Gas-phase synthesis of the rare-gas carbene cation $ArCH_2^+$ using doubly ionised bromomethane as a superelectrophilic reagent

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The bimolecular reaction of mass-selected CH_3Br^{2+}/CH_2BrH^{2+} dications with argon leads to the rare-gas carbene cation $ArCH_2^+$, which represents an example of a new kind of organo rare-gas compound.

Ever since their discovery in 1962,[1] rare-gas compounds have constituted a challenging area of research. From only a few examples in the beginning, now hundreds of rare-gas compounds have been synthesized.[2] The key to promoting the formation of (covalent) chemical bonds by rare gases lies in the use of strong oxidation agents (*e.g.* F_2). Most rare-gas compounds known so far therefore have bonds to the most electronegative elements (F, O, and derivatives thereof). For xenon, however, compounds with a variety of other elements are also known, including those with Xe–C bonds, *e.g.* $C_6F_5Xe^+$ salts.[3,4] The Kr–C compounds $KrCH_3^+$ and HKrCN have been observed in mass-spectrometric experiments[5] and low-temperature matrices,[6] respectively. Except for an early report on $ArCH_n^+$ cations formed in plasma,[7] the formation of $ArCH_3^+$ by endothermic methyl-cation transfer from protonated fluoromethane to argon,[8] and the diatomic dication ArC^{2+} formed in the endothermic reactions of argon with CO^{2+} dications[9] and of CO with Ar^{2+},[10] no compounds with covalent Ar–C bonds have so far been observed.

Obviously, the formation of rare-gas compounds requires the use of very electrophilic reagents which are capable of attacking the closed-shell configuration of the rare-gas atoms. A particularly strong class of oxidizing agents are small multiply charged ions,[11–15] which may also be classified as superelectrophiles.[16] Previous studies of CH_nX^{2+} dications ($X =$ F–I, $n = 1$–3)[17–22] suggested that some of these species may also strongly interact with rare gases.[22] Here, we report the generation of the argon–carbene cation $ArCH_2^+$ in collisions of argon with mass-selected $[C,H_3,Br]^{2+}$ dications formed upon double ionization of neutral bromomethane.

Before addressing the reactions leading to $ArCH_2^+$, the nature of the superelectrophilic reagent $[C,H_3,Br]^{2+}$ is summarized briefly.[22] Experimental and theoretical studies have established that ionization of neutral bromomethane to the molecular dication CH_3Br^{2+} is easily followed by a rearrangement to the tautomer CH_2BrH^{2+} which is considerably more stable than CH_3Br^{2+} (*i.e.* $\Delta E \approx 1.7$ eV for the dications in the singlet states). Although the isomerisation of CH_3Br^{2+} into CH_2BrH^{2+} is associated with an energy barrier of 0.35 eV, this is likely to be surmounted if the dication is formed by electron ionization, given the characteristics of double ionization in which a deposition of such a small amount of excess energy is likely to occur.[23] In the following, we hence assume that the $[C,H_3,Br]^{2+}$ dications formed upon double ionization of neutral bromomethane correspond to a mixture of the tautomeric ions CH_2BrH^{2+} and CH_3Br^{2+}.

In order to probe the potential of $[C,H_3,Br]^{2+}$ as a superelectrophile, it was reacted with rare gases.† With helium and neon, only electron- and proton-transfer reactions[21] as well as collision-induced dissociation of the dication[22] were observed, which are not pursued any further here. The reaction of mass-selected $[C,H_3,Br]^{2+}$ with argon is shown in Fig. 1. The major reactions observed are associated with (i) proton transfer from

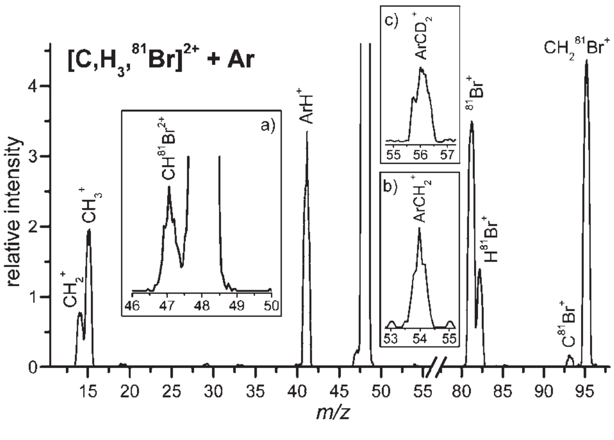

Fig. 1 Reaction of mass-selected $[C,H_3,^{81}Br]^{2+}$ dications with argon recorded at a collision energy of 0.95 eV in the centre-of-mass frame and $p(Ar) = 8 \times 10^{-4}$ mbar; the ^{81}Br isotope is chosen because $[C,H_3,^{79}Br]^{2+}$ has a mass overlap with $CH^{81}Br^{2+}$. The vertical scale refers to the precursor dication with an intensity of 100 (off-scale). Inset (a) shows an expanded view of the region *m*/*z* 46–50 recorded with an increased resolution on Q2 to resolve product ions at *m*/*z* 47 from the parent ion at *m*/*z* 48. Inset (b) shows the mass region of the bond-forming product $ArCH_2^+$ (*m*/*z* 52.8–55.2) amplified by a factor of 50. Inset (c) shows an expanded view of the region *m*/*z* 54.7–57.3 for the reaction of $[C,D_3,^{81}Br]^{2+}$ with argon.

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the dication to the rare gas to afford the product pair ArH^+ + CH_2Br^+, (ii) collision-induced dehydrogenation of the dication to yield the $CHBr^{2+}$ dication concomitant with neutral dihydrogen, and (iii) dissociation of $[C,H_3,Br]^{2+}$ to the product pairs $CH_3^+ + Br^+$ and $CH_2^+ + HBr^+$, of which the former pair is indicative of the molecular dication CH_3Br^{2+} and the latter can be assigned to the tautomer CH_2BrH^{2+}. Typical of all channels associated with charge separation is a mass discrimination of the lighter fragment ions, *i.e.* less ArH^+ than CH_2Br^+, less CH_3^+ than Br^+, and less CH_2^+ than HBr^+.[24,25]

$$CH_2BrH^{2+} + Ar \rightarrow ArCH_2^{+} + HBr^{+} \qquad (1)$$

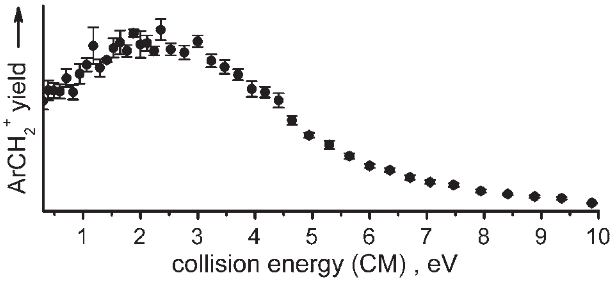

Fig. 2 Relative yield of $ArCH_2^+$ in the reaction of mass-selected $[C,H_3,Br]^{2+}$ dications with argon as a function of the collision energy (centre-of-mass frame) of the incident dications.

Of particular interest is the weak signal at *m*/*z* 54, which indicates the occurrence of reaction (1). The observation of the peak at *m*/*z* 54, which is shifted to *m*/*z* 56 when using $[C,D_3,Br]^{2+}$ (see inset (c) in Fig. 1),‡ demonstrates the formation of the rare-gas carbene $ArCH_2^+$ in the monocationic form and thus the occurrence of Ar–C bond formation. The collision-energy dependent yield of $ArCH_2^+$ has a non-zero cross section already at thermal energies, passes a maximum at about 2 eV, and then the yield drops at higher energies (Fig. 2).

Calculations employing density functional theory provide deeper insight into the mechanism of the Ar–C bond formation and also account for the various competing reactions (Fig. 3).§ The most stable isomer of $[C,H_3,Br]^{2+}$, the ylide CH_2BrH^{2+} in the singlet ground state, forms a reasonably stable encounter complex with argon coordinated to carbon, species $^1\mathbf{1}^{2+}$, from which the loss of HBr^+ concomitant with charge separation leads to $ArCH_2^+$ with an overall exothermicity of 2.18 eV. The energy released is significantly larger than the energy of the Ar–C bond in the product, $D(Ar\text{–}CH_2^+) = 0.84$ eV. Accordingly, the consecutive fragmentation into Ar + CH_2^+ is energetically feasible, and it is most probably responsible for the low yield of the bond-forming product $ArCH_2^+$. In contrast, direct electron transfer of the reactants to afford $CH_2BrH^+ + Ar^+$ is almost thermoneutral (−0.2 eV) and moreover hindered by a Coulomb barrier.[11–15,21,26] Proton transfer to yield CH_2Br^+ + ArH^+ is the most exothermic pathway which coincides with the large yield of this channel in the experiment. In addition to CH_2Br^+, the isomer $CHBrH^+$ can also be formed, which lies more than 3 eV higher in energy than CH_2Br^+, however.[22]

Both electronic states of the tautomeric dication CH_3Br^{2+} form encounter complexes of similar stabilities in which argon is coordinated to bromine, $^1\mathbf{2}^{2+}$ and $^3\mathbf{2}^{2+}$, respectively. Charge separation of both electromers can lead to $CH_3^+ + ArBr^+$, but the latter species is only very slightly bound in its electronic ground state and subsequent dissociation into Ar + Br^+ is thus likely to occur. Proton transfer to afford $CH_2Br^+ + ArH^+$ is again the most exothermic channel for $^1\mathbf{2}^{2+}$ and $^3\mathbf{2}^{2+}$. These energetics can account for the central experimental findings: (i) the major products in the experiment, *i.e.* $CH_2Br^+ + ArH^+$, are those predicted to be most exothermic by theory, (ii) the complementary product pairs $CH_3^+ + Br^+$ and CH_2^+ + HBr^+ can be ascribed to an argon-triggered charge separation of the isomers CH_3Br^{2+} and CH_2BrH^{2+}, respectively,[27,28] (iii)

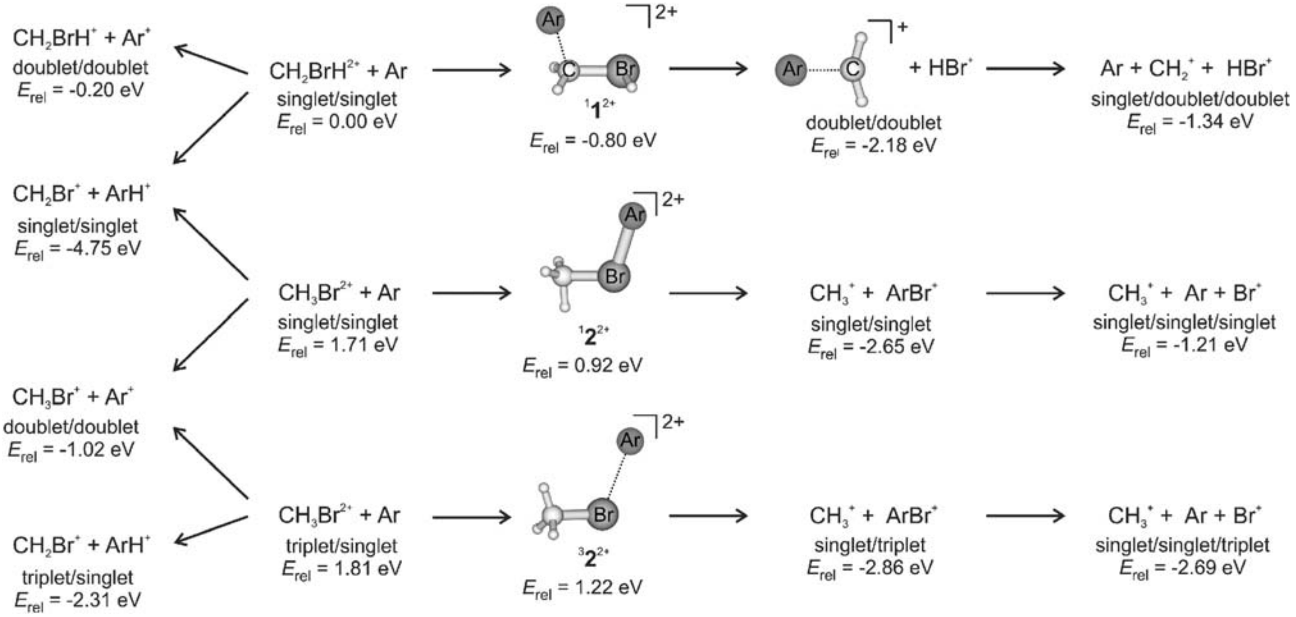

Fig. 3 Computed CCSD(T)/cc-pVTZ//B3LYP/6-311+G(2d,p) energetics of the CH_3Br^{2+}–Ar system given in eV relative to the lowest-lying entrance channel CH_2BrH^{2+} + Ar. The corresponding electronic states of reactants and products are indicated below the molecular formulae.

$ArCH_2^+$ arises from intermediate $^1\mathbf{1}^{2+}$ in an overall exothermic reaction, and (iv) electron transfer to yield $CH_3Br^+ + Ar^+$, though thermochemically allowed, cannot compete kinetically with the more exothermic channels and is thus suppressed in the experiment. With respect to the energy-dependent cross section of $ArCH_2^+$ (Fig. 2), the theoretical data suggest that isomer $^1CH_2BrH^{2+}$ can undergo reaction (1) already at thermal energies, while the tautomeric CH_3Br^{2+} dications first need to isomerise. This scenario may account for the initial rise of the $ArCH_2^+$ yield, which may alternatively be explained by the more effective competition of the bond-forming pathway to yield $ArCH_2^+$ with proton transfer. In both cases, the decrease of the cross section of $ArCH_2^+$ above 2 eV can be ascribed to consecutive dissociation into $Ar + CH_2^+$.

We note that similarly to argon, krypton and xenon also afford the corresponding carbene cations $KrCH_2^+$ and $XeCH_2^+$, respectively, when reacted with mass-selected $[C,H_3,Br]^{2+}$. Hence, doubly ionized methyl bromide can act as a superelectrophilic reagent for the activation of the rare gases Ar–Xe and provides access to the rare-gas carbenes in the gas phase. In future work we will try to increase yields in order to address the bimolecular reactivity of the $RgCH_2^+$ cations.

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Notes and references

† Most reactions have been studied by using a laboratory-built tandem mass spectrometer at the University of Trento having a OQOQ configuration (where O stands for octopole and Q stands for quadrupole).[29] Ions are generated by electron ionization of methyl bromide at an electron energy of 100 eV. In the present experiments, the first octopole O1 is used only as an ion guide. Parent ions are injected into O2 filled with a known pressure of rare gas. The ion beam kinetic energy, which determines the collision energy between parent ions and rare gas molecules in the laboratory frame, can be varied from about 0 to 100 eV by changing the octopole voltage. Product ions are mass analyzed by Q2 and detected by an electron multiplier.

‡ Additional experiments in Prague used a TSQ mass spectrometer which has an exchangeable ion source and a QOQ configuration.[30,31] Here, Q1 is used for selection of CH_3Br^{2+} (or CD_3Br^{2+}) generated by EI, the octopole serves as a collision cell to which the rare gases are admitted, and Q2 is scanned for product-ion analysis. Compared to the Trento apparatus, the TSQ has a higher mass resolution,[25] thereby enabling a better selection of the dicationic precursors and of the mono- and dicationic products.

§ The theoretical calculations were performed using the B3LYP[32–35] method with 6-311+G(2d,p) basis sets as implemented in Gaussian03.[36] All minima and transition structures were characterized by frequency analysis and energies were further refined by single-point calculations at the CCSD(T)/cc-pVTZ level of theory.[37–40] The energies reported below refer to 0 K, including corrections for zero-point vibrational energy (ZPVE) calculated at the B3LYP level of theory, and are given relative to $E_{0\ \mathrm{K}}(CH_2BrH^{2+} + Ar) = -3138.551572$ Hartree.

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