Remarkably Stable Trications and Tetracations: The Triheliomethyl Trication ($CHe_3{}^{\cdot 3+}$) and Tetraheliomethane Tetracation ($CHe_4{}^{4+}$)

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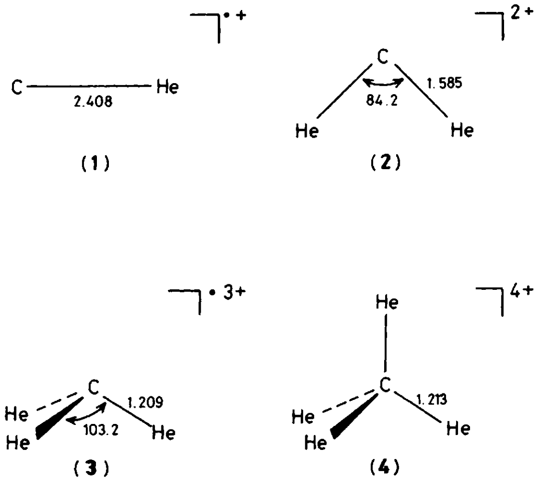
High-level *ab initio* calculations predict that the triheliomethyl trication ($CHe_3{}^{\cdot 3+}$) and tetraheliomethane tetracation ($CHe_4{}^{4+}$) should be experimentally observable, despite the availability of extremely exothermic fragmentation processes.

There has been intense recent interest in the chemistry of multiply-charged polyatomic ions as a result of the development of sophisticated experimental procedures and the application of high-quality theoretical calculations.[1] Most of the studies to date have been concerned with doubly-charged ions. For the dications, fragmentation is generally highly exothermic but is often inhibited by a barrier sufficiently large to permit their experimental observation. More highly charged ions, on the other hand, are expected to be less stable and have consequently attracted less attention.[2] In this



Optimized structures (MP4/6-311G**) for CHe_n^{n+} cations. Bond lengths in Å, bond angles in degrees.

communication theoretical evidence for the remarkable stability of two such highly charged ions, the triply-charged triheliomethyl trication and the quadruply-charged tetraheliomethane tetracation is presented.

The stability of helium-containing polyatomic ions was first noted by Wilson *et al.*[3] and more recently by Koch and Frenking.[4] Other than for the diatomic CHe, however, attention in these previous studies was restricted to singly- or doubly-charged ions. We have been particularly interested recently in more highly charged ions. Our examination of the tetraheliomethane tetracation, reported here, represents part of a wider study of multiply-charged analogues of methane.[5]

Optimized geometries were obtained for the $CHe^{\cdot+}$ (**1**), CHe_2^{2+} ($^1A_1$) (**2**), $CHe_3^{\cdot 3+}$ (**3**), and CHe_4^{4+} (**4**) ions and for appropriate transition structures for dissociation of (**3**) and (**4**) at moderately high levels of theory: fourth-order Møller–Plesset theory[6] with the 6-311G** basis set[7] (MP4/6-311G**) and full-valence CASSCF[8] with the 6-31G* basis set[9] (CAS/6-31G*). The latter procedure is necessary to give a satisfactory description of the dissociation of these species. The Gaussian 82[10] and GAMESS[11,12] programs were used. Unless otherwise noted, structural comparisons refer to MP4/6-311G** values and relative energies to MP4/6-311G** values corrected by MP2/6-31G* estimates (scaled by 0.93[13]) of zero-point vibrational energies. The barriers for dissociation were calculated at the CAS/6-311G** level using CAS/6-31G* structures, again with a correction for zero-point vibrational energy.

The results are consistent with previous studies,[3,4,14] in that the $CHe^{\cdot+}$ monocation (**1**) and CHe_2^{2+} dication (**2**) are characterized by long C–He bonds: 2.408 and 1.585 Å, respectively. Our striking new result is that the more highly charged $CHe_3^{\cdot 3+}$ trication (**3**) and CHe_4^{4+} tetracation (**4**) have very short C–He bonds of 1.209 and 1.213Å, respectively.

How stable are $CHe_3^{\cdot 3+}$ (**3**) and CHe_4^{4+} (**4**)? The exothermicities of the fragmentations to CHe_2^{2+} + $He^{\cdot+}$ and to $CHe_3^{\cdot 3+}$ + $He^{\cdot+}$ are enormous: 1030 and 1605 kJ mol^{-1}, respectively. However, the barriers for such processes, 152 and 72 kJ mol^{-1} (CAS/6-311G**), are sufficiently large that we believe experimental observation will be feasible.

Finally, we ask: how might the tetraheliomethane tetracation be prepared? One seemingly attractive possibility is through radioactive decay from tetratritiomethane, equation (1).

$$CT_4 \xrightarrow{\beta\text{-decay}} C^3He_4^{4+} + 4e^- \qquad (1)$$

Unfortunately, the (tritiated) monoheliomethane monocation which would be formed in the first step of reaction (1) is not very stable.[5] The C · · · He bond in $CH_3He^{\cdot+}$ is very long (2.053 Å) and the barrier for expulsion of He is less than 1 kJ mol^{-1}. Indeed, it is found experimentally[15] that less than 0.1% of $CH_3He^{\cdot+}$ is observed in the β-decay of CH_3T, the major product (82% yield) being the methyl cation, equation (2).

$$CH_3T \rightarrow [CH_3He]^{\cdot+} \rightarrow CH_3^+ + {}^3He + e^- \qquad (2)$$

It is rather ironic that it is the instability of the monocation which inhibits the preparation of the tetracation in this manner.

Our conclusion, that it is the more highly charged trication and tetracation in the series CHe_n^{n+} which have the shorter C–He bonds and greater kinetic stability, is consistent with a previous observation[3] for the diatomic CHe^{n+} ions.†

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† *Note added in proof:* Since submission of this manuscript, we have become aware of related calculations on helium-containing ions carried out by Professor P. v. R. Schleyer: P. v. R. Schleyer, *Adv. Mass Spectrom.*, 1985, 287. We thank Professor Schleyer for bringing this matter to our attention.