond but a C_{2v} symmetrical structure with two 2e—3c bonds. The C_s symmetrical structure is not even an energy minimum at this higher levels of calculations. We also report the results of our theoretical investigations of the reactions of $CH_4^{+\bullet}$ **4** with $H^{\bullet}$ and for comparison the related reaction of protonation of methane.

The geometry optimizations and frequency calculations were performed at the *ab initio* unrestricted UHF/6-31G**, UMP2/6-31G**, and UQCISD(T)/6-311G** levels (restricted calculations were performed for CH_4, C_2H_6 and CH_5^+) (22; note that all calculations were performed by using Gaussian 94). From calculated frequencies, the optimized structures were characterized as minima or transition structure. For improved energy, single point energies at UMP4(SDTQ)/6-31G** level on UMP2/6-31G** optimized geometries and at UCCSD(T)/cc-pVTZ (23) level on UQCISD(T)/6-311G** optimized geometries were computed. Calculated energies are given in Table 1. The *ab initio* calculation using unrestricted

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Table 1. Total energies (-au) and relative energies (kcal/mol)

	Energies†			Relative energies		
	1	**2**	**3**	**1**	**2**	**3**
HF/6-31G**//HF/6-31G**	39.63641 (0)	39.63486 (0)	39.62709 (1)	0.0	1.0	5.9
MP2/6-31G**//MP2/6-31G**	39.77365 (0)	39.77153 (1)	39.76819 (1)	0.0	1.3	3.4
ZPE‡	(25.7)	(24.6)	(22.8)			
MP4(SDTQ)/6-311G**//MP2/6-31G**	39.81563	39.81296	39.80950	0.0	1.7	3.9
QCISD(T)/6-311G**//QCISD(T)/6-311G**	39.81777 (0)	39.81493 (1)	39.81129 (1)	0.0	1.8	4.1
CCSD(T)/cc-pVTZ//QCISD(T)/6-311G**	39.84519	39.84258	39.83903	0.0	1.6	3.9
Final relative energies§				0.0	0.5	1.0

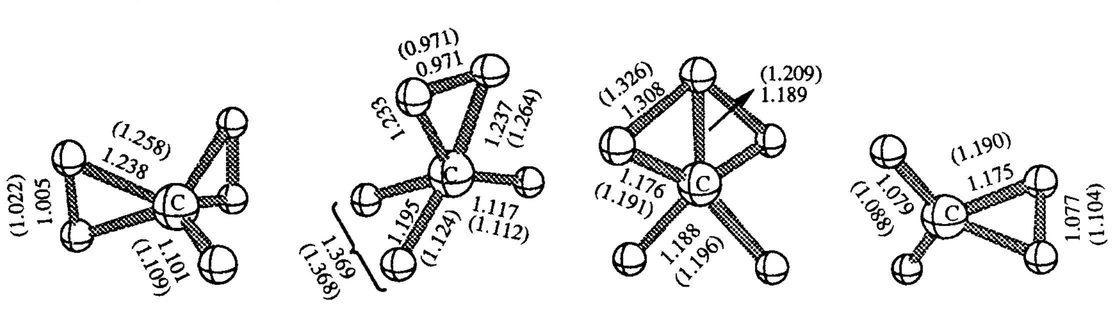
†Number of imaginary frequencies in parentheses.

‡Zero point vibrational energies (ZPE) at MP2/6-31G**//MP2/6-31G** scaled by a factor of 0.93.

§Final relative energies based on CCSD(T)/cc-pVTZ//QCISD(T)/6-311G**+ZPE.

(U) approach and frozen-core (fc) approximation were performed throughout. The symbols U and fc have been dropped for simplicity.

The C_{2v} symmetrical structure **1** and C_s symmetrical structure **2** were found to be minima on the potential energy surface (PES) of $CH_5^{2+\bullet}$ at the HF/6-31G** level as indicated by their frequency calculations (NIMAG = 0) at the same level.



1 (C_{2v}) **2** (C_s) **3** (C_2) TS **4** (C_{2v})

Structure **3**

The structure **2** lies 1.0 kcal/mol higher than **1** at this level of calculations (Table 1). At the higher correlated level of MP2/6-31G** structure **1** was found to be the only minimum on the potential energy surface of $CH_5^{2+\bullet}$. At the MP2/6-31G** level **2** is not even a minimum on the PES. The structure **2** turned out to be the transition state of the rotation of one of the 2e—3c unit around its axis as indicated by the frequency calculations (NIMAG = 1) at the same level. The structure **2** lies only 1.3 kcal/mol higher than **1** at the this level of calculations. Rotation of 2e—3c unit of **1** around its axis therefore would be facile. We have located C_2 symmetrical transition structure **3** for intramolecular hydrogen transfer in the cation **1**. For comparison we also calculated the structure of $CH_4^{+\bullet}$ **4**. Structure **1** can be viewed as a proton inserted into one of the σ non-2e—3c C—H bonds of $CH_4^{+\bullet}$ **4** to form an additional 2e—3c bond between carbon and a hydrogen atom. The dissociation of **1** into $CH_4^{+\bullet}$ **4** and H^+ was found to be exothermic by 80.1 kcal/mol (Eq. **1**). We also calculated the adiabatic ionization energies (IE_a) of CH_4 and CH_5^{2+} (Table 2). Calculated IE_a of CH_4 and CH_5^+ are 12.6 eV and 21.7 eV, respectively, agree very well with the experimental ionization energies of 12.6 eV (24) and 21.6 eV (10).

Table 2. Theoretical and experimental ionization energies in eV (kcal/mol) of CH_4 and CH_5^+

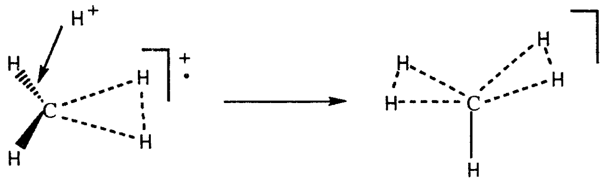
	Theoretical IE_a	Experimental
CH_4	12.6† (289.6)	12.6‡ (290.6)
CH_5^+	21.7† (4.97)	21.6§ (496.8)

†At the CCSD(T)/cc-pVTZ//QCISD(T)/6-311G** + ZPE level.

‡Taken from ref. 27.

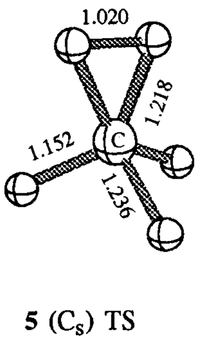
§Taken from ref. 10.

Another possible C_s structure **5** of $CH_5^{2+\bullet}$ was found to be 1.6 kcal/mol less stable than the structure **1** at the MP4(SDTQ)/6-31G**//MP2/6-31G** level. This is also a transition state of the rotation of the 2e—3c unit around its axis as indicated by its frequency calculations (NIMAG = 1) at the MP2/6-31G**//MP2/6-31G** level which again indicates the facile rotation of 2e—3c unit around its axis in **1**.



Structure **4**

Calculations at even higher level of theory also favor the C_{2v} structure **1**. Optimization at the QCISD(T)/6-311G** level shows



5 (C_s) TS

Structure **5**

that structure **1** is 1.8 kcal/mol more stable than the structure **2**. Frequency calculations at the QCISD(T)/6-311G**//QCISD(T)/6-311G** level again show that structure **1** is a minimum and structure **2** is a transition state. Our highest level of calculations [at the CCSD(T)/cc-pVTZ//QCISD(T)/6-311G** level] similarly show that **1** is more stable than **2** by 1.6 kcal/mol.

Structure **1** resembles a complex between $CH^{2+\bullet}$ and two hydrogen molecules resulting in the formation of two 2e-3c bonds. The sp^2-hybridized carbon atom of **1** possesses a formal p-orbital (containing a single electron) perpendicular to the plane of the molecule. The plane of each of the 2e—3c units are rotated 90° around its axis from the plane of the molecule. The C—H bond distance in the 2e—3c bonds is 1.238 Å at the MP2/6-31G** level. This is slightly longer than that found in the 2e—3c C—H bonds (1.181 Å) of $CH_4^{+\bullet}$ **4** at the same theoretical level. The non-2e—3c interacting C—H bond distance of 1.101 Å in **1** is also slightly longer than that of **4**. On the other hand, the calculated H—H distance in the 2e—3c interactions of 1.005 Å is only slightly shorter than that of 2e—3c interaction of **4** (1.077 Å).

Optimizations of the structures **1**–**4** at the QCISD(T)/6-311G** level changed the geometries very little. The C—H and H—H bonds become slightly longer. The transition structure **3** for intramolecular hydrogen transfer in the cation **1** lies only 3.9 kcal/mol higher in energy than structure **1** at the CCSD(T)/cc-pVTZ//QCISD(T)/6-311G** level. However, including zero point vibrational (ZPE) energy this is reduced to 1.0 kcal/mol (Table 1). Hydrogen scrambling in **1** therefore is extremely facile. This type of facile hydrogen scrambling was also found for CH_4^{2+} (12), CH_5^+ (16–18), CH_6^{2+} (25, 26), and CH_7^{3+} (27). Thus, it is clear that the most of the C_1 carbocations containing one or more 2e—3c bond can undergo very readily low energy bond to bond rearrangements as postulated in case of CH_5^+ by Olah *et al.* as early as 1969 (19, 20).

We have also investigated the related reactions of $CH_4^{+\bullet}$ **4** with $H^\bullet$ and with methane, as well as the protonation of methane. The reaction of $H^\bullet$ with $CH_4^{+\bullet}$ **4** (Eq. **2**; see Table 3) was found to be exothermic by 105.1 kcal/mol. In comparison the reaction of H^+ with CH_4 is exothermic by 129.2 kcal/mol (Eq. **3**). These results suggest that the gas phase dissociation of CH_5^+ into $CH_4^{+\bullet}$ **4** and $H^\bullet$ is about 24 kcal/mol more favorable than the gas phase dissociation of CH_5^+ into CH_4 and H^+. On the other hand, the reaction of $CH_4^{+\bullet}$ **4** with methane to form CH_5^+ and $CH_{3\bullet}$ is only exothermic by 1.2 kcal/mol (Eq. **4**).

In fact, the radiolysis of solid methane in liquid argon at 77 K by γ rays was shown by Libby and coworkers (28–30) to give polycondensates of an average molecular formula $C_{20}H_{40}$. It was considered that the radiolysis of methane gives $CH_4^{+\bullet}$, which in the presence of excess methane reacts according to $CH_4^{+\bullet} + CH_4 = CH_5^+ + CH_3$. Subsequent polymerization would involve ion molecule reactions ($CH_4 + C_n^+H_{2n+1} = H_2 + C_{n+1}^+H_{2n+3}$) followed by neutralization to form the heavier hydrocarbons (29, 30).

Table 3. Computed thermodynamic energies for various reactions

No.	Equation	ΔH† (kcal/mol)
1	$CH_4^{+\bullet}$(**4**) + $H^+ \rightarrow CH_5^{2+\bullet}$(**1**)	+80.9
2	$CH_4^{+\bullet}$(**4**) + $H \rightarrow CH_5^+$	−105.1
3	$CH_4 + H^+ \rightarrow CH_5^+$	−129.2
4	$CH_4^{+\bullet}$(**4**) + $CH_4 \rightarrow CH_5^+ + CH_3^\bullet$	−1.2
5	$CH_4 + CH_3^\bullet \rightarrow C_2H_6 + H^\bullet$	+12.6
6	$2\,CH_4 \rightarrow C_2H_6 + H_2$	+15.4

†At the CCSD(T)/cc-pVTZ//QCISD(T)6-311G** + ZPE level.

The exothermic protonation of methane offers a possibility for subsequent more facile homolytic cleavage resulting in overall exothermic formation of $CH_4^{+\bullet}$ by 24.1 kcal/mol.
In contrast, the one electron oxidation of methane requires 289.6 kcal/mol.

$$\left.\begin{array}{ll} CH_4 + H^+ \rightleftharpoons CH_5^+ & \Delta H = -129.2\ \text{kcal/mol} \\ CH_5^+ \longrightarrow CH_4^{+\bullet} + H^\bullet & \Delta H = +105.1\ \text{kcal/mol} \end{array}\right\rangle \Delta H = -24.1\ \text{kcal/mol.}$$

$$CH_4 \xrightarrow{-e} CH_4^{+\bullet} \qquad \Delta H = +289.6\ \text{kcal/mol.}$$

Subsequent reaction with neutral methane while reforms CH_5^+ gives the methyl radical enabling reaction with excess methane to give ethane. The overall reaction is endothermic by 11.4 kcal/mol.

$$CH_4^{+\bullet} + CH_4 \rightarrow CH_5^+ + CH_3^\bullet \quad \Delta H = -1.2\ \text{kcal/mol.}$$

$$CH_4 + CH_3^\bullet \rightarrow C_2H_6 + H^\bullet \quad \Delta H = +12.6\ \text{kcal/mol.}$$

H· can give subsequently H_2 ($2\,H^\bullet \rightarrow H_2$) or react further with CH_4 ($CH_4 + H^\bullet \rightarrow CH_3^\bullet$ + H2). The protolytic activation of methane with subsequent homolytic cleavage offers an alternative to the carbocationic higher energy conversion of methane.

$$CH_4 + H^+ \rightleftharpoons CH_5^+ \xrightarrow{-H_2} CH_3^+ \xrightarrow{CH_4} C_2H_7^+ \xrightarrow{-H^+} C_2H_6.$$

Hydrogen must be oxidatively removed as the overall reaction of $2\,CH_4 \rightarrow C_2H_6 + H_2$ is endothermic by 15.4 kcal/mol.

In conclusions, the present high level *ab initio* study at the HF/6-31G**, MP2/6-31G**, and QCISD(T)/6-311G** levels indicates that the C_{2v} symmetrical structure **1** is the only minimum on the potential energy surfaces of $CH_5^{2+\bullet}$. This is in contrast to the previously reported *ab initio* calculated C_s symmetrical structure of $CH_5^{2+\bullet}$ at the HF/6-31G* level (with only one 2e—3c bond) (10). The optimized structure shows that the four hydrogen atoms in **1** are bonded to the carbon atom by two 2e—3c bonds and the fifth by a 2e—3c bond. The sp^2-hybridized carbon atom of **1** possesses a formal p-orbital (containing an unpaired electron) perpendicular to the plane of the molecule. The plane of each of the 2e—3c units are rotated 90° around its axis from the plane of the molecule. The transition structure, **3**, was located for the intramolecular hydrogen transfer in the cation **1**, which indicates that the hydrogen scrambling in **1** should be facile. It was also pointed out that the protonation of methane to CH_5^+ offers a possibility for subsequent faciliated homolytic cleavage resulting in the overall exothermic formation of $CH_4^{+\bullet}$ by 24.1 kcal/mol. Subsequent reaction with neutral methane gives the methyl radical-enabling reaction with excess methane to give ethane offering an alternative for the carbocationic condensation of methane. Oxidative removal of hydrogen allows the otherwise overall endothermic (by 11.4 kcal/mol) reaction to proceed.

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