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International Journal of Mass Spectrometry 249–250 (2006) 130–137

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Unimolecular reactions of halogeno phenylarsenium ions: Kinetic energy release during the elimination of halogen hydride

Dirk Kirchhoff [a], Hans-Friedrich Grützmacher [a,*], Hansjörg Grützmacher [b]

[a] *Fakultät für Chemie der Universität Bielefeld Postfach 10 01 31, D-33501 Bielefeld, Germany*
[b] *Department of Chemistry and Applied Biosciences, HCI H 131 ETH-Hönggerberg, CH-8093 Zuerich, Switzerland*

Received 12 October 2005; accepted 3 January 2006
Available online 14 February 2006

In memoriam of Prof. Chava Lifshitz, a great scientist and a brave lady.

Abstract

The four dihalogeno phenylarsanes $C_6H_5AsF_2$, **1**, $C_6H_5AsCl_2$, **2**, $C_6H_5AsBr_2$, **3**, and $C_6H_5AsI_2$, **4**, produce in the 70 eV-EI mass spectra by loss of a halogen atom abundant halogeno phenylarseniun ions $C_6H_5As^+$–X, **1a**$^+$–**4a**$^+$. The further fragmentation reactions of ions **1a**$^+$–**4a**$^+$ are elimination of a molecule halogen hydride HX and/or loss of a halogen atom $X^\bullet$. The preferred route of fragmentation depends clearly on the strength of the As–X bond. The metastable fluoro ion **1a**$^+$ and chloro ion **2a**$^+$, respectively, fragment only by loss of HF and HCl, the metastable bromo derivative **3a**$^+$ exhibits losses of HBr and $Br^\bullet$ of about equal intensity, and the metastable iodo ion **4a**$^+$ fragments only by loss of an I atom. The loss of HX is associated with a large kinetic energy release (KER) which yield a dish-topped peak in the MIKE spectrum of **1a**$^+$ ($\langle T\rangle = 845$ meV) and **2a**$^+$ ($\langle T\rangle = 550$ meV) and a broad round-topped peak on the MIKE spectrum of **3a**$^+$ ($\langle T\rangle = 369$ meV). Theoretical calculations (UBHLYP/6-311 + G(2d,p)/-/UBHLYP/6-31 + G(d)) confirm that the elimination of HX requires an enthalpy of activation $\Delta H^{\#}$, and that in the case of **3a**$^+$ this $\Delta H^{\#}$ and the reaction enthalpy for loss of $Br^\bullet$ are of similar size. The $\Delta H^{\#}$ of HX elimination is also responsible for the reverse enthalpy of activation $\Delta H^{\#}_{\text{rev}}$ and the KER during this process. The observed $\langle T\rangle$ amounts to 78% (**1a**$^+$), 55% (**2a**$^+$), and 40% (**3a**$^+$) of the calculated value of $\Delta H^{\#}_{\text{rev}}$. Thus, the KER as well as the distribution of the KER (KERD) and the competition between elimination of HX and loss of $X^\bullet$ are very specific for the halogen ligand at the As atom. Metastable (4-fluorophenyl) arsenium ions **1b**$^+$, F–$C_6H_4As^+$–H, and (4-chlorophenyl) arsenium ions **2b**$^+$, Cl–$C_6H_4As^+$–H^+, eliminate HF or HCl with virtually identical KERD as metastable **1a**$^+$ or **2a**$^+$, $C_6H_5As^+$–Cl, proving an identical transition state for both isomers. Accordingly, **1b**$^+$ and **2b**$^+$ rearrange to **1a**$^+$ and **2a**$^+$ prior to HCl elimination. Such a rearrangement by a reductive elimination/oxidative insertion of As^+ into C─H and C─X bonds has been observed before and appears to be typical of arylarsane radical cation and arylarsenium cations.

Keywords: Phenylarsane; Fragmentation mechanism; Tandem mass spectrometry; Kinetic energy release; DFT calculation

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1. Introduction

The study of unimolecular reactions of gaseous phenylarsane radical cations and phenylarsenium cations by tandem mass spectrometry has given a wealth of new information about possible reaction modes of such ionized elementorganic compounds [1–3]. Of special interest are rearrangements of the radical cations of aryl arsanes by reductive elimination of the central As atom and bond formation between the aryl ligand and another ligand of the As atom. Such a rearrangement seems to be typical of ionized aryl derivatives of heavy main group elements. An analogous rearrangement by reversible reductive elimination/oxidative insertion of As has been detected in the fragmentation reactions of gaseous halogeno-(4-halogenophenyl) arsenium cations, $YC_6H_4As^+X$, which interchange the halogen substituents at the phenyl group and at the As atom prior to elimination of a molecule of halogen hydride (HX or HY) [3]. This observation shows that reductive As elimination and ligand coupling may also occur in unsaturated even electronic ions. The main evidence for the halogen interchange reaction $YC_6H_4As^+X \leftrightharpoons XC_6H_4As^+Y$ is the observation of kinetic energy release (KER) which accompanies the elimination of HX and HY, from metastable $YC_6H_4As^+X$ and which depends

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[*] Corresponding author.
E-mail address: hans-friedrich.gruetzmacher@uni-bielefeld.de (H.-F. Grützmacher).

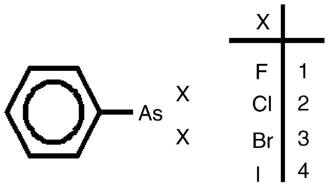
doi:10.1016/j.ijms.2006.01.011

only on the nature of the halogen atom but not on its position in the precursor ion. It is well established that KER and especially the kinetic energy release distribution (KERD) is a characteristic property of the transition state of the fragmentation reaction [4]. Important contributions to this field of gaseous ion chemistry have been made by C. Lifshitz. She has shown how very detailed information about ion structures, reaction mechanisms, and reaction dynamics can be obtained by a careful analysis of KER and KERD. Recently, she has documented and discussed these methods in a comprehensive review [5]. In particular it is known, that identical KERD for analogous reactions prove unambiguously identical transition states and identical reaction mechanisms of fragmentations. The elimination of HX (or HY) from isomeric metastable ions $YC_6H_4As^+X$ and $XC_6H_4As^+Y$ exhibits identical KERD, consequently the elimination occurs in both isomers by an identical critical configuration of the transition state. We have suggested that the elimination of HX and HY involves only the halogen ligand located at the As atom which requires an interchange of X and Y in the ions $YC_6H_4As^+X$ and $XC_6H_4As^+Y$ prior to the elimination [3]. This rearrangement involves likely an ion/neutral complex of As^+ and a dihalogeno benzene YC_6H_4X which arises by a reductive elimination of As from either ion $YC_6H_4As^+X$ and $XC_6H_4As^+Y$. A corollary of a halogen hydride elimination of only the halogen ligand at the As atom is that this process should be observed with identical KERD also for metastable halogeno phenylarsenium ions $C_6H_5As^+X$. Therefore, to complete the experimental results and to substantiate the suggested elimination mechanism, we present in this paper the results of a study of the mass spectrometric fragmentations of dihalogeno phenyl arsanes $C_6H_5AsX_2$ and halogeno phenylarsenium ions $C_6H_5As^+X$ (X = F, Cl, Br, I). It will be shown that elimination of HX from the halogeno phenylarsenium ions $C_6H_5As^+X$ displays indeed the same KERD as HX elimination from the halogeno(-4-halogenophenyl)arsenium ions $YC_6H_4As^+X$ and $XC_6H_4As^+Y$, in agreement with the suggested reaction mechanism.

2. Experimental

2.1. Compounds

The dihalogeno phenylarsanes **1–4** (for structures see Scheme 1) are known compounds. The synthesis by using standard techniques of synthetic chemistry is described elsewhere [6]. The structure of all compounds was verified by ^1H and ^{13}C NMR spectroscopy.



Scheme 1.

2.2. Mass spectrometry

70 eV-EI mass spectra of all compounds were recorded with a double focusing Auto Spec mass spectrometer of Micromass VG with EBE geometry at an acceleration voltage of 8 kV. For introduction into the ion source (ion source temperature about 250 °C) by using the temperature controlled sample probe.

The mass analyzed ion kinetic energy (MIKE) spectra of selected ions from the 70 eV-EI mass spectra were obtained by using the double focusing ZAB-2F mass spectrometer of Micromas VG with BE geometry at an acceleration voltage of 8 kV. The samples were introduced into the ion source (ion source temperature about 200 °C) using the solid sample probe and absorbing **1–7** to powdered Na_2SO_4. For measuring the MIKE spectra, the ion beam of the selected precursor ion was focused onto the slit of the second field free region between magnet and electrostatic analyzer (ESA) by an appropriate setting of the magnet current, and the MIKE spectrum was recorded by varying continuously the deflecting voltage of the ESA. For a better signal/noise ratio 30–50 scans were accumulated for each MIKE spectrum. The kinetic energy release distribution (KERD) during the fragmentation of the metastable ions was calculated from the peak shapes of the relevant fragment ions using the META program of Szilagyi and Vekey [7] with a set of parameters adjusted to the VG ZAB-2F mass spectrometer.

The mass spectra from collision induced decomposition (CID) of selected ions of the 70 eV-EI mass spectra were measured with the VG Auto Spec mass spectrometer using the experimental condition described above. For measuring a CID mass spectrum, the ion beam of the selected precursor ion was focused into the collision cell in the third field free region between the magnet and the second ESA of the Auto Spec mass spectrometer. He gas was introduced into the collision cell until the main ion beam intensity was reduced by about 50%. Then, the CID spectrum was recorded by varying continuously the deflecting voltage of the ESA.

2.3. Computational methods

All calculations were performed with *Gaussian 98* [8]. The minimum energy reaction pathway (MERP) of the HX elimination from arsenium ion $C_6H_5As^+X$ was explored by calculation of stationary points using the split valence all electron 6-31 + G(d) basis set in combination with the hybrid density functional Becke-half-and-half-LYP (BHLYP) [9]. This level of theory has been used with good results in the previous study of radical cations of dihalogeno-(4-halogenophenyl) arsanes [3]. Relative energies have been obtained by single point calculations using the BHLYP functional in combination with the 6-311 + G(2d,p) basis set. Combination with zero point energy (ZPE) correction and thermochemical corrections to the enthalpy H^{298} at 298 K, based on the BHLYP/6-31 + G(d) harmonic vibrational analysis, yield total energies at 0 K denoted as E_{tot} and enthalpies at 298.15 K designated as ΔH^{298}. All stationary points exhibit the correct number of negative frequencies, i.e., none for minima of the energy hyper surface and one negative frequency for transition states. It was ascertained by visualizing the negative frequency using the GAUSS VIEW program that this frequency corresponds to the correct movement of the atoms along the MERP in the neighborhood of the relevant transition state.

3. Results and discussion

The 70 eV EI mass spectra of difluorophenylarsane **1**, dichlorophenylarsane **2**, dibromophenyl-arsane **3**, and diiodophenylarsane **4** are shown in Fig. 1. The primary fragmentations of the molecular ions $\mathbf{1}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ corresponds to losses of ligands at the As atom.

In the case of the difluoro derivative **1**, which has a strong As–F bond, the main fragmentation pathway is cleavage of the As–C bond and formation of the $C_6H_5^+$ ion *m/z* 77. Accordingly, the peak of the ion $[C_6H_5AsF]^+$ at *m/z* 171 is rather small. With decreasing strength of the As–halogen bond the loss of a halogen ligand from the molecular ion is preferred and the ion $[C_6H_5AsX]^+$ (X = Cl: *m/z* 176/178; X = Bt: *m/z* 233/235; X = I: *m/z* 278) starts to dominate the EI mass spectrum. The further decomposion of ion $[C_6H_5AsX]^+$ proceeds by elimination of $X^\bullet$ or HX, which yields ions $[C_6H_5As]^{\bullet+}$, *m/z* 152, and $[C_6H_4As]^+$, *m/z* 151. The relative abundances of these ions depends clearly on the strength of the As–X bond and the thermodynamic stability of HX. Thus, only the loss of $I^\bullet$ is observed for $[C_6H_5AsI]^+$, while only loss of HF takes place for $[C_6H_5AsF]^+$. Minor signals in the mass spectra arise from ions AsX_2^+ and $AsX^{\bullet+}$, so that the interpretation of the EI mass spectra is straight forwards, in agreement with published data [10]. Note however, that the mass spectra of **1**, **2**, and **3** display small but significant peaks of halogenobenzene radical cation $C_6H_5X^{\bullet+}$ (X = F: *m/z* 96; X = Cl: *m/z* 112/114: X = Br: *m/z* 154/156) which indicates that a rearrangement by reductive elimination of AsX from $C_6H_5As–X_2^{\bullet+}$ does occur. Nonetheless, the structure of a halogenophenylarsenium ion $C_6H_5As^+X$ can be safely assigned to the ions $[M-X]^+$ since additional experiments have shown [6] that ions of identical properties are also obtained by loss of $^\bullet CH_3$ from the molecular ions of methylhalogenophenylarsanes $C_6H_5As(CH_3)X$. The unimolecular reactions of metastable arsenium ions $C_6H_5As^+X$ are discussed in the following sections (see Scheme 2).

The MIKE spectra of the arsenium ions $C_6H_5As^+F$, $\mathbf{1a}^+$,$C_6H_5As^+F$, $\mathbf{1a}^+$,$C_6H_5As^+Cl$, $\mathbf{2a}^+$,$C_6H_5As\text{-}^+Br$, $\mathbf{3a}^+$, and $C_6H_5As^+I$, $\mathbf{4a}^+$, are shown in Fig. 2. The only significant signal in the MIKE spectra of $\mathbf{1a}^+$ and $\mathbf{2a}^+$is due to the elimination of HF or HCl. The MIKE spectrum of the bromo derivative $\mathbf{3a}^+$ displays overlapping signals for the losses of $Br^\bullet$ and HBr, while metastable $\mathbf{4a}^+$ eliminates only $I^\bullet$.

The loss of $I^\bullet$ gives rise to a sharp signal of Gaussian peak shape which shows no special effects of the KERD associated with this process. Enlarged versions of the peaks of the MIKE spectra of $\mathbf{1a}^+$–$\mathbf{3a}^+$are presented in Fig. 3 together with a graph showing the KERD derived from the peaks using the META program of Szilagyi and Vekey [7]. The loss of HF and HCl from

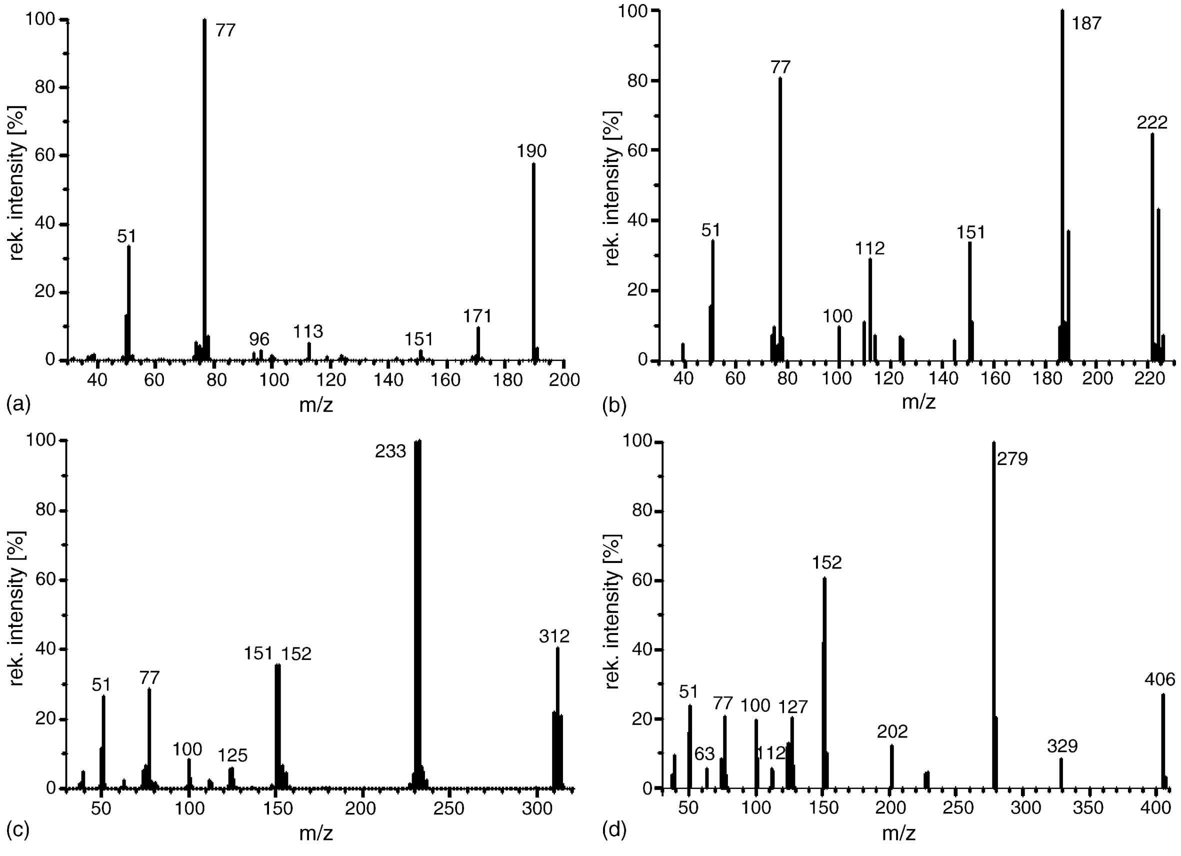
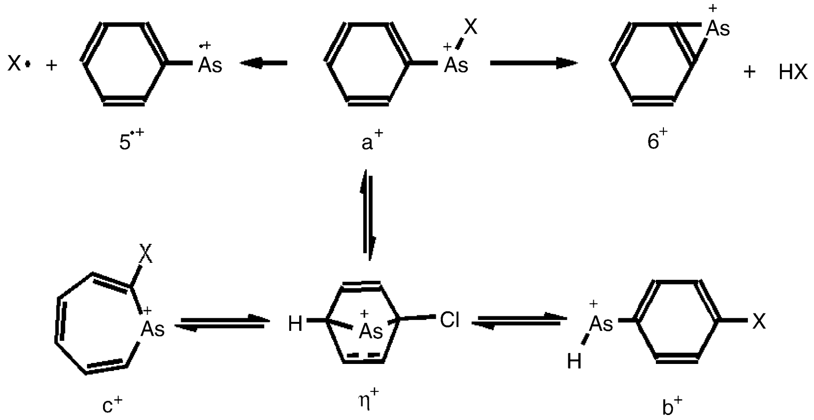


Fig. 1. 70 eV-EI mass spectrum of (a) difluoro phenylarsane **1**; (b) dichloro phenylareane **2**; (c) dibromo phenylarsane **3**; (d) diiodo phenylarsane **4**.



Scheme 2.

1a$^+$ and **2a**$^+$, respectively, gives rise to a dish-shaped peak which indicates the presence of a considerable reverse activation energy for these eliminations. Further, the minimum value of KER is about 400 meV in the case of **1a**$^+$ and about 150 meV for **2a**$^+$. Thus, a large fraction of the reversed activation energy is always released as kinetic energy of the departing fragments. The overlapping signals at *m/z* 152 and *m/z* 151 have been resolved using the Origin program [11] into a narrow peak at *m/z* 152 owing to loss of Br$^\bullet$ and a broad round-topped component at *m/z* 151 for the loss of HBr. By peak area both fragmentations of metastable **3a**$^+$ exhibit about equal intensity. The KERD calculated for the elimination of HBr shows again the presence of a reversed activation energy for this process, although no fixed minimum value of the KER is found.

The shapes of the peaks observed in the MIKE spectra of arsanyl cations **1a**$^+$–**4a**$^+$ for the elimination of HX or X$^\bullet$ as well as the mean values of the KER calculated from the peaks agree very well with those found for the same eliminations from metastable halogeno-(4-halogeno-phenyl)arsanyl cations [3]. This result confirm the suggestion that HX elimination from these arsanyl cations involves only a halogen ligand at the As atom. Thus, if elimination of the halogen substituent originally located at the phenyl group is observed, the fragmentation requires a preceding migration of the halogen substituent

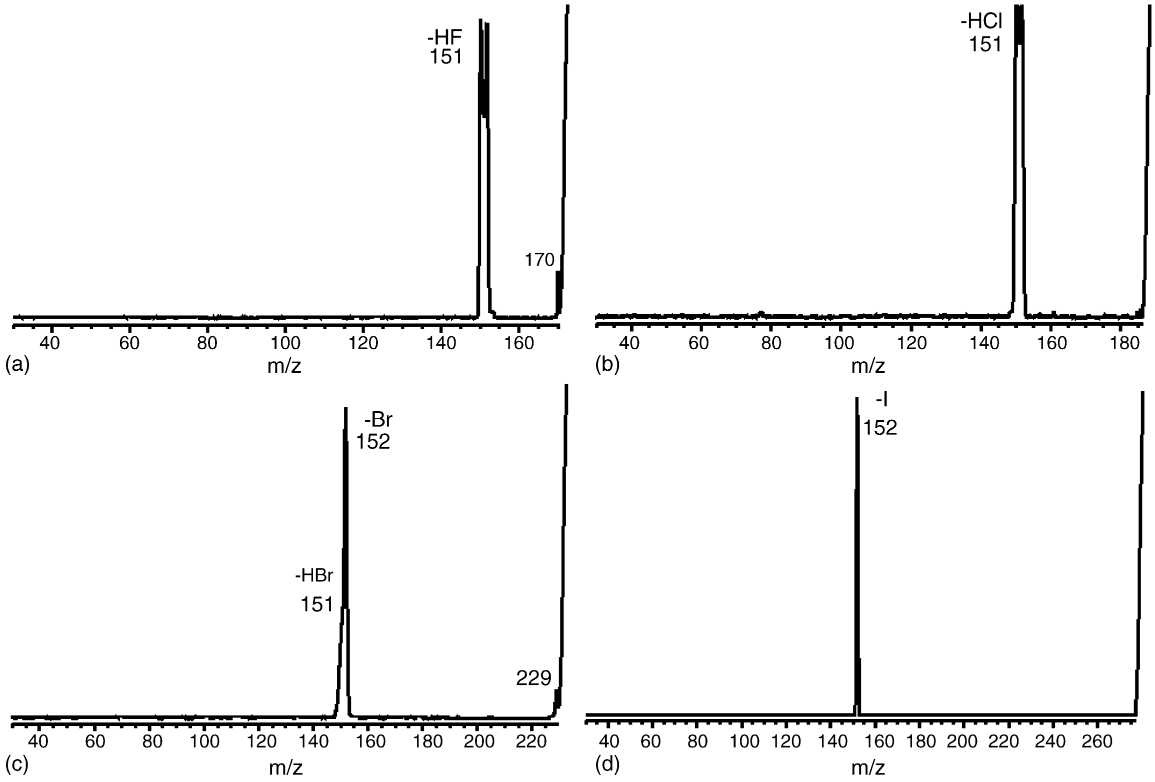


Fig. 2. MIKE spectrum of (a) fluoro phenylarsenium ion **la**$^+$; (b) chloro phenylarsenium ion **2a**$^+$; (c) bromo phenylarsenium ion **3a**$^+$; (d) iodo phenylarsenium ion **4a**$^+$.

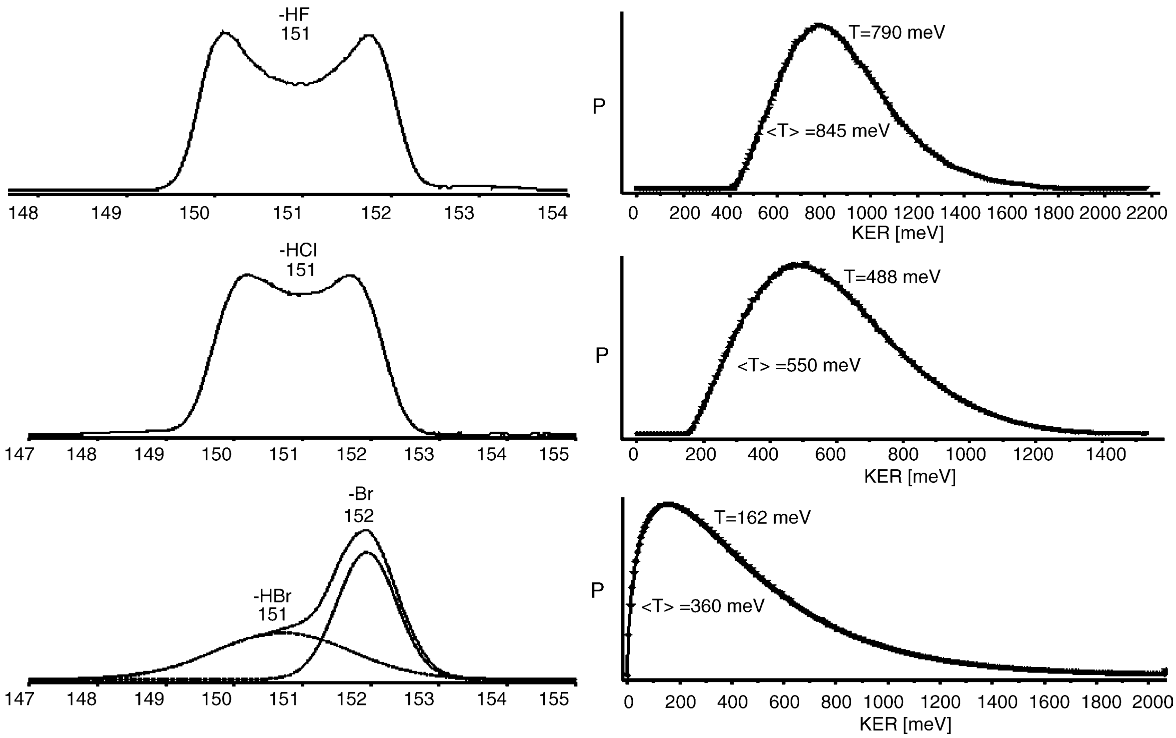


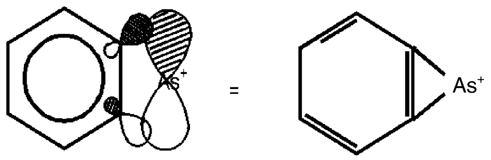
Fig. 3. Peak shape and KERD for loss of HX from metastable (a) fluoro phenylarsenium ion **1a**$^+$; (b) chloro phenylarsenium ion **2a**$^+$; (c) bromo phenyl arsenium ion. **3a**$^+$; (d) iodo phenylarsenium ion **4a**$^+$.

to the As atom via an intermediate ion/neutral complex of As$^+$ and a dihalogenobenzene [3]. An analogous rearrangement of a halogenophenylarsenium ion $C_6H_5As^+X$ by reductive elimination of As would result probably in an ion/molecule complex of As$^+$ and halogenobenzene C_6H_5X. A reinsertion of the As$^+$ into one of the C–H bonds would generate the isomeric arsenium ion X–$C_6H_4As^+H$ (Scheme 2). This possibility was checked by a study of the decomposition of metastable (4-fluorophenylarsenium ion **1b**$^+$, F–$C_6H_4As^+$–H, and (4-chlorophenyl) arsenium ion **2b**$^+$, $ClC_6H_4As^+H$. These isomers of **1a**$^+$ and **2a**$^+$ were obtained in the ion source of the mass spectrometer by fragmentation of the molecular ion of diethyl-(4-halogenophenyl) arsanes, 4-$XC_6H_4As(C_2H_5)_2$, (X = F, Cl), by loss of a $C_2H_5^\bullet$ radical followed by β-elimination of C_2H_4.

The MIKE spectra of the isomeric arsenium ion **1a**$^+$/**1b**$^+$ and **2a**$^+$/**2b**$^+$ are identical. In particular, the KERD observed for the elimination of HF and HCl are virtually identical (**1a**$^+$ $\langle T\rangle = 845$ meV, **1b**$^+$ $\langle T\rangle = 820$ meV and **2a**$^+$ $\langle T\rangle = 550$), **2b**$^+$ $\langle T\rangle = 575$ neV). Clearly, the elimination of HF and HCl occurs from the isomers via identical transition states, and at least **1b**$^+$ and **2b**$^+$ isomerize by an exchange of the H atom at the As and the X atom at the phenyl group prior to HX elimination. Further, the enthalpy of activation of both steps of the isomerization, reductive elimination of As$^+$ from the As–H bond and oxidative insertion of As$^+$ into the C–X bond, should be comparable to the enthalpy of activation of the respective HX elimination for a competition of isomerozation $\mathbf{a}^+ \rightleftarrows \mathbf{b}^+$ and the loss of HX.

The loss of an atom X$^\bullet$ from the halogenophenylarsenium ions **1a**$^+$–**4a**$^+$ by a direct cleavage of the As–X bond yields the phenylarsanediyl radical cation $C_6H_5As^{\bullet+}$ **5**$^{\bullet+}$ which is the most stable isomer according to the "heavy atom exclusion rule". [12] The most plausible mechanism of the elimination of HX from the arsanyl cation $C_6H_5As^+X$ is 1,3-elimination involving one of the *ortho*-H atoms of the phenyl group. This results in a $C_5H_4As^+$ cation with the structure of a 1,2-phenylenearsenium cation **6**$^+$. This is a stable structure which is composed of an As$^+$ cation overlapping with its vacant 4p orbital the two in-plane $2sp_2$ orbitals ("arine orbitals") of a 1,2-didehydrobenzene ligand as shown in Scheme 3. The formation of stable **6**$^+$ is associated with a substantial activation enthalpy barrier as indicated by the large KER during this process.

Experimental enthalpies of formation of phenylarsane radical cations **1**$^{\bullet+}$–**4**$^{\bullet+}$ and arsanyl cations **1a**$^+$–**4a**$^+$, **5**$^{\bullet+}$, and **6**$^+$ are not available for a calculation of the energetics of the fragmentation reactions and for a more quantitative description of the competition between loss of X$^\bullet$ and elimination of HX. Therefore, the enthalpies of relevant stationary points of the minimum energy reaction path (MERP) of the formation and decomposition of ions **1a**$^+$–**3a**$^+$ were calculated by the DFT method at the



6$^+$

1,2-phehylenearsenium cation
(benzoarsacyclopropenyl cation)

Scheme 3.

Table 1
Total electronic energy at 0 K, E_{total}, of stationary points of the MERPs of radical cations $[6C,5H,2X,As]^{\bullet+}$ and of cations $[6C,5H,X,As]^{+}$, and the reaction enthalpy, ΔH_r^{298}, relative to the enthalpy of dihalogeno phenylarsane radical cation $C_6H_5AsX_2^{\bullet+}$ and halogeno phenylarsanyl cation $C_6H_5As^+X$ (X = F, Cl, Br; calculated by UBHLYP/6-31 1 + G(2d,p)/-/UBHLYP/6-31 + G(d))

Species	**1**, X = F		**2**, X = Cl		**3**, X = Br	
	E_{total} (hartree)	ΔH_r^{298} (kJ mol^{-1})	E_{total} (hartree)	ΔH_r^{298} (kJ mol^{-1})	E_{total} (hartree)	ΔH_r^{298} (kJ mol^{-1})
$C_6H_5AsX_2^{\bullet}$+	−2666.65318	0.00	−3387.44183	0.0	−7615.32690	0.0
$X^{\bullet}$	−99.73457		−460.15567		−2574.06239	
$C_6H_5As^+X + X^{\bullet}$	−2666.58165	191.6[a]	−3387.38899	142.4[a]	−7615.28480	113.0[a]
$C_6H_5As^+X$ (**a**$^+$)	−2566.84708	0.0	−2927.23332	0.0	−5041.22241	0.0
4-X-C6H5As$^+$H (**b**$^+$)	−2566.91427	72.3	−2927.28890	98.7	−5041.17572	114.7
X-arsatropylium (**c**$^+$)	−2566.79414	139.1	−2927.17590	151.0	−5041.15376	177.1
$\eta^{4-}(C_6H_5X)As^+$ (**η**$^+$)	−2566.78843	152.5	−2927.16575	175.9	−5041.14830	188.8
$C_6H_5As^{\bullet+}$ (**5**$^{\bullet+}$)	−2467.04486					
5$^{\bullet+}$ + $X^{\bullet}$	−2566.77943	429.2[a]	−2927.20053	336.7[a]	−5041.10725	297.8[a]
$C_6H_4As^+$ (**6**$^+$)	−2466.43916					
HX	−100.44113		−460.81576		−2574.70238	
6$^+$ + HX	−2566.88029	160.1[a]	−2927.25492	183.3[a]	−5041.14154	195.2[a]
(**6**$^+$ + HX)$_{\mathrm{complex}}$	−2566.89383	125.5	−2927.26409	160.7	−5041.15262	169.9
a$^+$-TS(elim)	−2566.83344	269.4	−2927.21309	284.2	−5041.10582	283.4
a$^+$-TS1	−2566.81372	334.3	−2927.22145	276.7	−5041.12119	258.4
b$^+$-TS1	−2566.81895	314.6	−2927.19400	339.8	−5041.08085	355.4
c$^+$-TS1	−2566.82053	315.9	−2927.20755	310.6	−5041.09924	
a$^+$-TS2	−2566.78546	404.4	−2927.19098	336.7		

[a] 2.47 kJ mol^{-1} added to account for RT.

level UBHLYP/6311 + g(2d,p)//UBHLYP/6-31g(d). The results are shown in Table 1. The data of Table 1 were used to construct a schematic reaction enthalpy profile which is shown in Fig. 4. Further, a selection of the calculated structures are depicted in Fig. 5.

The halogeno phenylarsenium ions $C_6H_5As^+X$, **a**$^+$, were found to be the most stable isomers. This and the rather low dissociation enthalpy calculated for the loss of $X^{\bullet}$ from the molecular ions of **1**–**3** support the assumption that arsenium ions of structure a$^+$ are formed by the fragmentation. As expected, the reaction enthalpy of the further fragmentation of ions a$^+$ to the 1,2-phenylene arsenium ion $C_6H_4As^+$, **6**$^+$, and HX is distinctly smaller than the reaction enthalpy of a generation of $C_6H_5As^{\bullet+}$, **5**$^{\bullet+}$, and $X^{\bullet}$. However, contrary to the loss of $X^{\bullet}$, the elimination of HX requires an extra activation barrier. In the case of the fluoro and chloro derivative **1a**$^+$ and **2a**$^+$, the corresponding transition state is located below the reaction enthalpy of the dissociation to $5^{\bullet+}$ and $X^{\bullet}$. Thus, only elimination of HX is predicted to occur for metastable **1a**$^+$ and **2a**$^+$, in agreement with the MIKE spectra of these ions. In the case of the bromo derivative **3a**$^+$, the reaction enthalpy for the loss of $Br^{\bullet}$ is calculated to be only 14.4 kJ mol^{-1} greater than the enthalpy of the transition state **3a**$^+$-TS(elim) of the HBr elimination. According to QET, the rate constant of a simple dissociation with a "loose" transition state rises more steeply with excess energy of the ions than the rate constant of a HX elimination with a "tight" transition state. Hence, ions of some excess energy should prefer simple dissociation even if this process requires somewhat more enthalpy. This prediction is again in agreement with the observation of competing losses of $Br^{\bullet}$ and HBr in the MIKE spectrum of **3a**$^+$. Therefore, the DFT calculations reflect correctly the experimental results of the fragmentations of ions **1a**$^+$–**3a**$^+$.

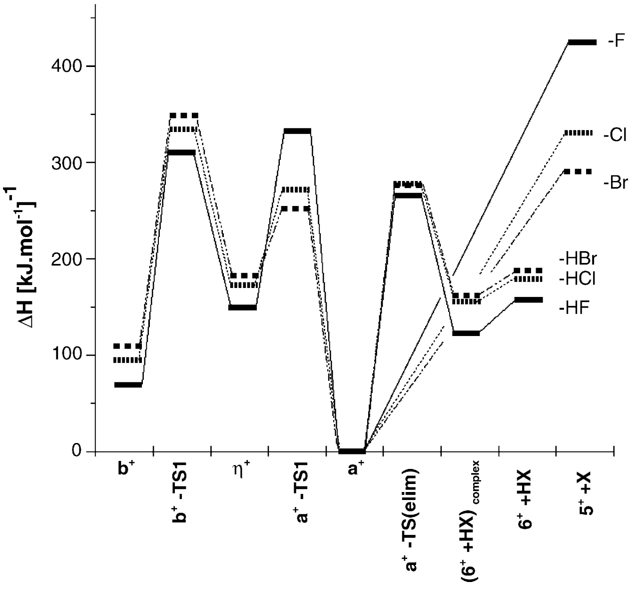


Fig. 4. Minimum reaction enthalpy pathway (MERP) of fragmentation and isomerization of halogeno phenylarsenium cations **1a**$^+$–**3a**$^+$ (arsa-tropylium ion **c**$^+$ not included). (▬) **1a**$^+$, (┅) **2a**$^+$, (▪▪▪) **3a**$^+$.

The reverse reaction enthalpy, $\Delta H_{\mathrm{rev}}^{\#}$, for the elimination of HX can be estimated from the data of Table 1 by the difference between ΔH_r^{298} of the transistion state **a**$^+$ TS(elim) and of the products **6**$^+$ + HX. In agreement with the experimental results $\Delta H_{\mathrm{rev}}^{\#}$, decreases in the series –HF (109.3 kJ mol^{-1}); –HCl (100.9 kJ mol^{-1}); –HBr (88.2 kJ mol^{-1}). The mean value of the KER, $\langle T \rangle$ of 845 meV (85 kJ mol^{-1}) is measured for **1a**$^+$ → **6**$^+$ + HF. This corresponds to about 78% of the calculated $\Delta H_{\mathrm{rev}}^{\#}$ so that a large fraction of $\Delta H_{\mathrm{rev}}^{\#}$ is released during the elimination. In the case of the elimination of HCl or HBr from **2a**$^+$ or **3a**$^+$, this fraction decreases to 55 and 40%. Thus, not

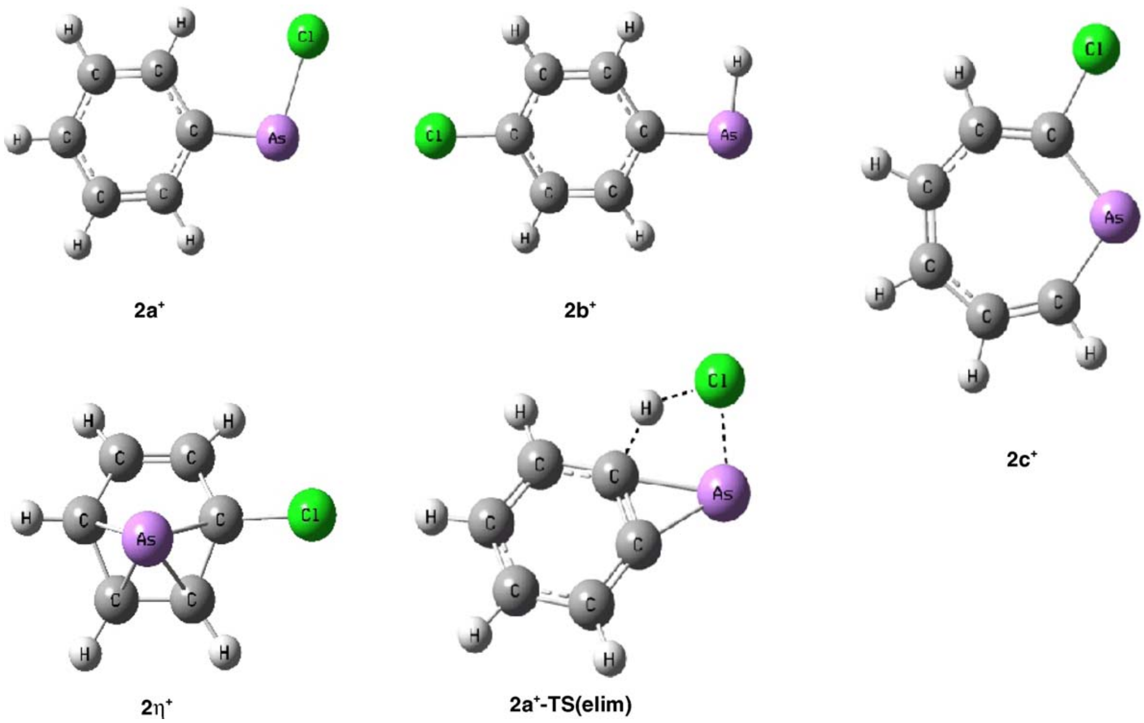


Fig. 5. Calculated structures (UBHLYP/6-311 + g(2d,p)//UBHLYP/6-31 + g(d)): chloro phenylarsenium cation **2a**$^+$, 4-chlorophenylarsenium cation **2b**$^+$, 1-chloro-7arsatropylium cation **2c**$^+$, 1-chloro-7-arsa-bicyclo[2.2.1]heptadien-7-yl cation **2η**$^+$, transition state **2a**$^+$-TS(elim) of HCl eliminatiom.

only the value of $\Delta H^{\#}_{\mathrm{rev}}$ decreases along the series **1a**$^+$–**2a**$^+$–**3a**$^+$ but also the fraction which is observed as KER during the elimination of HX. Such a behavior of the KER in a series of analogous fragmentations was repeatedly observed before [13] and was attributed to a shift of the position of the transition state along the reaction coordinate from a late position to an early one with a decreasing strength of the bond which is cleaved.

In view of the observation of identical KER during the elimination of HF and HCl from the isomers **1a**$^+$ **1b**$^+$ and **2a**$^+$/**2b**$^+$ which points to an interconversion of these isomers the MERP of this isomerization has also been analyzed by DFT calculations. The structure **a**$^+$ was always found to be more stable than isomer **b**$^+$ (see Table 1, Scheme 2, and Fig. 5). This reflects just the differences of the strength of the bonds As–H and As–X on the one side and C–H and C–X on the other side. In particular the weak As–H bond destabilizes structure **b**$^+$. The isomerization **a**$^+$ $\leftrightharpoons$ **b**$^+$ may occur in principle via the seven-membered ring structure of the arsatropylium ion **c**$^+$ (Table 1 and Fig. 5). This isomer **c**$^+$ is stable for all three systems $[C_6H_5AsX]^+$, X = F, Cl. Br although at distinctly higher enthalpies than **a**$^+$ and **b**$^+$. A direct rearrangement **a**$^+$ → **c**$^+$ via transition state **a**$^+$-TS2 needs high $\Delta H_{\mathrm{r}}^{298}$, so that this route of the isomerization is not very plausible. In fact, the prototype of an isomerization of aromatic cations, the interconversion of the benzyl cation and the tropylium ion, proceeds via an intermediate of the bicyclic structure of bicyclo [4.1.0] heptadienyl [14]. The corresponding 7-arsa-bicyclo [4.1.0] cycloheptatrienyl (not shown) is only in the case of [6C,5H, As,F]$^+$ a minimum of the potential energy hypersurface. In the other systems optimization of this structure produces structure **η**$^+$ (Scheme 2 and Fig. 5) which is also a stable isomer for [6C,5H,As,F]$^+$. Structure **η**$^+$ can be depicted as a distorted 7-arsa-bicyclo-[3.3.2]heptadien-7-yl cation, in which As$^+$ bridges a halogenobenzene ring in 1,4-position. This As-bridge is somewhat inclined towards C(2) and C(3) indicating a binding contact of As$^+$ also to these C atoms. This gives the isomer **η**$^+$ some character of a η^4-$C_6H_5XAs^+$ species in which As$^+$ is capping a halogenobenzene molecule. Structures of this type have been proposed Jemmis and Schleyer [15] and gain stability by a "three-dimensional aromaticity". In the present context one should note that isomer **η**$^+$ arises from **a**$^+$ and **b**$^+$, respectively, by a reductive elimination of As$^+$ from an As–X and As–H bond, and that **η**$^+$ replaces the electrostatically bonded ion/neutral complex as the central intermediate of the isomerization **a**$^+$ $\leftrightharpoons$ **b**$^+$ (Scheme 2). However, the isomer **η**$^+$ is always separated from **a**$^+$ and **b**$^+$ by large enthalpy barriers (Fig. 4) which prohibit a fast interconversion of all isomers before elimination of HX from **a**$^+$. An identical activation enthalpy of 241 ± 1 kJ mol^{-1} is calculated for the reductive elimination of As from the As–H bond of **1b**$^+$–**3b**$^+$. Even so, since **b**$^+$ becomes increasingly less stable than **a**$^+$ in this series, the transition state **b**$^+$-TS1 of the step **b**$^+$ → **η**$^+$ as well as transition state **a**$^+$-TS1 of step **a**$^+$ → **η**$^+$ are located above the transition state **a**$^+$-TS(elim) of the elimination of HX from **a**$^+$ (see Table 1 and Fig. 4). Thus, the DFT calculations predict an uni-directional rearrangement of **b**$^+$ to **a**$^+$ via **η**$^+$ instead of a fast mutual interconversion **a**$^+$ $\leftrightharpoons$ **η**$^+$ $\leftrightharpoons$ **b**$^+$ prior to the elimination of HX.

4. Conclusion

Ions [6C,5H,X,As]$^+$, (X = F, Cl, Br, I), corresponding to halogeno phenylarsenium ions of structure **a**$^+$ can be generated in the ion source of a tandem mass spectrometer by loss of $X^{\bullet}$ from the molecular ions of dihalogeno phenylarsanes $C_6H_5AsX_2$. Metastable ions $\mathbf{a}^+$ fragment by elimination of an HX molecule and/or by loss of an X atom. The preferred fragmentation route depends clearly on the strength of the As–X bond. As metastable ions, the fluoro and chloro derivative $\mathbf{1a}^+$ and $\mathbf{2a}^+$, respectively, eliminate only HF and HCl, while the bromo derivative $\mathbf{3a}^+$ undergoes losses of HBr and $Br^{\bullet}$ with similar intensities. The metastable iodo derivative $\mathbf{4a}^+$ decomposes only by loss of $I^{\bullet}$. The elimination of HX is accompanied by the release of substantial amount of kinetic energy (KER), so that dish-topped peaks are observed for this process in the MIKE spectra of $\mathbf{1a}^+$ and $\mathbf{2a}^+$ and a broad round-topped peak in the MIKE spectrum of $\mathbf{3a}^+$.

Further, the mean value $\langle T\rangle$ of KER decreases from 845 meV for $\mathbf{1a}^+$ to 550 meV for $\mathbf{2a}^+$ and 360 meV for $\mathbf{3a}^+$. Clearly, the competition between elimination of HX and of $X^{\bullet}$ as well as the KERD during the loss of HX from metastable arsenium ions $\mathbf{a}^+$ are diagnostic for the halogen X bonded to the As arom. This is of importance since an identical behavior, in particular identical KERD, has been observed for metastable halogeno (4-halogenophenyl)arsenium ions $Y–C_6H_4As^+–X$ and $X–C_6H_4As^+–Y$ during the loss of HX and HY, irrespectively whether X or Y was originally bonded to the As atom [16]. Therefore, the present results confirm the earlier supposal that only the halogen (either X or Y) at the As atom is lost from metastable $Y–C_6H_4As^+–X$ and $X–C_6H_4As^+–Y$, and that both isomers mutually interchange before the elimination of HX and HY. This isomerization proceeds by a reductive elimination of As^+ from the As–X bond or As–Y bond followed by an oxidative insertion of As^+ into the C–X or C–Y bond. In fact, an analogous rearrangement is observed in this study for halogeno phenylarsenium ions $\mathbf{a}^+$ since an identical KERD is found for the elimination of HF and HCl, respectively, from the metastable fluoro chloro phenylarsenium ions $C_6H_5As^+X$, $\mathbf{1a}^+$ and $\mathbf{2a}^+$, and the (4-fluorophenyl-) and (4-chlorophenyl)arsenium ion $XC_6H_5As^+–H$, $\mathbf{1b}^+$ and $\mathbf{2b}^+$.

The conclusions which are derived from the experimental results are substantiated by the results of a calculation of the thermochemistry of fragmentations and isomerization. The DFT calculations reveal the isomer $\boldsymbol{\eta}^+$ with a distorted structure of a 7-arsa-bicyclo[2.2.1]heptadien-7-yl as the central intermediate of the isomerization $\mathbf{a}^+ \leftrightharpoons \mathbf{b}^+$ by a reductive elimination/oxidative insertion cycle of As^+. An ion of structure $\boldsymbol{\eta}^+$ has already been found as an intermediate in the reactions of the phenylarsenium ion $C_6H_5As^+H$ [2]. Although the present results show that the rearrangement of phenylarsenium ions $\mathbf{a}^+$ and $\mathbf{b}^+$ to the isomer $\boldsymbol{\eta}^+$ requires substantial activation enthalpies, it is sensible to assume that ions of type $\boldsymbol{\eta}^+$ play an important role in the reactions of gaseous arylarsenium ions. In this respect ion $\boldsymbol{\eta}^+$ is a counterpart to the tropylium ion in the chemistry of gaseous aromatic hydrocarbon ions which has been extensively studied by Lifshitz [17].

Acknowledgment

The financial assistance of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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