# Structure and Stability of Diprotonated Methane, $CH_6^{2+}$ [1]

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**Abstract:** The prototype of hexacoordinate carbodications $CH_6^{2+}$ has been investigated by ab initio molecular orbital theory with inclusion of electron-correlation effects. The geometries were determined with the HF/6-31G* basis set and their energies were calculated at the MP3/6-31G** level. A $C_{2v}$ symmetry structure with two stabilizing 3c-2e interactions is found to be a minimum on the potential energy surface. Two transition structures ($C_{2v}$) as well as several hilltop structures ($D_{3h}$, $D_{2d}$, $C_{5v}$, and $O_h$) for polytopal intramolecular hydrogen rearrangements have been located. Hydrogen scrambling should be very rapid. $CH_6^{2+}$ is thermodynamically unstable toward deprotonation, loss of $H_2^{+}\cdot$, and loss of $H_3^+$ by 63.1, 18.6, and 126.8 kcal/mol, respectively. The deprotonation barrier was calculated to be 35.4 kcal/mol. A high barrier of 59.9 kcal/mol for loss of $H_3^+$ was established. The heat of formation, $\Delta H_f(CH_6^{2+})$, is estimated to be 651 ± 3 kcal/mol. The kinetic stability combined with the favorable heat of hydrogenation of $CH_4^{2+}$ of 79 kcal/mol suggests that $CH_6^{2+}$ may be adaptable to experimental observation in the gas phase.

Protonated methane $CH_5^+$, the prototype for five-coordinate carbocations,[2] is of substantial significance in the electrophilic reactions of methane.[3] Carbodications are an increasingly prominent class of organic ions.[4] Hence we considered if doubly protonated methane, $CH_6^{2+}$, might be a viable species.

Hexacoordinated carbon has so far, however, hardly been considered in the carbodication chemistry[4] except for, e.g., Hogeveen's pyramidal dication,[5] its unsubstituted $(CH)_6^{2+}$ ($C_{5v}$) analogue,[6] and $CLi_6^{2+}$ ($O_h$).[7] We now report on a calculational study of the structure and stability of the prototype $CH_6^{2+}$ and show it to be a viable species.[1]

The trivalent $C_1$ dications have been the subject of recent studies. Beynon et al.[8] reported the observation of $CH^{2+}\cdot$, $CH_2^{2+}$, $CH_3^{2+}\cdot$, and $CH_4^{2+}$ obtained from methane and $CH_5^{2+}\cdot$ from $CH_5^+$ by the mass-spectroscopic charge-stripping technique. In a subsequent theoretical study[9] the barriers for proton loss for $CH_2^{2+}$, $CH_3^{2+}\cdot$, and $CH_4^{2+}$ were calculated to be 30.8, 2.9, and 16.8 kcal/mol, respectively, but $CH^{2+}\cdot$ was found to be only repulsive in character. Despite the unfavorable heats of formation of these dications, the binding energy prevails over the strong electrostatic repulsion of the two charges at short internuclear distances. Hence, metastable, but experimentally observable species result.[8] This trend is even more pronounced in the $C_2$ series. For example, the deprotonation barriers of the acetylene dication ($C_2H_2^{2+}$)[10] and the ethylene dication ($C_2H_4^{2+}$)[11] were calculated to be 65.0 and 68.8 kcal/mol, respectively. Theoretical calculations have shown that the ethane dication, $C_2H_6^{2+}$, may have three minima on the potential energy surface with a maximum deprotonation barrier of ca. 30 kcal/mol.[1a,12,13]

Electron-deficient species can be stabilized effectively by hydrogen complexation, leading to an increase of the carbon coordination number, i.e., hypercoordination, to give a total of 8 valence electrons.[1a] The experimentally deduced heat of hydrogenation of the trivalent methyl cation, $CH_3^+$, to the tetravalent pentacoordinate methonium ion, $CH_5^+$, of 42 kcal/mol is illustrative for the stabilization.[14] A value of 34.5 kcal/mol is obtained by theoretical calculations at the level employed in the present paper (MP3/6-31G** + ZPE).[15] Two of the ligands of the pentacoordinated carbon are involved in a 3-center-2-electron (3c-2e) interaction.[15] Similar bonding nature characterizes numerous other nonclassical ions,[2b] including the norbornyl cation.[16]

The present study extends this concept to dicationic species and

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(1) (a) For a preliminary communication, see: Lammertsma, K.; Olah, G. A.; Barzaghi, M.; Simonetta, M. *J. Am. Chem. Soc.* **1982**, *104*, 6851. After appearance of this communication the authors learned of independent studies on the same species by Schleyer and Pople's groups. It was decided to combine our studies in a joint full paper. (b) The Erlangen group regards the present paper as Carbodications. 7. For part 6 see ref 6b.

(2) (a) Olah, G. A.; Klopman, G. A.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261. (b) Olah, G. A. *Pure Appl. Chem.* **1981**, *53*, 201. (c) Radom, L.; Poppinger, D.; Haddon, R. C. "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1976; Vol. 5, p 2303. (d) Kutzelnigg, W. "Einführung in die Theoretische Chemie"; Verlag Chemie, Weinheim, 1978; Vol. 2, p 348.

(3) (a) Olah, G. A.; Mo, Y. K.; Olah, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4939. (b) Siskin, M.; Schlosberg, R. H.; Kocsi, W. P. *ACS Symp. Ser.* **1977**, *55*, 186.

(4) (a) For a recent review, see: Prakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem.* **1983**, *95*, 356. (b) Lammertsma, K.; Schleyer, P. v. R., to be published.

(5) Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.* **1975**, *8*, 413.

(6) (a) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781. (b) Lammertsma, K.; Schleyer, P. v. R. *Ibid.* **1983**, *105*, 1049.

(7) Jemmis, E. D.; Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R.; Chin, J. W., Jr.; Landro, F. J.; Lagow, R. J.; Luke, B.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4275.

(8) (a) Ast, T.; Porter, C. J.; Proctor, C. J.; Beynon, J. H. *Chem. Phys. Lett.* **1981**, *78*, 439. (b) Proctor, C. J.; Porter, C. J.; Ast, T.; Bolton, P. D.; Beynon, J. H. *Org. Mass Spectrom.* **1981**, *16*, 454.

(9) Pople, J. A.; Tidor, B.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *88*, 533. Siegbahn (Siegbahn, P. E. M. *Chem. Phys.* **1982**, *66*, 443) calculates the deprotonation of $CH_4^{2+}$ to be exothermic by 109.2 kcal/mol with a barrier of 17.7 kcal/mol by using a basis set with polarization functions on hydrogen and carbon.

(10) Pople, J. A.; Frisch, M. J.; Raghavachari, K.; Schleyer, P. v. R. *J. Comp. Chem.* **1982**, *3*, 468.

(11) Lammertsma, K.; Barzaghi, M.; Olah, G. A.; Pople, J. A.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.*, preceding paper in this issue.

(12) Olah, G. A.; Simonetta, M. *J. Am. Chem. Soc.* **1982**, *104*, 330.

(13) Schleyer, P. v. R.; Kos, A. J.; Pople, J. A.; Balaban, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 3771.

(14) Derived from the most recent data reviewed by Walder and Franklin: Walder, R.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 85. Also see: Bohme, D. K.; Mackay, G. I.; Schiff, H. I. *J. Chem. Phys.* **1980**, *73*, 4978; Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119.

(15) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

(16) (a) Olah, G. A.; Prakash, G. K. S.; Arvanaghi, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1982**, *104*, 7105. (b) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41. (c) Goddard, J. D.; Osamura, Y.; Schaefer, H., III *J. Am. Chem. Soc.* **1982**, *104*, 3258. (d) Raghavachari, K.; Schleyer, P. v. R. *Ibid.*, submitted.

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Table I. HF/6-31G* Optimized Geometries of $CH_6^{2+}$ Structures[a]

| structure | geometry |
|---|---|
| 1, $C_{2v}$ | $C\text{-}H_a = 1.123$; $C\text{-}H_c = 1.208$; $H_aCH_b = 97.8$; $H_cCH_d = 47.5$; $H_cCH_e = 98.6$ |
| 2, $C_{2v}$ | $C\text{-}H_a = 1.217$; $C\text{-}H_c = 1.151$; $H_aCH_b = 45.3$; $H_cCH_d = 76.5$; $H_cCH_e = 88.1$ |
| 3, $D_{3h}$ | $C\text{-}H_a = 1.162$; $H_aCH_b = 64.5$ |
| 4, $C_{2v}$ | $C\text{-}H_a = 1.232$; $C\text{-}H_c = 1.156$; $C\text{-}H_e = 1.143$; $H_aCH_b = 43.1$; $H_cCH_d = 138.4$; $H_eCH_f = 137.8$ |
| 5, $C_{5v}$ | $C\text{-}H_a = 1.093$; $C\text{-}H_b = 1.183$; $H_aCH_b = 113.6$ |
| 6, $D_{2d}$ | $C\text{-}H_a = 1.199$; $C\text{-}H_b = 1.150$; $H_aCH_b = 67.0$ |
| 7, $O_h$ | $C\text{-}H = 1.175$ |
| 8, $C_s$ | $C\text{-}H_a = 1.216$; $C\text{-}H_c = 1.095$; $C\text{-}H_e = 1.132$; $H_e\text{-}H_f = 1.462$; $H_aCH_b = 43.9$; $H_cCH_d = 110.3$; $H_aCH_e = 104.8$; $H_cCH_e = 112.0$; $H_fH_eC = 160.8$ |
| 8a, $C_{4v}$ | $C\text{-}H_a = 1.203$; $C\text{-}H_c = 1.141$; $H_a\text{-}H_b = 0.865$; $H_aCH_c = 105.3$ |
| 8b, $C_{4v}$ | $C\text{-}H_a = 1.222$; $C\text{-}H_c = 1.127$; $H_a\text{-}H_b = 1.489$; $H_aCH_c = 111.6$ |
| 9, $C_s$ | $C\text{-}H_a = 1.093$; $C\text{-}H_b = 1.186$; $H_b\text{-}H_c = 1.072$; $H_c\text{-}H_d = 1.111$; $H_d\text{-}H_e = 0.847$; $H_aCH_b = 114.3$; $CH_bH_c = 79.5$; $H_bH_cH_d = 134.9$; $H_cH_dH_e = 145.8$; $HCH_a = 110.4$ |

[a] Bond lengths are in angstrom and bond angles in degrees.

demonstrates that the smallest possible hexacoordinated carbodication, $CH_6^{2+}$, may be experimentally accessible. The doubly positive charge is ameliorated in this thermodynamically very unstable electron-deficient species, so that spontaneous fragmentation of the hexacoordinate carbon does not take place. Since intuitively one would expect $CH_6^{2+}$ to be purely repulsive in character, how can the doubly positive charge be accommodated to prevent spontaneous fragmentation?

Hexacoordinate charged species are known for the elements of main groups 3 to 0 of the periodic table.[17] These inorganic salts are $AB_6$ complexes with 12 or 14 valence electrons and all have an (close to) octahedral conformation.[17] Theoretical studies have focused on the qualitative relative stabilities of octahedral ($O_h$) and trigonal prismatic ($D_{3h}$) structures of such complexes.[17] In contrast $CH_6^{2+}$ has 8 valence electrons and favors $C_{2v}$ symmetry.

## Methods

The ab initio calculations were performed by the spin-restricted Hartree–Fock method using the GAUSSIAN 80 series of programs.[18] The geometries of both equilibrium and transition structures were completely optimized within each assumed symmetry using the standard 3-21G and 6-31G* basis sets;[19] a conjugate gradient method based on analytical first derivatives was used.[20] Single-point calculations at the 6-31G** level,[16] which has additional polarized (p type) functions on hydrogen to those (d type) on carbon, were carried out on the 6-31G* optimized structures. They are designated as HF/6-31G**//6-31G*. Valence-shell electron-correlation corrections were calculated with second- and third-order Møller–Plesset perturbation theory[21] at both the 6-31G* and 6-31G** levels. The final energies correspond to MP3/6-31G**//HF/6-31G*. Harmonic force constants over internal coordinates were computed by numerical differentiation of the analytical energy gradient at both the HF/3-21G//3-21G and HF/6-31G*//6-31G* levels using the corresponding optimized geometries. A two-point forward formula with a step size of 0.0053 Å for bond lengths and 0.57° for bond and dihedral angles was used in numerical derivatives. The derived vibrational harmonic frequencies[22] were used to calculate the zero-point vibrational energies (ZPE). For transition structures the imaginary frequency is neglected in the zero-point summation. Reaction paths connecting two minima through a transition structure were calculated at the HF/3-21G level as the steepest descent paths (i.e., orthogonal to the energy equipotential contour surface) in the $(3N - 6)$-dimensional space of internal coordinates. The initial direction at a transition or hilltop was given by the vibrational normal coordinate corresponding to the imaginary frequency.[23] We employed this procedure to ensure full characterization of the stationary points.

Chart I

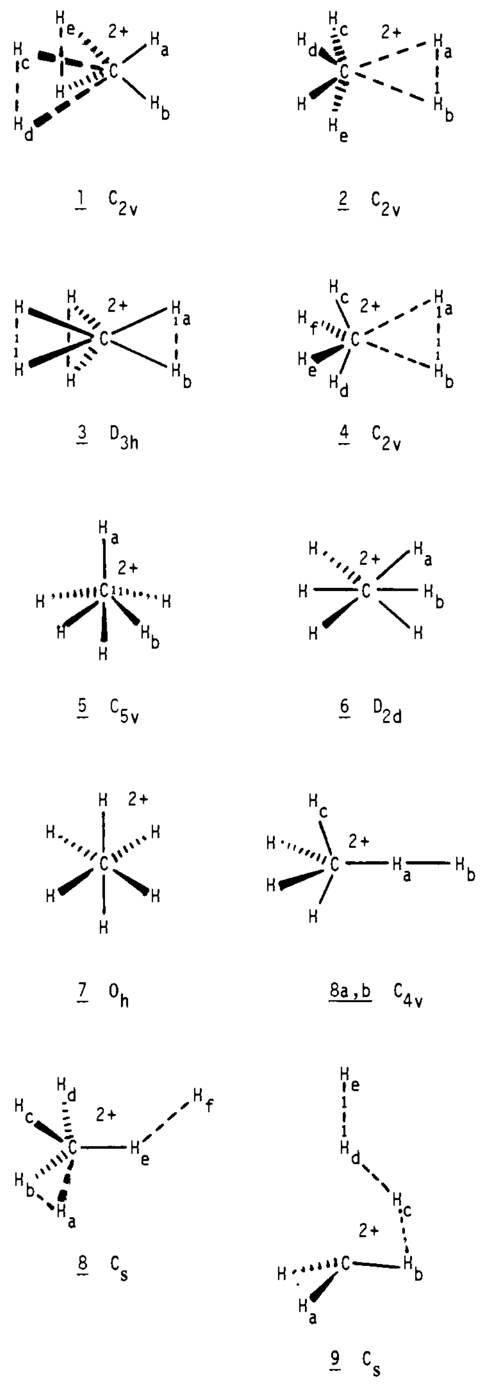

Table I gives the HF/3-21G and HF/6-31G* equilibrium, transition, and hilltop structures of the species studied. Their absolute and relative energies at the various levels of Hartree–Fock theory are summarized in Table II, with the effect of electron correlation included in Table III. The

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(17) Gimarc, B. M.; Liebman, J. F.; Kohn, M. *J. Am. Chem. Soc.* **1978**, *100*, 2334. Gimarc, B. M. "Molecular Structure and Bonding—the qualitative molecular orbital approach"; Academic Press: New York, 1979, and references cited therein.

(18) (a) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; De Frees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406. (b) Van Kampen, P. N.; Smits, G. F.; De Leeuw, F. A. A. M.; Altona, C. *QCPE* **1982**, *14*, 437.

(19) (a) 3-21G basis: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (b) 6-31G* and 6-31G** basis: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(20) Schlegel, H. B. *J. Comp. Chem.* **1982**, *3*, 214.

(21) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem., Symp.* **1975**, *9*, 229. (c) Pople, J. A.; Binkley, J. S.; Seeger, R. *Ibid.* **1976**, *10*, 1.

(22) Wilson, E. B., Jr.; Cross, P. C. "Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra"; McGraw-Hill: New York, 1955.

(23) (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363. (b) Sana, M.; Reckinger, G.; Leroy, G. *Theor. Chim. Acta (Berlin)* **1981**, *58*, 145. (c) Lammertsma, K.; Barzaghi, M.; Olah, G. A., to be published.

Table II. Hartree–Fock Total (in au) and Relative Energies (in kcal/mol, in parentheses) of $CH_6^{2+}$ Structures

| geometry | HF/3-21G//3-21G | HF/6-31G*//6-31G* | HF/6-31G**//6-31G* |
|---|---|---|---|
| 1, $C_{2v}$ | −40.04648 (0.0) | −40.27675 (0.0) | −40.30397 (0.0) |
| 2, $C_{2v}$ | −40.04844 (−1.2) | −40.27388 (1.7) | −40.29730 (4.2) |
| 3, $D_{3h}$ | −40.04534 (0.7) | −40.27062 (3.8) | −40.29481 (5.7) |
| 4, $C_{2v}$ | −40.04697 (−0.3) | −40.27210 (2.9) | −40.29499 (5.6) |
| 5, $C_{5v}$ | −40.02039 (16.4) | −40.25746 (12.1) | −40.28486 (12.0) |
| 6, $D_{2d}$ | −40.02817 (11.5) | −40.25138 (15.9) | −40.27628 (17.4) |
| 7, $O_h$ | −40.01778 (18.0) | −40.22349 (33.4) | −40.23781 (41.5) |
| 8, $C_s$ |  | −40.22672 (31.4) | −40.24484 (37.1) |
| 8a, $C_{4v}$ | −40.01918 (17.8) | −40.23535 (25.9) | −40.24948 (35.2) |
| 8b, $C_{4v}$ | −39.99966 (29.3) | −40.22083 (36.3) | −40.23499 (43.3) |
| 9, $C_s$ | −39.96356 (52.0) | −40.19172 (53.4) | −40.21111 (58.3) |

HF/6-31G* harmonic frequencies and zero-point vibrational energies are listed in Table IV.

## Results and Discussion

In the calculational survey of the potential energy hypersurface of $CH_6^{2+}$ we have found nine stationary points, whose geometries have $O_h$ (**7**), $D_{3h}$ (**3**), $D_{2d}$ (**6**), $C_{5v}$ (**5**), $C_{2v}$ (**1**, **2**, **4**), and $C_s$ (**8**, **9**) symmetry (Table I).

Structure **1** ($C_{2v}$) is the only $CH_6^{2+}$ minimum at the HF/6-31G* level, since only for **1** are all calculated harmonic vibrational frequencies real. The stationary points **2**, **4**, **8**, and **9** are transition structures at that level, characterized by one imaginary frequency. The remaining geometries **3**, **5**, **6**, and **7** are hilltop structures, characterized by one imaginary degenerate frequency.[24]

## Geometries and Energies

The global energy minimum structure **1** has two 3c-2e interactions with the carbon participating in both. Each of these interactions, characterized by the long C–H bond length of 1.208 Å and the small H–C–H bond angle of 47.5°, accommodate positive charge, leaving the two remaining C–H bonds (1.123 Å) rather unaffected. The similarity with protonated methane, $CH_5^+$, having one 3c-2e interaction, is clear. Regarding $CH_6^{2+}$ as protonated $CH_5^+$ or as diprotonated methane it may be argued that each of these protons goes into a stabilizing 3c-2e interaction. The transition structures **2** and **4** ($C_{2v}$) have only one such interaction and are 2.6 and 4.3 kcal/mol, respectively, higher in energy than **1** at the MP3/6-31G**//6-31G* level. Qualitatively the absence of the stabilizing three-center interactions renders the higher symmetry geometries as higher energetic species. The boundaries for these hilltop structures are given by the trigonal prism **3** and the octahedron **7**. Three H–H interactions are bonding in **3**, while all are nonbonding in **7**; the 6-31G* overlap populations[25] are 0.056 and 0.000, respectively.[26] At the MP3/6-31G**//6-31G* level the energy differences of **3** and **7** with **1** are 2.9 and 34.4 kcal/mol, respectively. Both geometry **5** ($C_{5v}$), resembling Hogeveen's pyramidal dication, and **6**, representing double protonation of methane at opposite sides, are of intermediate energy.

The deprotonation transition structure **8** at 6-31G* has a cyclic 3c-2e interaction. The dissociating H–H bond length is 1.462 Å with a connecting C–H bond length of 1.132 Å. The MP3/6-31G**//6-31G* energy difference with **1** amounts to 38.8 kcal/mol.

The transition structure **9** has a bent $H_3^+$ unit complexed to $CH_3^+$ via one of the hydrogens in $C_s$ symmetry. The energy of **9** is 63.9 kcal/mol (MP3/6-31G**//6-31G*) higher than that of **1**.

An attractive but only qualitative representation of hypercoordinate cations is by means of hydrogenated complexes. The H–H distances are indicative for the interaction in these 3c-2e complexes.[27] For example, $CH_5^+$ may be regarded as the hydrogenated methyl cation, H–H = 0.853 Å vs. 0.730 Å in hydrogen (HF/6-31G*).[15] The stabilization results from interaction of the two s orbitals of $H_2$ with the empty $p_z$ orbital of planar trivalent $CH_3^+$.[2] Similarly structures **2** and **4**, with $H_a$–$H_b$ distances of 0.937 and 0.904 Å, respectively, can be visualized as the cyclic complexes of $H_2$ with the $p_z$ orbital of planar-trivalent $CH_4^{2+}$. In this approach structure **8a** ($C_{4v}$, 3-21G) is the linear complex, resulting from interaction of one s orbital of $H_2$ with the $p_z$ orbital of $CH_4^{2+}$. Taking the 3c-2e presentation to extremes one may formally regard the global minimum **1** as a dihydrogenated complex of $CH_2^{2+}$, H–H being 0.972 Å. In this context one is tempted to picture structure **3** as a tight complex between $H_3^+$ and $CH_3^+$.

More quantitatively the structural nature of the 8-valence-electron $CH_6^{2+}$ may be understood from inspection of the molecular orbital framework at, e.g., the HF/6-31G* level. Converting the octahedron **7** into the trigonal prism **3** is accompanied by splitting the triple-degenerate $t_{1u}$ HOMO ($E = -1.22059$ au) into the $a_2''$ ($E = -1.20714$ au) and the double-degenerate e′ MO's ($E = -1.29155$ au).[17] The energy decrease from $t_{1u}$ to e′ overrules the small increase from $t_{1u}$ to $a_2''$, and determines quantitatively the stabilization of **3** ($D_{3h}$) over **7** ($O_h$), being 29.6 kcal/mol at this level (HF/6-31G*). In **1** ($C_{2v}$) the significantly enhanced overlap between the s orbitals of two pairs of hydrogens further lowers the energy of one of the e′ MO's of **3** to −1.35334 au, reducing the total energy by 3.8 kcal/mol (HF/6-31G*). This $b_1$ MO is the main contributor to the 3c-2e interactions in the $CH_6^{2+}$ minimum-energy structure **1**.

## Effect of Basis Set and Correlation Energies

The use of different basis sets and the inclusion of correlation corrections influences markedly the potential energy hypersurface of $CH_6^{2+}$, as shown schematically in Figure 1 and in Tables II and III. At the lower HF/3-21G level of calculation, both **2** and **4** are energetically favored over **1** by 1.2 and 0.3 kcal/mol, respectively.[28] Inclusion of d-polarization functions on carbon (HF/6-31G*) reverses the relative stability of **2** and **4**, with respect to **1**, and significantly enhances the stability of **1** with respect to all the remaining structures. This effect is even more pronounced by extending the polarization with p functions on hydrogen (HF/6-31G**//6-31G*). This finding confirms the necessity to include d- and p-polarization functions for a proper description of hypercoordinate ions, and in particular of the 3c-2e stabilization.[15,29] The transition structure for deprotonation also illustrates this point. Thus the HF/6-31G* optimized geometry **8** ($C_s$) accommodates the positive charges in the departing proton and in a 3c-2e interaction. The latter is absent at the HF/3-21G level where a $C_{4v}$ transition structure **8b** is obtained instead; also only at this level is there a local minimum, **8a**, with $C_{4v}$ symmetry.[30]

The effect of correlation interaction is relevant. The use of correlated wave functions has a slightly larger effect on transition structures than on equilibrium geometries. The resulting energy separations are reduced significantly as compared to the Hartree–Fock values. The changes are somewhat higher at the second than at the third order Møller–Plesset perturbation theory. At the MP2 and MP3/6-31G*//6-31G* levels of theory, the energies of **1**, **2**, **3**, and **4** become virtually equal. However, upon introduction of MP2 and MP3 correlation corrections on the larger 6-31G**//6-31G* basis set the energy differences between these structures are again significant. At the MP3 level, the calculated stabilization energy of **1** over **2**, **3**, and **4** is 2.6, 2.9, and 4.3

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[24] McIver, J. W., Jr. *Acc. Chem. Res.* **1974**, *7*, 72.

[25] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343.

[26] The Mulliken population analysis also shows that the carbon in $CH_6^{2+}$, despite its formal charge of +2, is strongly *negative*, see also: Greenberg, A.; Winkler, R.; Smith, B. L.; Liebman, J. F. *J. Chem. Educ.* **1982**, *59*, 367. The carbon carries the highest negative charge at 6-31G* in the octahedron **7** (−2.17) and the lowest in the $C_{2v}$ minimum **1** (−1.22).

[27] Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3436.

[28] At the HF/3-21G level all frequencies for **2** are real, while both **1** and **4** have one imaginary frequency.

[29] Lischka, H.; Köhler, H.-J. *J. Am. Chem. Soc.* **1978**, *100*, 5297. Köhler, H.-J.; Lischka, H. *Ibid.* **1979**, *101*, 3479.

[30] At the HF/3-21G level two additional equilibrium structures, closely related to **8a**, were localized with $C_{2v}$ and $C_{4v}$ symmetry. These were not investigated at the higher theoretical levels because of their unfavorable energy and geometrical characteristics.

Table III. Electron Correlation Corrected Total (in au) and Relative Energies (in kcal/mol in parentheses) of $CH_6{}^{2+}$ Structures

| | 6-31G*//6-31G* | | 6-31G**//6-31G* | |
|---|---|---|---|---|
| geometry | MP2 | MP3 | MP2 | MP3 |
| **1**, $C_{2v}$ | −40.42713 (0.0) | −40.44512 (0.0) | −40.47763 (0.0) | −40.49674 (0.0) |
| **2**, $C_{2v}$ | −40.42742 (−0.2) | −40.44503 (0.1) | −40.47422 (2.1) | −40.49264 (2.6) |
| **3**, $D_{3h}$ | −40.42652 (0.4) | −40.44351 (1.0) | −40.47444 (2.0) | −40.49215 (2.9) |
| **4**, $C_{2v}$ | −40.42502 (1.3) | −40.44283 (1.4) | −40.47123 (4.0) | −40.48987 (4.3) |
| **5**, $C_{5v}$ | −40.41191 (9.6) | −40.42887 (10.2) | −40.46427 (8.4) | −40.48220 (9.1) |
| **6**, $D_{2d}$ | −40.40793 (12.0) | −40.42512 (12.5) | −40.45642 (13.3) | −40.47439 (14.0) |
| **7**, $O_h$ | −40.38678 (25.3) | −40.40488 (25.3) | −40.42412 (33.6) | −40.44186 (34.4) |
| **8**, $C_s$ | −40.37319 (33.8) | −40.39031 (32.6) | −40.41605 (38.6) | −40.43485 (38.8) |
| **8a**, $C_{4v}$ | −40.38569 (26.0) | −40.40462 (25.4) | −40.42480 (33.1) | −40.44524 (32.3) |
| **8b**, $C_{4v}$ | −40.37371 (33.5) | −40.39036 (34.4) | −40.41236 (40.9) | −40.43010 (40.7) |
| **9**, $C_s$ | −40.32510 (64.0) | −40.34640 (61.9) | −40.37127 (66.7) | −40.39488 (63.9) |

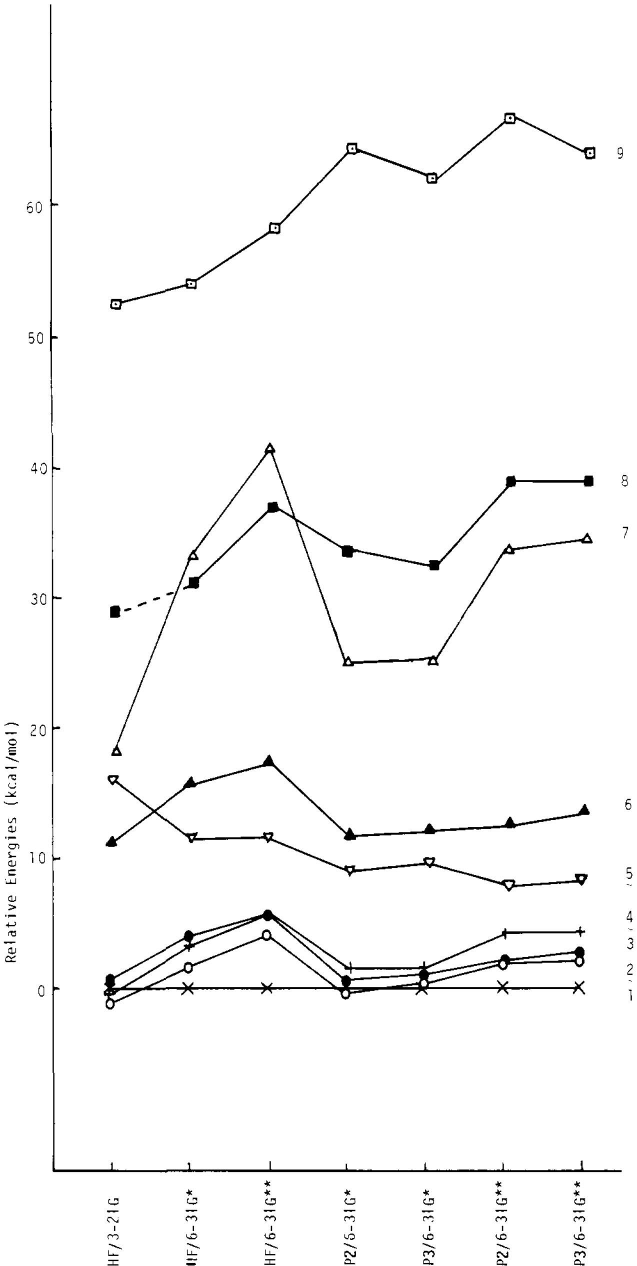

Figure 1. Plot of relative energies (in kcal/mol) vs. basis set. All the energies are relative to **1**.

kcal/mol, respectively. For the higher energy structures studied the largest stabilizing influence is observed for octahedral **7**. At the 6-31G** level the relative energy of **7** to **1** (41.5 kcal/mol) is reduced by 7.9 (MP2) and 7.1 (MP3) kcal/mol. The opposite effect is found for the "demethylation" structure **9**, for which the energy difference with **1** of 58.3 kcal/mol (6-31G**) is augmented by 8.4 (MP2) and 5.6 (MP3) kcal/mol. It has regularly been applied and recently[31] evaluated that changes in relative energies due to the addition of correlation corrections to the basis set are roughly additive. Our results on the 6-31G* and 6-31G** basis sets confirm this. We find the additivity of MP corrections accurate to about 1 kcal/mol. Although the energy differences between the studied structures might be somewhat affected by employing higher theoretical levels and optimizations including correlation, we anticipate this to be marginal and not to seriously affect the relative orderings (see, e.g., Figure 1), with the possible exception of **3** and **4**.

## Polytopal Rearrangements

Once the stationary points of a potential energy hypersurface are located and characterized as equilibrium and transition structures, mapping of the potential energy hypersurface by curves that connect two minima through a transition state provides a reasonable description of the reaction paths for the chemical processes that the investigated system may undergo.[23]

Usually a simple analysis of the normal coordinate corresponding to the imaginary frequency is sufficient to characterize a transition structure with respect to the associated minima. Such a type of analysis (at the HF/6-31G* level) indicates **2** as the transition for the cyclic transfer of the 3c-2e interactions and **4** as the transition for a 3c-2e rotation. The small energy barriers for these rotating processes demonstrate the ease of making and breaking the 3c-2e interactions in a dynamic way. Consequently hydrogen scrambling in $CH_6{}^{2+}$ will be a very facile process.

The structures **3**, **5**, **6**, and **7** are all hilltop structures for polytopal rearrangement; the normal mode of one of the degenerate reaction pathways is illustrated for each. Analysis of the normal mode of the triple-degenerate reaction-frequency coordinate of **7** is the least clear. Calculation at the 3-21G level of the reaction pathway from the stationary point confirms **7** to be a hilltop structure for internal rearrangement of the hydrogens in $CH_6{}^{2+}$.

## Stability

To assess the stability of **1** we have examined the heat of reaction (thermodynamic stability) and the associated energy barriers (kinetic stability) for four modes of dissociation: (1) loss of a proton to give $CH_5{}^+$, (2) loss of $H_2{}^{+\cdot}$ to give the methane radical cation, (3) loss of $H_3{}^+$ to give a methyl cation, and (4) loss of molecular hydrogen. The reaction energies for these processes, evaluated at the MP3/6-31G**//6-31G* level + scaled[32] ZPE, are given in Scheme I.[33]

### Scheme I

$$CH_6{}^{2+} \rightarrow CH_5{}^+ + H^+ \qquad \Delta E = -63.1\ \text{kcal/mol} \qquad (1)$$

$$CH_6{}^{2+} \rightarrow CH_4{}^{+\cdot} + H_2{}^{+\cdot} \qquad \Delta E = -18.6\ \text{kcal/mol} \qquad (2)$$

$$CH_6{}^{2+} \rightarrow CH_3{}^+ + H_3{}^+ \qquad \Delta E = -126.8\ \text{kcal/mol} \qquad (3)$$

$$CH_6{}^{2+} \rightarrow CH_4{}^{2+} + H_2 \qquad \Delta E = +79.4\ \text{kcal/mol} \qquad (4)$$

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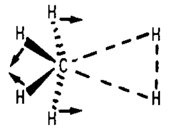
(31) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673.

Table IV. 6-31G* Harmonic Frequencies[a] ($cm^{-1}$) and Zero-Point Energies[b] (kcal/mol)

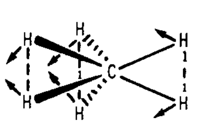
| geometry | frequency | ZPE |
|---|---|---|
| 1, $C_{2v}$ | 741 ($b_2$), 859 ($a_2$), 911 ($a_1$), 1208 ($b_1$), 1239 ($b_2$), 1388 ($a_2$), 1434 ($a_1$), 1445 ($b_1$), 1841 ($a_1$), 2145 ($a_2$), 2217 ($b_2$) 2611 ($a_1$), 2635 ($b_1$), 2910 ($b_2$), 2941 ($a_1$) | 37.9 (33.5) |
| 2, $C_{2v}$ | 555 ($a_2$), 892 ($b_1$), 1068 ($a_1$), 1165 ($a_2$), 1326 ($b_1$), 1375 ($a_1$), 1405 ($b_2$), 1851 ($a_1$), 2107 ($b_1$), 2478 ($a_2$), 2621 ($a_1$), 2701 ($b_1$), 2741 ($b_2$), 2763 ($a_1$), 364* ($b_2$) | 35.8 (31.7) |
| 3, $D_{3h}$ | 1022 ($a''$), 1048 ($a_1''$), 1162 ($a_2''$), 1369 ($e'$), 1607 ($a_1'$), 2416 ($e''$), 2563 ($a_1'$), 2646 ($a_2''$), 2695 ($e'$), 840* ($e'$) | 34.4 (30.4) |
| 4, $C_{2v}$ | 542 ($b_2$), 686 ($b_1$), 1179 ($a_1$), 1304 ($a_1$), 1339 ($b_1$), 1409 ($b_2$), 1487 ($a_2$), 1816 ($a_1$), 2019 ($b_1$), 2457 ($a_1$), 2667 ($b_1$), 2681 ($a_1$), 2776 ($b_2$), 2879 ($a_1$) | 36.1 (31.9) |
| 5, $C_{5v}$ | 1087 ($e_2$), 1180 ($e_1$), 1208 ($a_1$), 1526 ($e_1$), 2281 ($e_2$), 2444 ($a_1$), 2498 ($e_1$), 3203 ($a_1$), 875* ($e_2$) | 34.3 (30.4) |
| 6, $D_{2d}$ | 659 (e), 1248 ($a_2$), 1357 ($b_2$), 1421 (e), 1550 ($b_1$), 2146 ($b_2$), 2270 ($b_2$), 2617 ($a_1$), 2667 ($b_2$), 2729 (e), 1124* (e) | 33.6 (29.7) |
| 7, $O_h$ | 1210 ($t_{1u}$), 1612 ($t_{2g}$), 2256 ($e_g$), 2458 ($a_{1g}$), 2485 ($t_{1u}$), 1032* ($t_{2u}$) | 32.7 (28.9) |
| 8, $C_s$ | 406 ($a''$), 430 ($a'$), 592 ($a''$), 1092 ($a'$), 1240 ($a''$), 1410 ($a'$), 1457 ($a'$), 1472 ($a''$), 1685 ($a'$), 2234 ($a''$), 2540 ($a'$) 2853 ($a'$), 3163 ($a'$), 3215 ($a''$), 976* ($a'$) | 34.0 (30.1) |
| 8a, $C_{4v}$ | 458 (e), 1088 ($a_1$), 1160 ($b_2$), 1168 (e), 1397 ($a_1$), 1466 ($b_1$), 2517 ($b_2$), 2680 ($a_1$), 2784 (e), 3121 ($a_1$), 217* (e) | 31.8 (28.1) |
| 8b, $C_{4v}$ | 425 (e), 1110 ($b_2$), 1284 ($a_1$), 1351 (e), 1462 ($b_1$), 2578 ($a_1$), 2688 ($b_2$), 2847 ($a_1$), 2927 (e), 266* (e), 951* ($a_1$) | 30.6 (27.1) |
| 9, $C_s$ | 576 ($a''$), 586 ($a'$), 718 ($a''$), 946 ($a'$), 1261 ($a''$), 1308 ($a'$), 1369 ($a'$), 1400 ($a''$), 1531 ($a'$), 1606 ($a'$), 2436 ($a'$), 3071 ($a'$), 3149 ($a'$), 3318 ($a''$), 1407* ($a'$) | 33.3 (29.5) |

[a] The asterisk indicates the imaginary frequency. [b] The zero-point energies, scaled by 1/1.130 (see ref 32), are given in parentheses.

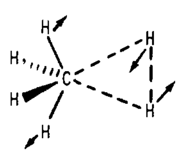
Chart II



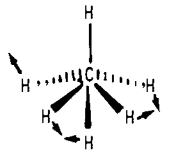
2 $C_{2v}$



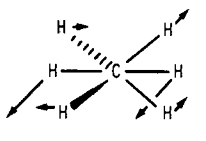
3 $D_{3h}$



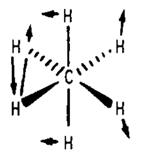
4 $C_{2v}$



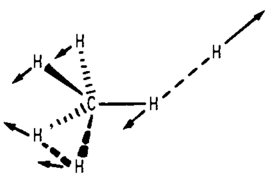
5 $C_{5v}$



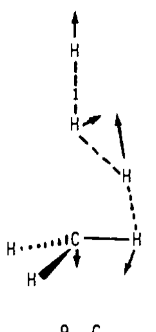
6 $D_{2d}$



7 $O_h$



8 $C_s$



9 $C_s$

**Heat of Formation of $CH_6^{2+}$.** The calculated energies of reactions 1–3 combined with the experimental heats of formation at 0 K (in kcal/mol) of $CH_5^+$ (218.2),[14] $CH_4^{+\cdot}$ (275),[34] $CH_3$ (262.7),[35] $H_3^+$ (264.2),[14] $H_2^{+\cdot}$ (355.7),[34] and $H^+$ (365.2)[34] can be used to estimate $\Delta H_f{}^\circ{}_0(CH_6^{2+})$ = 647.1, 649.3, and 653.2 kcal/mol, respectively. Equation 4, evaluated by using the theoretically estimated $\Delta H_f{}^\circ{}_0(CH_4^{2+})$ = 733 kcal/mol,[9] gives $\Delta H_f{}^\circ{}_0(CH_6^{2+})$ = 653.6 kcal/mol. Averaging these values, we obtain $\Delta H_f{}^\circ{}_0(CH_6^{2+}) = 651 \pm 3$ as our best estimate. This is the lowest heat of formation of any of the $CH_n^{2+}$ dications.[9]

**Deprotonation.** The deprotonation energy, reaction 1, being the proton affinity (PA) of $CH_5^+$ with a negative sign, amounts to −63.1 kcal/mol. This expected strong exothermicity of $CH_6^{2+}$ is comparable in magnitude to the deprotonation energy of −71.4 kcal/mol for $CH_2^{2+}$ (−PA of $CH^+$), but smaller than the −105.7 kcal/mol calculated for $CH_4^{2+}$ (−PA of $CH_3^+$) obtained at the MP4/6-31G**//6-31G* level of theory.[9] Despite the substantial driving force, sizable barriers for proton loss from $CH_2^{2+}$ and $CH_4^{2+}$ were calculated, 35.6 and 16.8 kcal/mol, respectively (same level + ZPE). The mass spectroscopic detection of these $CH_n^{2+}$ ($n$ = 1–5) dications demonstrates experimentally the kinetic stability of these metastable species.[36]

What is the barrier for proton loss from $CH_6^{2+}$? Since many geometries for the transition may exist and the lowest possible barrier is to be located, this is not a simple problem.

We first evaluated the deprotonation at the 3-21G level, where the $C_{4v}$ geometry **8b** is a transition structure (one imaginary frequency). Following the intrinsic reaction coordinate in both directions from this saddle point resulted in a local minimum (structure **8a**, also $C_{4v}$)[30] and deprotonation. The 3-21G deprotonation barriers **5** → **8** and **2** → **8** are 11.5 and 30.5 kcal/mol, respectively. Optimization at 6-31G* however negated this picture, since for both **8a** and **8b** a small additional degenerate imaginary frequency was obtained.

A transition structure for deprotonation could be located at the HF/6-31G* level within $C_s$ symmetry. The geometrical relationship between **8** and the product, $CH_5^+$ ($C_s$) is apparent. Single-point calculations at higher levels indicate the deprotonation barrier from **1** to be 35.4 kcal/mol (MP3/6-31G**//6-31G* + scaled ZPE). We cannot rigorously exclude the possibility that some lower barrier may exist, but believe this to be unlikely.

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(32) (a) A scaling factor of 1/1.130 is used: Pople, J. A.; Schlegel, H. B.; Krishnan, R.; De Frees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem., Symp.* **1982**, *15*, 269. (b) Hout, R. F.; Levi, B. A.; Hehre, W. J. *J. Comp. Chem.* **1982**, *3*, 234.

(33) The MP3/6-31G** energies (au) and 6-31G* zero-point vibrational energies (kcal/mol, in parentheses) of the fragments are as follows: $H_2^{+\cdot}$, $E$ = −0.59426 (3.3 exptl); $H_2$, $E$ = −1.16314 (6.6); $H_3^+$, $E$ = −1.33013 (13.9); $CH_3^+$, −39.36450 (21.1); $CH_4^{2+}$, $E$ = −39.19283 (21.4); $CH_4^{+\cdot}$ ($C_{2v}$), $E$ = −39.92087 (23.1 estimated); $CH_5^+$, $E$ = −40.59267 (34.7). The data of $H_2$ come from the following: Harding, L. B.; Schlegel, H. B.; Krishnan, R.; Pople, J. A. *J. Phys. Chem.* **1980**, *84*, 3394. Those of $CH_3^+$ and $CH_5^+$ result from ref 15. The ZPE of $H_3^+$ is reported in ref 9.

(34) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *1*, 6.

(35) McCulloh, K. E.; Dibeler, V. H. *J. Chem. Phys.* **1976**, *64*, 4445. See: Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647.

(36) The 3-21G barrier for proton loss from $CH_5^{2+}$ is 22.3 kcal/mol (G. W. Spitznagel, Erlangen, unpublished calculations).

**Demethylation.** A more favorable dissociation energy of −126.8 kcal/mol, reaction 2, is obtained by fragmenting $CH_6^{2+}$ into $H_3^+$ and $CH_3^+$. For this process, however, three "C–H bonds" have to be broken. Intuitively this suggests that an even higher barrier might be involved despite the larger exothermicity. After extensively searching at the 3-21G level we were able to locate this transition structure with $C_s$ symmetry.[37] Our final estimate of the dissociation barrier is 59.9 kcal/mol (MP3/6-31G**//6-31G* + scaled ZPE).

Similarly we assume a significant barrier for the fragmentation of $CH_6^{2+}$ into $H_2^{+\cdot}$ and $CH_4^{+\cdot}$ since two C–H bonds have to be cleaved in this near isothermic reaction 2. However, we did not investigate this process in detail.

**Prospects for the Experimental Realization of $CH_6^{2+}$.** Our work indicates that $CH_6^{2+}$ should be a metastable dication with quite high dissociation barriers. How can $CH_6^{2+}$ be generated? The reverse of reaction 4, the hydrogenation of $CH_4^{2+}$, may, because of the favorable thermodynamics ($\Delta E = 79.4$ kcal/mol), be viewed as a possible mode for formation of $CH_6^{2+}$. Since $CH_4^{2+}$ is reported to have a lifetime greater than 3 μs, and is generated by the mass-spectroscopic charge-transfer stripping technique from methane by a neutral collision gas ($N_2$),[8] mixing in of hydrogen might provide the conditions for the formation of $CH_6^{2+}$. Although electron transfer from $H_2$ to $CH_4^{2+}$ (eq 5) and proton transfer from $CH_4^{2+}$ to $H_2$ (eq 6) are even more favorable, they are likely to have $CH_6^{2+}$ as the intermediate species. We encourage mass spectrometrists to seek this dication.

$$CH_4^{2+} + H_2 \rightarrow CH_4^{+\cdot} + H_2^{+\cdot} \qquad \Delta E = -102 \text{ kcal/mol} \quad (5)$$

$$CH_4^{2+} + H_2 \rightarrow CH_3^{+} + H_3^{+} \qquad \Delta E = -206 \text{ kcal/mol} \quad (6)$$

## Conclusions

The prototype of hexacoordinate carbon, $CH_6^{2+}$, is a minimum on the potential energy surface. Its $C_{2v}$ geometry (**1**) has two stabilizing 3c-2e interactions. Despite the favorable thermodynamics for dissociation $CH_6^{2+}$ appears to have sizable barriers for deprotonation and for loss of $H_3^+$. Within these barriers two polytopal rearrangements were established, rendering $CH_6^{2+}$ subject to very fast H scrambling. Hydrogenation of $CH_4^{2+}$, by means of mass-spectroscopic charge stripping of $CH_4$ with inert gas and hydrogen, is suggested as a possible experimental approach to $CH_6^{2+}$.

**Acknowledgment.** The cooperation of the USC computer center greatly facilitated the present investigation. M.B. thanks the Consiglio Nazionale delle Ricerche (CNR) for the award of a National Scholarship for research abroad. The project benefited from senior scientist awards of the von Humboldt Foundation (to G.A.O. and J.A.P.) and support from the Fonds der Chemischen Industrie. We thank W. J. Hehre and G. A. Segal for constructive discussions and T. Clark, A. Sawaryn, and G. W. Spitznagel for some computations.

**Registry No.** $CH_6^{2+}$, 83561-00-6.

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[37] The following procedure proved successful: in a first approach at the 3-21G level $H_3^+$ was separated from $CH_3^+$ by imposing $C_{3v}$ symmetry. The resulting geometry had an $a_1$ vibration corresponding to the dissociation, but also an imaginary degenerate (e) vibration for rotation of the $H_3$ planes. Adjusting the geometry according to the normal mode of this e vibration led via a stepwise procedure to the desired transition structure.

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# CASSCF Study of Reaction of Singlet Molecular Oxygen with Ethylene. Reaction Paths with $C_{2v}$ and $C_s$ Symmetries

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**Abstract:** The reaction of singlet molecular oxygen, $O_2(^1\Delta_g)$, with ethylene along four reaction paths of $C_{2v}$ and $C_s$ symmetries has been studied. The present calculations show that formation of the peroxirane intermediate, the first step on the peroxirane pathway to dioxetane, has lower activation energy than that of the biradical pathway. The multiconfiguration CASSCF (complete active space SCF) method and a double-ζ basis (in the final calculations augmented with a single d function on carbon and oxygen) were used. Contracted CI calculations were performed at the key points of the $C_s$ surfaces. Neither of the reaction paths of $C_{2v}$ symmetry were found feasible. In $C_s$ symmetry, the barrier for formation of the peroxirane intermediate is calculated to be 149 kJ/mol. The transition state of $C_s$ symmetry leading to dioxetane via a biradical species is analogous to the $C_{2v}$ one, showing formation of even the second C–O bond at a rather early stage, and has a barrier of 169 kJ/mol. No other low-energy transition states leading to dioxetane via a biradical species have been found in the present CASSCF-CCI calculations.

Since the "rediscovery" of singlet molecular oxygen by Foote and Wexler[1] and Corey and Taylor,[2] the reactions of $O_2(^1\Delta_g)$ with olefins have covered a wide spectrum of practical applications, ranging from polymer chemistry and paper industry to pharmacology.[3-19] The mechanisms of these reactions have been extensively studied, both experimentally and theoretically. However, for an attachment to a double bond, the results seem to be conflicting.[20-38]

The reactions of singlet oxygen with olefins can be classified into three groups: (A) 1,4 addition (endoperoxide formation); (B) 1,3 addition (ene reaction); and (C) 1,2 addition (dioxetane formation). The first one is generally believed to be a concerted [2 + 4] addition which proceeds through a six-membered-ring

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(1) Foote, C. S.; Wexler, S. *J. Am. Chem. Soc.* **1964**, *86*, 3879.

(2) Corey, E. J.; Taylor, W. C. *J. Am. Chem. Soc.* **1964**, *86*, 3881.

(3) Singlet molecular oxygen: Schaap, A. P., Ed. "Benchmark Papers in Organic Chemistry", Dowden, Hutchinson and Ross, Inc.: Stroudsburg, PA, 1976; Vol. 5.

(4) Singlet oxygen: "Reactions with Organic Compounds and Polymers"; Rånby, B., Rabek, J. F. Eds.; Wiley: New York, 1978.

(5) Singlet oxygen: *Photochem. Photobiol.* **1978**, *28*, No. 4–5.

(6) Singlet oxygen: Wasserman, H. H., Murray, R. W., Eds. "Organic Chemistry"; Academic Press: New York, 1979; Vol. 40.

(7) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395.

(8) Harrison, J. E.; Watson, B. D.; Schultz, J. *FEBS Lett.* **1978**, *92*, 327.

(9) Keevi, T.; Mason, H. S. *Methods Enzymol.* **1978**, *52*, 3.

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