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Reactivity of the $CHBr^{2+}$ Dication toward Molecular Hydrogen

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Structural aspects as well as the stability and reactivity of the $CHBr^{2+}$ dication are studied both experimentally and theoretically. Translational energy distributions of the $CHBr^{+}$ products from charge transfer between $CHBr^{2+}$ and Kr indicate that the dication exists in two isomeric forms, $H{-}C{-}Br^{2+}$ and $C{-}Br{-}H^{2+}$. In the reaction of $CHBr^{2+}$ with H_2, the dominant channel corresponds to proton transfer leading to $CBr^{+} + H_3^{+}$. Other reaction channels involve the formation of the intermediates CH_3Br^{2+} and CH_2BrH^{2+}, respectively. Both of the latter dications can either lose a proton to form CH_2Br^{+} or undergo a spin-isomerization followed by cleavage of the C−Br bond. The proposed mechanisms are supported by DFT calculations and deuterium labeling experiments.

Introduction

Small molecular dications often represent models for reactive intermediates under extreme conditions. The research concerning dications addresses chemical processes relevant to interstellar space,[1] planetary atmospheres,[2] etching technology,[3] or reactions in superacidic media,[4] just to mention a few examples. The accumulation of charge very often leads to thermodynamic instabilities of the molecular dications; i.e., there exists at least one exothermic fragmentation pathway, which yields two singly charged products.[5,6] Nevertheless, over the past decade an increasing number of small, thermodynamically stable dications has been reported.[6−8]

A fundamental process occurring upon the encounter of a dication and a neutral reaction partner corresponds to electron transfer (reaction 1). This process leads to a pair of singly charged ions and is associated with a considerable translational energy release, often referred to as Coulomb explosion.[6] Electron transfer proceeds effectively at internuclear distances larger than those typically required for chemical reactions and therefore is kinetically favored.[9] The simplest chemical reaction corresponds to proton transfer from a hydrogen-containing dication to a neutral reaction partner (reaction 2, B = H). Proton transfer, in comparison with electron transfer, often leads to thermochemically more favored products. Nevertheless, proton transfer can only compete with the kinetically preferred electron transfer, if the exothermicity of electron transfer is lower than 2 eV[9−11] or if the neutral partner has a significantly large permanent dipole moment.[12]

$$AB^{2+} + C \rightarrow [ABC]^{2+} \rightarrow AB^{+} + C^{+} \tag{1}$$

$$AB^{2+} + C \rightarrow [ABC]^{2+} \rightarrow A^{+} + BC^{+} \tag{2}$$

Here, we report an investigation of the reaction of $CHBr^{2+}$ with molecular hydrogen. For the closely related $CHCl^{2+}$ dication, a series of studies[12−16] has demonstrated that the $CHCl^{2+}$ dication is formed as two isomers, $HCCl^{2+}$ and $CClH^{2+}$, upon electron ionization of methyl chloride. The reaction of $CHCl^{2+}$ with H_2 is dominated by proton transfer to form CCl^{+} and H_3^{+} with a minor channel leading to the products CH_2Cl^{+} and H^{+}. In addition to these, a novel process is presented here for $CHBr^{2+}/H_2$ which does not occur in the related system $CHCl^{2+}/H_2$. Another difference between the dications involved here evolves from the fact that both isomers of the $CHCl^{2+}$ dication are metastable, whereas the $HCBr^{2+}$ dication belongs to a family of thermodynamically stable dications.[12] On the other hand, the role of excited states of $CHBr^{2+}$ might be enhanced due to a larger spin−orbit interaction associated with bromine compared to the lighter congener chlorine. The comparison of both systems thus affords new insights into the relationship between the stability and the reactivity of dicationic species.

Experimental Section

The electron-transfer experiments were performed using the crossed beam apparatus EVA II.[9] The $CHBr^{2+}$ dications were formed by dissociative electron ionization (130 eV) of methyl bromide.[17] Ions were extracted, mass-selected, and decelerated to a specific laboratory energy. The $CHBr^{2+}$ beam was then crossed at 90° with a beam of Kr emerging from a multichannel jet. The angular and energy spread of the $CHBr^{2+}$ beam was 1° and 0.5 eV (full width at half-maximum, fwhm), respectively. The angular spread of the neutral beam was about 6° (fwhm), and the energy distribution corresponded to the thermal distribution at 300 K. Reactant and product ions were further analyzed behind a detection slit (2.5 cm from the scattering center). First,

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the translational energy distribution was determined in a stopping potential analyzer, next, the ions were accelerated, mass-analyzed, and detected by a channeltron-type electron multiplier. The neutral beam was modulated by a chopper and phase-sensitive detection was used to diminish background effects. The energy profiles of the $CHBr^+$ product were measured at the laboratory scattering angle of −1.5° relative to the primary beam. Only the forward scattering of the product ions was measured. Energy profiles are plotted in dependence on the reaction exoergicity $\Delta E = T' - T$ (T' and T are center-of-mass translational energies of the products and reactants, respectively).

Another series of experiments was carried out on the Berlin tandem SIFT-GIB apparatus,[18] which consists of a multifunctional ion source, a selected-ion flow tube (SIFT), and a quadrupole−octopole−quadrupole (QOQ) unit. In the present study, only the QOQ part was used as a regular guided-ion beam mass spectrometer. For ionization, an additional electron−ionization source situated directly in front of the QOQ unit was used. The $CHBr^{2+}$ dications were formed by dissociative electron ionization (100 eV) of CH_3Br and mass-selected by means of the first quadrupole. The background spectrum contained a small monocation signal at m/z 46 (less than 1% of $CHBr^{2+}$). The reactions were conducted in the octopole-reaction cell at variable kinetic energies of $CHBr^{2+}$ defined by the voltage applied to the octopole (U_{oct}). The kinetic energy spread of the ion beam was about 12 eV (fwhm). The pressure of the collision gas was 3×10^{-4} mbar; the same product branching was recorded when the pressure was 0.8×10^{-4}, except that the signal-to-noise ratio was lower. Products of the reactions were mass-analyzed by means of the second quadrupole and detected. Throughout these studies, Q1 and Q2 were both kept at mass resolutions of $m/\Delta m \geq 200$, ensuring proper mass-selection and permitting the analysis of ions with a different number of hydrogen atoms, i.e., CH_xBr^{2+} ($x = 0, 1, 2$). The collision energy-dependent measurements were conducted at lower resolution of Q2 in order to avoid mass discrimination effects. Data acquisitions were done with the Merlin Automation Software (ABB Extrel).

All calculations were performed with the Gaussian 98 suite[19] using the hybrid density functional method B3LYP[20] in conjunction with 6-311+G(3df,3pd) triple-ζ basis set. For all optimized structures, frequency analysis at the same level of theory allowed to assign them as genuine minima or transition structures as well as to calculate the zero-point vibrational energies (ZPVEs). All transition structures were further characterized by intrinsic reaction coordinate (IRC) calculations[21] performed at this level of theory. Relative energies (E_{rel}) are given for 0 K and thus include corrections for ZPVEs.

Results and Discussion

Electron Transfer with Krypton. In mass-spectrometric studies of mechanisms of ion−molecule reactions, the correct interpretation of experimental results depends heavily upon the knowledge of the structure of the reactant ion and for isomeric mixtures on the relative abundances of different isomers as well as on the electronic states of the reactant ions. For doubly charged ions, the exothermicities of electron transfer between the studied dications and neutral atoms/molecules can be obtained from determining the translational energy distributions of the product ions. Assuming that the exothermicity of electron transfer is released as translational energy of the product ion, the translational-energy distribution can be coupled with the calculated energetics of the charge-transfer processes between different isomers or electronic states of the studied dication and the neutral partner.[22] This, in turn, provides insight into the composition of the reactant-ion beam.

From the analogy with the lighter congener dication $CHCl^{2+}$, it can be expected that for $CHBr^{2+}$ also two isomers, $H{-}C{-}Br^{2+}$ and $C{-}Br{-}H^{2+}$, can be formed in both ground and electronically excited states.[12] Due to different exothermicities of electron transfer between different isomers and states of $CHBr^{2+}$ with a neutral partner, the translational energy spectrum of the corresponding product ions $CHBr^+$ can hence be used to monitor the isomer- and state compositions of the mass-selected $CHBr^{2+}$ dications.

The relative probability of electron transfer between a dication and a neutral partner can be estimated according to the "reaction-window" concept,[23] which is based on the Landau−Zener formalism developed decades ago for atomic systems.[24] Accordingly, electron transfer is supposed to be favored when the associated exothermicity falls into a "window" of 2−5 eV. The previous CCSD(T) calculations predict that the adiabatic ionization energy (IE_a) of $H{-}C{-}Br^+$ is 16.63 eV and that of the isomer $C{-}Br{-}H^+$ amounts to 17.30 eV.[12] Therefore, it can be expected that the corresponding dications $HCBr^{2+}$ and $CBrH^{2+}$ will both undergo efficient electron transfer with neutral partners that have IE roughly between 12.3 and 14.6 eV. Thus, the experiment with krypton[25] with the lowest IE of 14.00 eV is performed in order to show whether both isomers $H{-}C{-}Br^+$ and $C{-}Br{-}H^+$ are present in the ion beam or whether only the more stable isomer $H{-}C{-}Br^+$ is formed.

Figure 1 shows the translational energy spectra of the product ion $CHBr^+$ resulting from electron transfer between $CHBr^{2+}$ and Kr, obtained with the cross-beam apparatus at two collision energies (E_{coll} = 11.2 eV and 8.5 eV, respectively). The spectra are plotted in dependence on the translational energy released upon electron transfer, ΔE. The arrows show the exothermicities of electron transfer between the ground states of $H{-}C{-}Br^{2+}$ ($^1\mathbf{1}^{2+}$) or $C{-}Br{-}H^{2+}$ ($^1\mathbf{2}^{2+}$) and krypton. The exothermicity of the electron transfer between the ground state of $H{-}C{-}Br^{2+}$ ($^1\mathbf{1}^{2+}$) and Kr amounts to 2.6 eV. The consideration of the formation one or both products of electron transfer in the excited states leads to a smaller value of kinetic energy released. Thus, the formation of the ground-state $H{-}C{-}Br^+$ ($^2\mathbf{1}^+$) and the excited state of Kr^+ ($^2P_{1/2}$) provides exothermicity of 2.0 eV. This value is just at the border of the favored "window",[23] nonetheless a small signal corresponding to this process can be still identified in Figure 1b. The excited states of the singly charged product $H{-}C{-}Br^+$ ($^2\mathbf{1}^{+*}$) have not been studied theoretically, but by analogy with the $H{-}C{-}Cl^+$ ion the excitation energy is expected in a range of 0.3−0.5 eV.[15] Thus, the formation of $^2\mathbf{1}^{+*}$ concomitant with Kr^+ ($^2P_{3/2}$) would lead to exothermicity by 0.3−0.5 eV lower than the formation of product in their ground states (2.6 eV).

This analysis demonstrates that if the $CHBr^{2+}$ dication would be formed exclusively as the more stable isomer $H{-}C{-}Br^{2+}$, the electron transfer with Kr would lead to product ions with kinetic energy around 2.6 eV and lower. On the contrary, the translational energy distributions in Figure 1, parts a and b, quite clearly show that there is a significant population of ions with larger translational energy than 3 eV. Thus, these data cannot be explained by the reactions of the ground state of the $H{-}C{-}Br^{2+}$ isomer only. We note in passing that the triplet state of $H{-}C{-}Br^{2+}$ ($^3\mathbf{1}^{2+}$) lies considerably higher in energy (3.66 eV higher in energy than $^1\mathbf{1}^{2+}$),[12] thus the corresponding exothermicities of electron transfer with Kr would lie well above 5 eV and would not be observable in this experiment.[23]

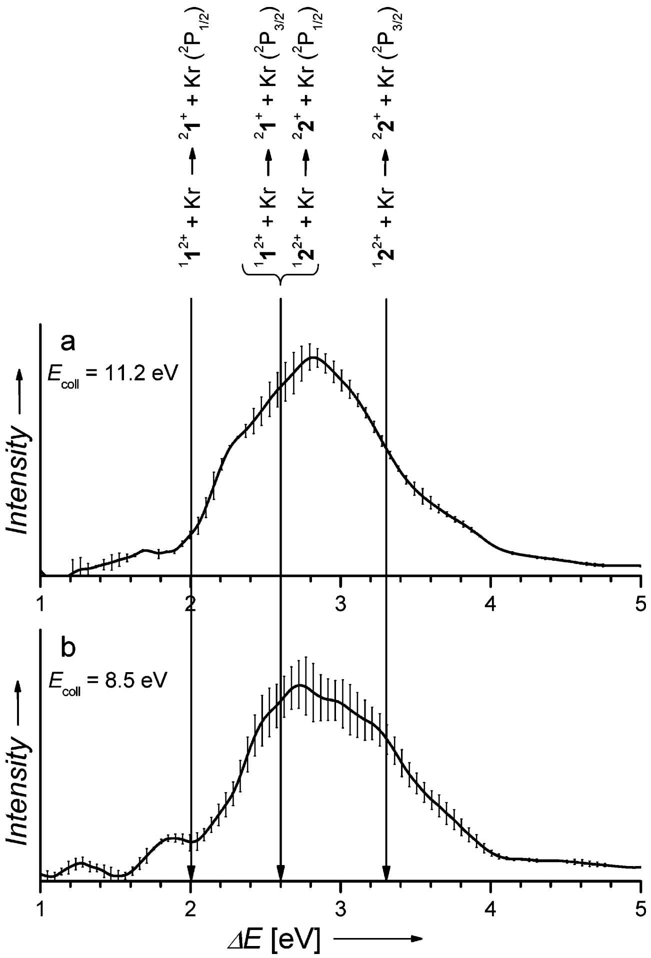


Figure 1. Relative translational energy distributions of the $CHBr^+$ and Kr^+ products from electron transfer between $CHBr^{2+}$ and Kr at collision energies of (a) 11.2 and (b) 8.5 eV. The vertical arrows depict the exothermicities of charge transfer between $H-C-Br^{2+}$ ($^1\mathbf{1}^{2+}$) and Kr and $C-Br-H^{2+}$ ($^1\mathbf{2}^{2+}$) and Kr, respectively; formation of the product ions either in their ground states or Kr in the spin−orbit excited state is considered. Vertical bars indicate standard error of the mean of experimental data.

To explain the electron transfer between reactants leading to ions with kinetic energies higher than 3 eV, the nonnegligible population of the less stable isomer $C-Br-H^{2+}$ is proposed. Charge transfer between the ground state of $C-Br-H^{2+}$ ($^1\mathbf{2}^{2+}$) and Kr leading to the products in the ground states is associated with exothermicity $\Delta E = 3.3$ eV.[12] Hence, this process can account for the formation of the $CHBr^+$ ions with kinetic energies larger than 3 eV. Similarly to the process described above, the charge transfer leading to one or both products in the excited state is further considered. The formation of the ground state of $C-Br-H^{2+}$ ($^2\mathbf{2}^+$) and spin−orbit excited state of krypton, Kr ($^2P_{1/2}$), leads to exothermicity 2.6 eV. With the similar assumption as for $^2\mathbf{1}^{+*}$, the formation of the excited state of $C-Br-H^{2+}$ ($^2\mathbf{2}^{+*}$) and Kr ($^2P_{1/2}$) leads to exothermicities in a range of 2.8−3.0 eV.

In summary, the molecular beam experiments reveal that not only the most stable isomer of $CHBr^{2+}$, $H-C-Br^{2+}$, is formed upon electron ionization of CH_3Br, but also a more energetic $CHBr^{2+}$ ions must be formed. These ions are not electronically excited $H-C-Br^{2+}$, because they lie too high in energy.[12] Instead, the data are consistent with a conjoint abundance of $H-C-Br^{2+}$ and $C-Br-H^{2+}$ in the reactant beam.

Formation of excited states of $CHBr^{2+}$ could be probed by studies of electron transfer with rare gases with higher IE than Kr, e.g., Ar or Ne. Nevertheless, it has been shown earlier[12] that reactions between $CHBr^{2+}$ and Ar or Ne are dominated by proton transfer (94 and 99%, respectively); therefore, it is assumed that the population of excited states of $CHBr^{2+}$ is negligible.

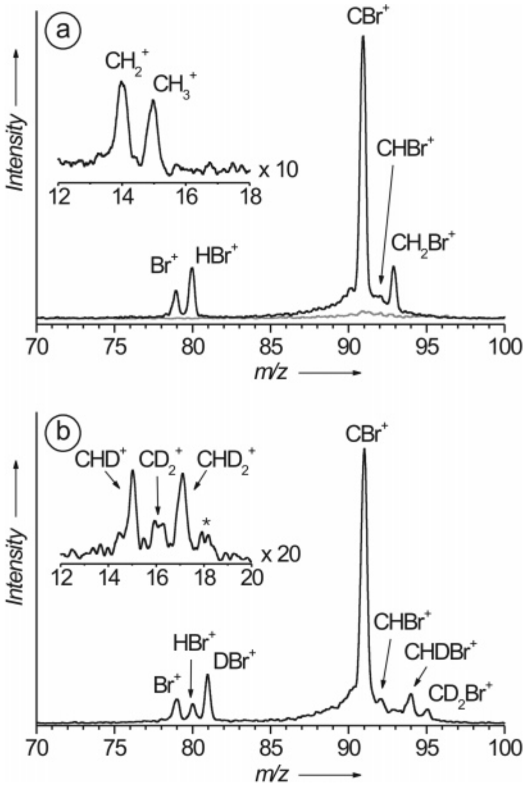


Figure 2. Mass spectra of product ions from the reactions of mass-selected $CHBr^{2+}$ with (a) H_2 and (b) D_2 at a collision energy nominally set to zero. The small signal in Figure 2b at m/z 18 (∗) most probably originates from a reaction of monocationic impurity isobaric with the parent dication (see Experimental Details).

Reaction with Molecular Hydrogen. The reaction between $CHBr^{2+}$ and H_2 was investigated in a guided ion beam (GIB) experiment. To decrease possible collision-induced dissociations and at the same time to increase product yields, the reaction was investigated at a laboratory kinetic energy of the $CHBr^{2+}$ reactant ion close to zero. The major reaction channel leads to the formation of the CBr^+ ion (Figure 2a). On the basis of the analogy with the $CHCl^{2+}/H_2$ system, it may be assumed that CBr^+ originates from proton transfer between $CHBr^{2+}$ and H_2. The other reaction product H_3^+ could not be detected due to a poor sensitivity of the quadrupole system in this particularly low mass range. Formation of $CHBr^+$ results from electron transfer between the reaction partners. As mentioned above, electron-transfer processes follow the “reaction window” concept, according to which the probability of electron transfer is more or less determined by the exothermicity of the reaction. As the ionization energy of molecular hydrogen (IE = 15.42 eV) is very close to that of Ar (IE = 15.76 eV), similar results are to be expected for electron transfer between $CHBr^{2+}$ and both neutral partners. Thus, electron transfer should in fact be negligible.[12] If the height of the $CHBr^+$ peak is evaluated with acknowledgment of the shape of the CBr^+ signal, its abundance amounts to only 1.4% relative to the sum of all products (Table 1).

Another reaction channel leads to the formation of $CH_2Br^+ + H^+$ products (10.0%); this bond-forming reaction[26] is also known from the system $CHCl^{2+} + H_2$.[13] Interestingly, there is

TABLE 1: Relative Abundances of Selected Ionic Products[a] in the Reactions CHBr^{2+} + H$_2$ and CHBr^{2+} + D$_2$

CHBr^{2+} + H$_2$	product branching[b]	CHBr^{2+} + D$_2$	product branching[b]
Br$^+$	6.6	Br$^+$	5.8
HBr$^+$	12	HBr$^+$	4.3
		DBr$^+$	12
CBr$^+$	70	CBr$^+$	69
CHBr$^+$	1.4	CHBr$^+$	1.4
CH$_2$Br$^+$	10	CHDBr$^+$	5.8
		CD$_2$Br$^+$	2.4

[a] For each pair of product ions formed in the reaction, only the heavier product is given. [b] Given as 100 × $I_{P+}/\Sigma I_{P+}$. Intensities of the products, I_{P+}, are determined from heights of the corresponding peaks in Figure 2a,b.

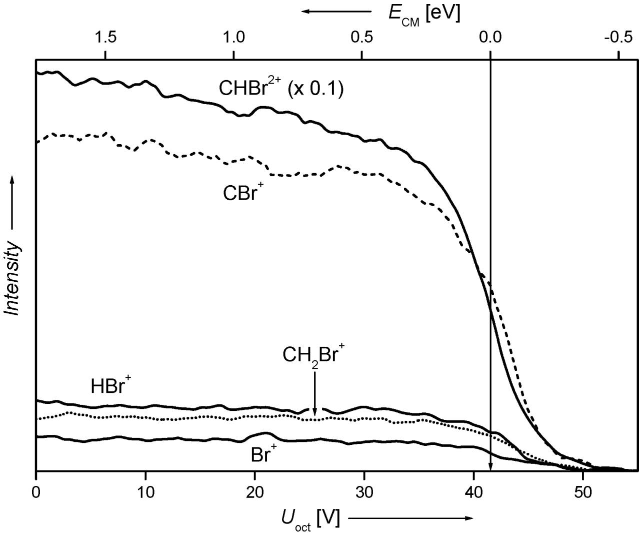


Figure 3. Yields of CBr$^+$, CH$_2$Br$^+$, HBr$^+$, and Br$^+$ products from the reaction CHBr^{2+} + H$_2$ as a function of the voltage applied to the octopole collision cell. The upper axis shows the collision energy between CHBr^{2+} and H$_2$ in the center-of-mass frame; zero was set to the point of inflection of the CHBr^{2+} intensity as a function of U_{oct}.

also abundant formation of Br$^+$ and HBr$^+$ ions (6.6% and 12%, respectively). The contribution of collision-induced dissociation (CID) of the precursor dication to the formation of these products was found to be negligible, as deduced from a control experiment with helium as a neutral collision partner under the same experimental conditions. To this end, the same pressures of the collision gases H$_2$ and He, respectively, were adjusted and the collision energy was in both experiments close to zero; the corresponding spectrum is shown as a gray line in Figure 2a. We note in passing that the interaction of CHBr^{2+} and He was further investigated under the same conditions, except that the collision energy was increased to 3.5 eV, and an almost identical spectrum was obtained. Thus, Coulomb explosions of CHBr^{2+} to the pairs CBr$^+$/H$^+$, CH$^+$/Br$^+$, or C$^+$/HBr$^+$ are not significantly induced even at higher collision energy. This finding is particularly interesting with respect to the population of the metastable isomer C−Br−H^{2+}, which has strongly exothermic dissociation limits: (i) CBr$^+$/H$^+$ with $\Delta E = -2.96$ eV, (ii) C$^+$/HBr$^+$ with $\Delta E = -2.79$ eV, and (iii) HC$^+$/Br$^+$ with $\Delta E = -1.30$ eV.[12] This observation accordingly highlights the existence of considerable Coulomb barriers for the respective fragmentation channels. In summary, it can be concluded that the Br$^+$ and HBr$^+$ products in the CHBr^{2+}/H$_2$ system are formed by a cleavage of the C−Br bond of the reaction intermediate [C,H$_3$,Br]$^{2+}$ (see below). This reasoning is also strongly supported by the low-mass region, in which signals for the complementary fragment ions CH$_2^+$ and CH$_3^+$ were detected (see inset in Figure 2a).

The mass spectrum of the products originating from the interaction of CHBr^{2+} and He also contains small amounts of CBr$^+$ and CHBr$^+$. Neither electron- nor proton transfer is expected in the reaction of CHBr^{2+} with He, because both processes are considerably endothermic. Thus, the signals of CBr$^+$ and CHBr$^+$ are most probably due to reactions of CHBr^{2+} with background gases and CBr$^+$ can also be formed by CID. A similar contribution of these processes can be expected also in the reaction of CHBr^{2+} with H$_2$. Thus, the actual abundance of CHBr$^+$ as the product from electron transfer between CHBr^{2+} and H$_2$ is expected to be in fact even smaller than listed in Table 1. As this finding does not influence the interpretation of the results and because the impact of the background reactions on the other channels is negligible, the intensities given in Table 1 are not corrected for possible background contributions.

The mechanism of the reaction between CHBr^{2+} and hydrogen was further probed in a reaction with D$_2$ (Figure 2b). Indeed, the major channel again corresponds to proton transfer from the dication to D$_2$ leading to the CBr$^+$ and D$_2$H$^+$ products (69%). The abundance of electron transfer is identical to that in the reaction of CHBr^{2+} with H$_2$ (1.4%). Quite notably, the formation of CX$_2$Br$^+$ (X = H or D) products is associated with hydrogen scrambling, thus pointing to the formation of a long-lived intermediate. The relative ratio between the possible products CHDBr$^+$ and CD$_2$Br$^+$ amounts to 2.4:1.0 (5.8% and 2.4%, respectively). Finally, the same trend is observed for the HBr$^+$ and DBr$^+$ products, which are formed in a 1.0:2.8 ratio (4.3% and 12%, respectively). Note that both CHDBr$^+$, and DBr$^+$ are statistically preferred products over CD$_2$Br$^+$ and HBr$^+$, respectively. The statistical ratio 2:1 is elevated in both cases, a finding to which we will return further below. Finally, the abundance of the Br$^+$ product (5.8%) is similar to that found in the reaction with H$_2$ (6.6%).

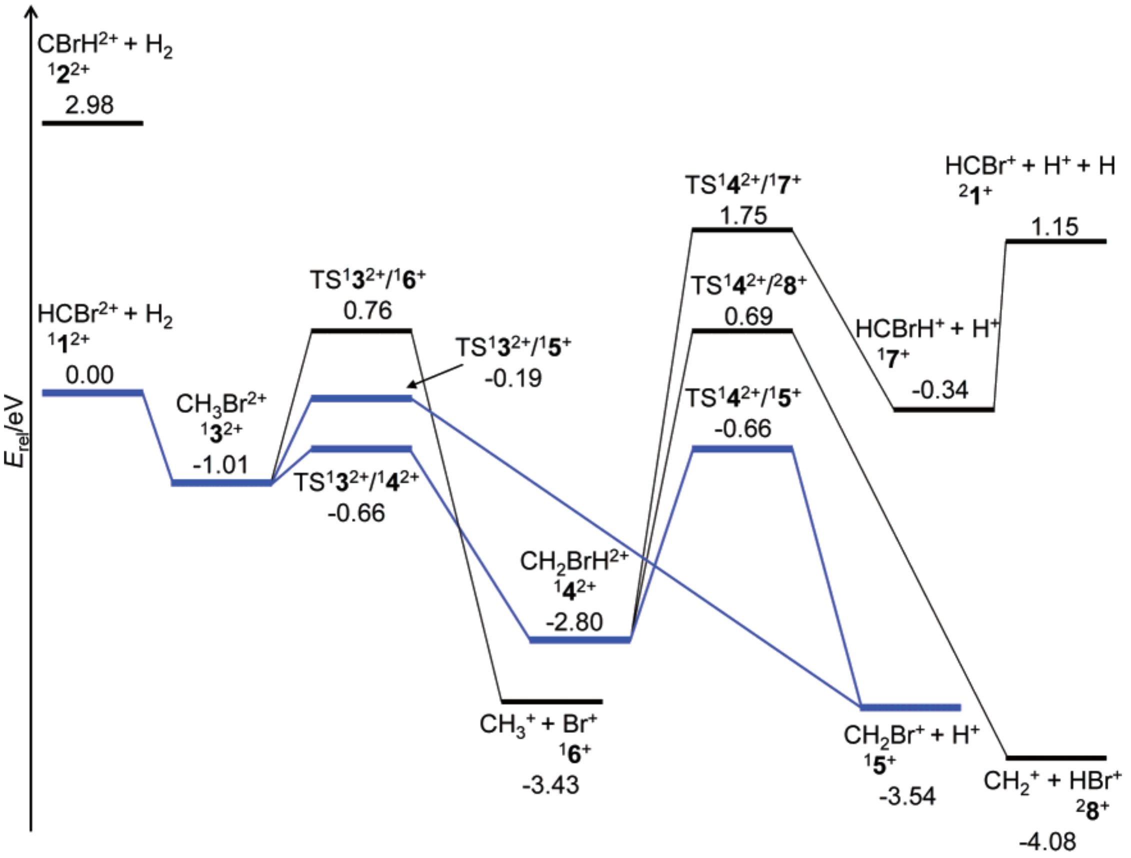
Further evidence for the proposed mechanism in the formation of Br$^+$, HBr$^+$, and DBr$^+$ products evolves from the inset shown in Figure 2b. Thus, the respective fragmentations of the [C,H,D$_2$,Br]$^{2+}$ intermediate yield (i) CHD$^+$/DBr$^+$, (ii) CD$_2^+$/HBr$^+$, and (iii) CHD$_2^+$/Br$^+$ pairs of products. Note that the sensitivity of the quadrupole analyzer is somewhat smaller for these low masses such that we refrain from an exact quantitative analysis of the intensities; notwithstanding, the overall picture is nicely confirmed.

The yields of CBr$^+$, CH$_2$Br$^+$, HBr$^+$, and Br$^+$ in the reaction of CHBr^{2+} with H$_2$ as a function of the voltage applied to the octopole cell (U_{oct}) are shown in Figure 3. The upper scale gives the collision energy in the center of mass frame; the origin was set to the point of inflection of the CHBr^{2+} intensity as a function of U_{oct}.[27] In the collision-energy range studied (0−1.7 eV), the respective branching ratios are almost constant. A slight increase of the product yields can be derived for collision energies close to zero, as expected for chemical reactions.

Theoretical Results

To understand the reaction mechanism in more detail, density functional calculations were performed. The most exothermic reaction between the CHBr^{2+} dication and H$_2$ corresponds to proton transfer to form CBr$^+$ and H$_3^+$. For the H−C−Br^{2+} (^{1}**1**$^{2+}$) isomer, the exothermicity of this process amounts to 4.27 eV. In the case of the less stable isomer C−Br−H^{2+} (^{1}**2**$^{2+}$), the exothermicity increases to 7.25 eV. It has been shown experimentally that the proton transfer between CHCl^{2+} and H$_2$ proceeds impulsively without formation of a long-lived inter-

SCHEME 1: Singlet Potential-Energy Surface of the $CHBr^{2+} + H_2$ System with Reaction Pathways Involving $[CH_3Br]^{2+}$ Intermediates[a]



[a] Blue lines emphasize the energetically favored pathways. The total energy of $HCBr^{2+} + H_2$ at 0 K amounts to −2612.936698 hartree (E_{rel} = 0.00 eV).

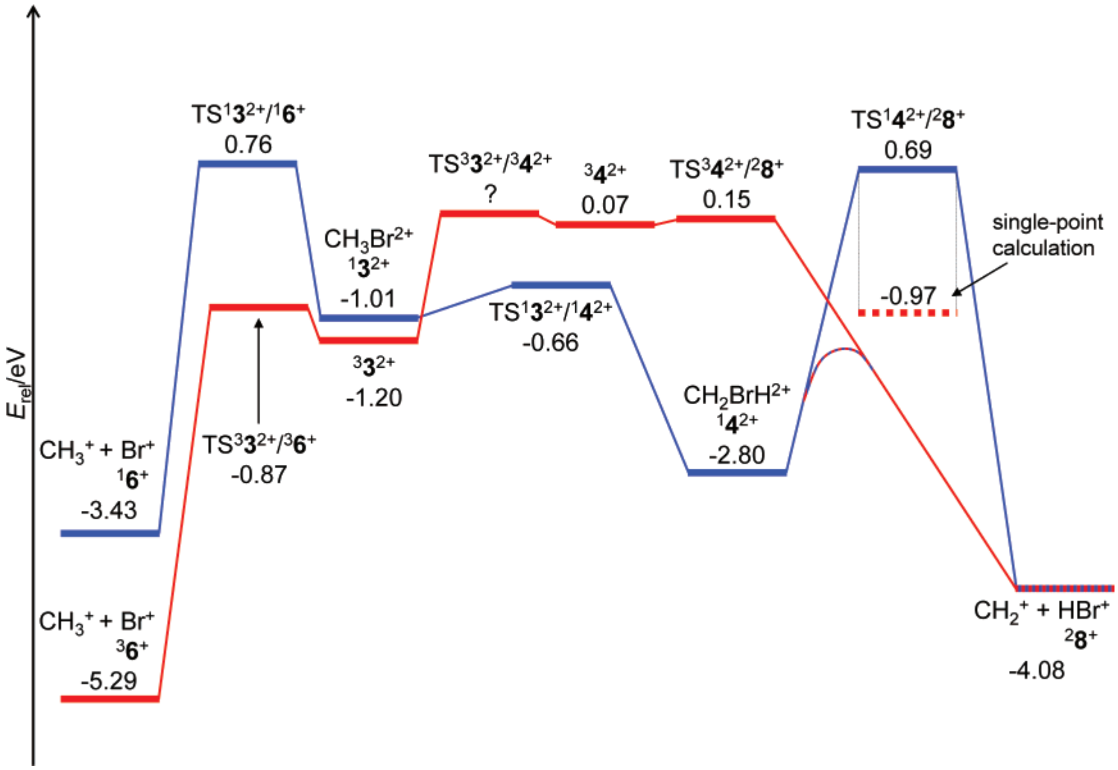
mediate.[13] With respect to the similar energy balances and similar nature of proton transfers in both systems, $CHCl^{2+}/H_2$ and $CHBr^{2+}/H_2$, it can be expected that proton transfer proceeds impulsively also in the reaction studied here. The transition structures for the proton-transfer either from $H-C-Br^{2+}$ or $C-Br-H^{2+}$ to H_2 were not found.

The other reaction pathways in the system of $CHBr^{2+}$ and H_2 (Scheme 1) most probably include the formation of an intermediate as evidenced also by hydrogen scrambling observed in the reaction with D_2 (Figure 2b). Two possible isomers of the intermediate $[CH_3Br]^{2+}$ can be formed: CH_3Br^{2+} ($^1\mathbf{3}^{2+}$, E_{rel} = − 1.01 eV; E_{rel} of $H-C-Br^{2+} + H_2$ is set to 0.00 eV) and CH_2BrH^{2+} ($^1\mathbf{4}^{2+}$, E_{rel} = − 2.80 eV). Thus, formation of both possible intermediates is associated with a considerable gain of energy. Whereas the more stable isomer $H-C-Br^{2+}$ can yield either CH_3Br^{2+} or CH_2BrH^2 via formal 1,1- or 1,2-additions of H_2, respectively, the reaction of the isomer $C-Br-H^{2+}$ with H_2 is expected to lead only to the more stable intermediate CH_2BrH^{2+} ($^1\mathbf{4}^{2+}$) in the first step. This reaction route would impart not less than 5.8 eV internal energy into the CH_2BrH^{2+} intermediate formed. Consequently, this intermediate is expected to be extremely short-lived, and the complete scrambling observed in the experiment is unlikely to occur. Given that $C-Br-H^{2+}$ is a metastable dication and proton transfer to H_2 is by 7.25 eV exothermic, it is assumed that this dication isomer reacts by simple proton transfer and does not form long-lived species. Following this line of reasoning, only reactions of the more stable reactant dication $H-C-Br^{2+}$ are considered in the following.

The intermediate CH_3Br^{2+} can decompose directly via expulsion of a proton, which leads to the products CH_2Br^+ ($^1\mathbf{5}^+$) + H^+ (E_{rel} = − 3.54 eV). This process is associated with an energy barrier, E_{rel}(TS$^1\mathbf{3}^{2+}/^1\mathbf{5}^+$) = − 0.19 eV, which is lower than the internal energy available upon formation of CH_3Br^{2+} (Scheme 1). The alternative fragmentation via cleavage of the C−Br bond requires a much larger amount of energy (E_{rel}(TS$^1\mathbf{3}^{2+}/^1\mathbf{6}^+$) = 0.76 eV). Accordingly, this pathway could be allowed only for those intermediates, which were formed from internally excited $H-C-Br^{2+}$ reactants with internal energy gained in the ionization process. Another possibility is represented by a rearrangement of CH_3Br^{2+} to the more stable ylide isomer CH_2BrH^{2+}. This process is subject to a low energy barrier (E_{rel}(TS$^1\mathbf{3}^{2+}/^1\mathbf{4}^{2+}$) = − 0.66 eV) and can therefore be expected to proceed rather efficiently.

The fragmentation of the ylide intermediate CH_2BrH^{2+} ($^1\mathbf{4}^{2+}$) can occur via (i) C−H bond cleavage, (ii) heterolysis of the Br−H bond, or (iii) dissociation of the C−Br bond. Cleavage of the C−H bond leads to $H-C-Br-H^+$ ($^1\mathbf{7}^+$). This process is associated with a high-energy barrier (E_{rel}(TS$^1\mathbf{4}^{2+}/^1\mathbf{7}^+$) = 1.75 eV). Therefore, it could contribute to the formation of $[CH_2Br]^+$ only if the intermediate $C-Br-H^{2+}$ reactant ion is involved as a reaction partner. Nevertheless, given the competition with two other energetically more favored fragmentation pathways, this mechanism can be excluded. The two other fragmentations proceed through cleavages of the Br−H or C−Br bonds. Similar to the fragmentation of CH_3Br^{2+}, dissociation of the C−Br bond is associated with an energy-demanding barrier (E_{rel}(TS$^1\mathbf{4}^{2+}/^2\mathbf{8}^+$) = 0.69 eV). Therefore, the energetically favored fragmentation of CH_2BrH^{2+} corresponds to the loss of a proton from bromine with a barrier of E_{rel}(TS$^1\mathbf{4}^{2+}/^1\mathbf{5}^+$) = −0.66 eV.

SCHEME 2: Singlet (Blue) and Triplet (Red) Potential-Energy Surface of the $CHBr^{2+} + H_2$ System Leading to the C−Br Bond-Cleavage Products[a]



[a] All energies are given relative to $HCBr^{2+}/H_2$ (in the singlet states) set to E_{rel} = 0.00 eV.

While the computational findings can rationalize the formation of the CH_2Br^+ product, they do not explain the relatively large abundances of Br^+ and BrH^+ in the spectra (Figure 2). As the analogous products were not observed in the reaction of $CHCl^{2+}$ with H_2, it can be assumed that their formation is associated with some special features of the bromine analogue. In fact, spin−orbit interaction plays a much more important role for bromine, and therefore, a possible involvement of triplet states in the reaction pathways is considered (Scheme 2).[28] The triplet state of the CH_3Br^{2+} intermediate is more stable than the singlet state, and the barrier for the C−Br bond cleavage amounts to only E_{rel}(TS^3**3**$^{2+}$/^{3}**6**$^+$) = −0.87 eV. Thus, it is proposed that due to a stronger spin−orbit coupling the initially formed singlet state of CH_3Br^{2+} interconverts to the triplet state, thereby allowing a competition between C−H and C−Br bond cleavages. For the more stable isomer CH_2BrH^{2+}, the triplet state (E_{rel}(^{3}**4**$^{2+}$) = 0.07 eV) lies 2.87 eV higher in energy than the singlet state. Nonetheless, the single-point energy of the singlet-state TS^1**4**$^{2+}$/^{2}**8**$^+$ associated with the BrH^+ loss calculated on the triplet surface amounts to only $E_{rel/SP}$(TS^3**4**$^{2+}$/^{2}**8**$^+$) = −0.97 eV. As indicated in Scheme 2, it is thus suggested that along the fragmentation pathway of the CH_2BrH^{2+} intermediate a spin isomerization occurs,[28] which results in a Coulomb explosion to produce CH_2^+ and HBr^+. We note in passing that the transition structure TS^3**3**$^{2+}$/^{3}**4**$^{2+}$ for the rearrangement of CH_3Br^{2+} to CH_2BrH^{2+} in the triplet states was not located; all optimization attempts led to dissociation into CH_2^+ and HBr^+.

Finally, let us address the isotope distributions in the reaction of $CHBr^{2+}$ and D_2. The products $CHDBr^+$ and CD_2Br^+ are formed in a 2.4:1.0 ratio. Both products can arise either from the fragmentation of the CHD_2Br^{2+} intermediate or the ylide intermediates $CD_2−BrH^{2+}$/$CHD−BrD^{2+}$. For $CHD_2−Br^{2+}$, the statistical ratio for D^+ to H^+ elimination (2:1) is expected to be somewhat smaller due to a kinetic isotope effect favoring H^+ elimination. If the ylide intermediate is formed by the rearrangement of initially formed $CHD_2−Br^{2+}$, the same is expected, except that the kinetic isotope effect would operate twice: first in the rearrangement of a hydrogen atom and then in the expulsion of a proton (deuteron). Accordingly, this scenario predicts that the ratio of D^+ to H^+ elimination should be smaller than 2, which is in contradiction to the experimental results. Instead, the observations can be rationalized consistently, if a specific mechanism for the formation of the intermediate $CHD−BrD^{2+}$ exists. Explicitly, we propose a 1,2-addition of D_2 to $H−C−Br^{2+}$ leading to $CHD−BrD^{2+}$. Alternatively, impulsive reaction mechanisms proceeding via high-energy barriers[13] may contribute to the formation of $CHDBr^+$. Nevertheless, the scenario with a preferential formation of $CHD−BrD^{2+}$ is further supported by the relative abundances of HBr^+ and DBr^+ (1.0:2.8). Last but not least, we note that the observation of a preferential formation of $CHD−BrD^{2+}$ strongly supports our assumption above that the isomeric dication $C−Br−H^{2+}$ does not play any role as far as long-lived intermediates of the ion−molecule reactions are concerned.

Conclusions

The $CHBr^{2+}$ dication has two constitutional isomers, the thermodynamically stable $H−C−Br^{2+}$ dication and the metastable isomer $C−Br−H^{2+}$, both of them are formed upon electron ionization of CH_3Br. The most abundant ion−molecule process in the $CHBr^{2+}/H_2$ system corresponds to proton transfer from the dication to the hydrogen molecule. Other processes proceed through a long-lived reaction intermediate $[CH_3Br]^{2+}$, which exists in two isomeric forms, $CH_3−Br^{2+}$ and $CH_2−BrH^{2+}$. Two general fragmentations schemes are possible for both of them: (i) they can lose a proton to form $CH_2−Br^+$ or (ii) they can undergo spin-isomerization followed by C−Br bond cleavages. These processes result in the formation of either CH_3^+

$+$ Br^+ or $CH_2^+ + BrH^+$ products. Whereas the first process has been already described for the related $CHCl^{2+}/H_2$ system, the second process is novel and is proposed to result from a more efficient spin−orbit coupling associated with the bromine atom. Thus, it can be stated that the reactivities of small molecular dications CHX^{2+} do not just follow the homologous trends in conjunction with the associated thermodynamic considerations but that the nature of the halogen atom has a rather pronounced influence.

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References and Notes

(1) Jenkins, E. B.; Bowen, D. V.; Tripp, T. M.; Sembach, K. R. *Astrophys. J.* **2005**, *623*, 767.

(2) Witasse, O.; Dutuit, O.; Lilensten, J.; Thissen, R.; Žabka, J.; Alcaraz, C.; Blelly, P. L.; Bougher, S. W.; Engel, S.; Andersen, L. H.; Seiersen, K. *Geophys. Res. Lett.* **2002**, *29*, 1263 and **2003**, *30*, 1360.

(3) Apel, P. Y. *Nucl. Tracks Radiat. Meas.* **1991**, *19*, 29.

(4) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1393.

(5) Mathur, D. *Phys. Rep.* **1993**, *225*, 193.

(6) Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **1999**, *103*, 7385.

(7) Schröder, D.; Loos, J.; Schwarz, H.; Thissen, R.; Roithová, J.; Herman, Z. *Int. J. Mass Spectrom.* **2003**, *230*, 113.

(8) Roithová, J.; Schröder, D.; Schwarz, H. *Chem.—Eur. J.* **2005**, *11*, 628.

(9) Herman, Z.; Žabka, J.; Dolejšek, Z.; Fárník, M. *Int. J. Mass Spectrom.* **1999**, *192*, 191.

(10) Bursey, M. M.; Pedersen, L. G. *Org. Mass Spectrom.* **1992**, *27*, 974.

(11) Petrie, S.; Javahery, G.; Wincel, H.; Böhme, D. K. *J. Am. Chem. Soc.* **1993**, *115*, 6290.

(12) Roithová, J.; Herman, Z.; Schröder, D.; Schwarz, H. *Chem.—Eur. J.* **2006**, *12*, 2465.

(13) Roithová, J.; Žabka, J.; Hrušák, J.; Thissen, R.; Herman, Z. *J. Phys. Chem. A* **2003**, *107*, 7347.

(14) Roithová, J.; Hrušák, J.; Herman, Z. *J. Phys. Chem. A* **2003**, *107*, 7355.

(15) Roithová, J.; Žabka, J.; Thissen, R.; Herman, Z. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2988.

(16) Roithová, J.; Hrušák, J.; Herman, Z. *Int. J. Mass Spectrom.* **2003**, *228*, 497.

(17) Rühl, E.; Price, S. D.; Leach, S.; Eland, J. H. D. *Int. J. Mass Spectrom. Ion Processes* **1990**, *97*, 175.

(18) Roithová, J.; Schröder, D.; Grüne, P.; Weiske, T.; Schwarz, H. *J. Phys. Chem. A* **2006**, *110*, 2970.

(19) Gaussian 98 (Revision A.11.4). Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr..; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 2001.

(20) (a) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys. (Paris).* **1980**, *58*, 1200. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (d) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(21) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(22) Herman, Z. *Int. Rev. Phys. Chem.* **1996**, *15*, 299.

(23) (a) Spears, K. G.; Fehsenfeld, F. C.; McFarland, F.; Ferguson, E. E. *J. Chem. Phys.* **1972**, *56*, 2562. (b) Ehbrecht, A.; Mustafa, N.; Ottinger, Ch.; Herman, Z. *J. Chem. Phys.* **1996**, *105*, 9833. (c) Lindinger, W.; Hansel, A.; Herman, Z. *Adv. Mol. Opt. Phys.* **2000**, *43*, 243, and references therein.

(24) (a) Landau, L. *Phys. Z. Sowjetunion* **1932**, *2*, 46. (b) Zener, C. *Proc. R. Soc. London A* **1932**, *137*, 696. (c) Olson, R. E.; Smith, F. T.; Bauer, E. *Appl. Opt.* **1971**, *10*, 1848. (d) Salop, A.; Olson, R. E. *Phys. Chem.* **1976**, *13*, 1312.

(25) Rare gases are usually used as most suitable neutral reactants for the following reasons: First, by definition, electron transfer cannot lead to vibrational excitation of the atomic product ion, and second, higher rare gases are relatively heavy with respect to the studied ions; therefore, a large momentum transfer in the collision leads to an improved resolution in the translational energy spectra.

(26) Price, S. D. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1717.

(27) The point of inflection of the $CHBr^{2+}$ intensity as a function of U_{oct} corresponds to the maximum of the respective differential intensity dependence. As this function shows the distribution of the laboratory kinetic energy of $CHBr^{2+}$, its maximum corresponds to the kinetic energy of the majority of ions. In turn, when exactly this stopping voltage is applied to the collision cell, it is reasonable to assume that the majority of ions have kinetic energy zero. Therefore, this point is set as the origin of collision energy in center-of-mass frame.

(28) Schwarz, H. *Int. J. Mass Spectrom.* **2004**, *237*, 75.