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Ion/molecule reactions of phenylarsandiyl radical cation $C_6H_5As^{\bullet +}$ with methyl halogenides CH_3X ($X = Cl, Br, I$)

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Dedicated to Professor Diethardt Böhme on the occasion of his 65th birthday.

Abstract

The ion/molecule reactions of the phenylarsandiyl radical cation $C_6H_5As^{\bullet +}$, **1**$^{\bullet +}$, with methyl-halides CH_3X, X = Cl, Br, I, have been investigated using Fourier transform ion cyclotron resonance (FT-ICR) spectrometry. The radical cation **1**$^{\bullet +}$ exhibits in its valence electron shell a vacant molecular orbital as well as a single occupied orbital and an orbital containing an electron pair. Consequently, reactivity of an electrophilic carbenoid and/or an electrophilic radical is expected. No reaction is observed with CH_3Cl, while CH_3Br undergoes a slow reaction (reaction efficiency 1.2%) and CH_3I a fast reaction (reaction efficiency 21.6%) with **1**$^{\bullet +}$. In both reaction systems, the main product ion $C_6H_5As^+X$ is produced by radical substitution with transfer of the halogen atom X to **1**$^{\bullet +}$. The methylphenylarsenium ion $C_6H_5As^+CH_3$ is found as a second product ion in both systems but with distinctly less intensity. Unexpectedly, an ion $C_7H_7^+$ is observed as a third product only of the reaction system **1**$^{\bullet +}$/CH_3Br. Information about reaction enthalpies was obtained by theoretical studies which show that the reaction with CH_3Cl would be only slightly exothermic, if at all. Further, generation of the less abundant product $C_6H_5As^+CH_3$ is the more exothermic pathway for CH_3Br and CH_3I. This proves that reaction mechanisms and not reaction exothermicity determines the total rate constant and the branching ratio of the ion/molecule reactions observed. It is suggested that the mechanism for generation of $G_6H_5As^+X$ is electrophilically assisted radical substitution via formation of an intermediate adduct of electrophilic **1**$^{\bullet +}$ to an electron lone pair of the halogen of CH_3X. In contrast, C6H5As$^+CH_3$ is generated via insertion of the carbenoid **1**$^{\bullet +}$ into the C–X bond which yields a halogenomethylphenylarsane radical cation $C_6H_5As(X)CH_3^{\bullet +}$ as intermediate. According to the calculations, this insertion is strongly exothermic but requires obviously a substantial activation energy. The investigation of the fragmentations of $C_6H_5As(X)CH_3$ by tandem mass spectrometry corroborates these suggestions. Notably, only $C_6H_5As(Br)CH_3^{\bullet +}$, but not $C_6H_5As(I)CH_3^{\bullet +}$, generates abundant $C_7H_7^+$ions on fragmentation.

Keywords: Ion/molecule reaction; FT-ICR spectrometry; Kinetics; Organoarsenic derivatives; Phenylarsandiyl radical cation

1. Introduction

The monovalent organoelement derivatives R–E of the elements of the group 15 of the periodic table of elements (the former Vth main group of the pnictogens N–Bi) are isoelectronic with carbenes [1] and their higher element homologues. However, while the electronic state of carbenes—singlet or triplet state—depends on the type of substituents, nitrenes [2] and phosphinidenes [3] strongly prefer a triplet state. The chemistry of arsinidenes and higher element homologues has not been described in the literature, but it can be safely assumed that these carbenoid species exist mainly as triplets, so that the correct name is “arsandiyl diradical”. An ion *m*/*z* 152 of elemental composition [6C,5H,As] is omnipresent in the EI mass spectra of phenylarsanes [4]. The two most likely structures of this ion are an ionized phenylarsandiyl and an ionized 1,2-phenylenearsane, respectively. Theoretical calculations show [5] that the former is the more stable isomer, in agreement with the “heavy atom exclusion rule” [6] stating that structures with a terminal heavy main group element are the most stable isomers. Additionally, the calculations show that the ground state of the phenylarsandiyl radical cation $C_6H_5As^{\bullet +}$ is a doublet state, i.e., the electron is removed from one of the singly

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occupied SOMOs of the arsanediyl on electron ionization. This gives the phenylarsandiyl radical cation an interesting array of reactant orbitals at the As: an empty orbital, a singly occupied orbital and an orbital containing an electron pair. Accordingly, the phenylarsandiyl radical cation may undergo reactions as an electrophilic carbenoid, as a radical, and less likely as a nucleophile. These considerations stimulated a study of the ion/molecule reactions of the phenylarsandiyl radical cation with methyl halogenides by Fourier-transform ion cyclotron resonance (FT-ICR) spectrometry. It will be shown that the main reaction is halogen abstraction which is expected for radical reactivity but that other reaction modes do play a role.

2. Experimental

2.1. Compounds

The reactants methylchloride, methylbromide, and methyliodide are commercially available as pure compounds. The organoarsenic compounds used in this work were synthesized by standard techniques of synthetic chemistry using procedures given in the literature. Gaseous phenylarsandiyl radical cations were obtained by electron ionization induced dissociation of diiodophenylarsane. This compound was prepared by treatment of a suspension of dichlorophenylarsane in acetone with excess of KI [7]. Dichlorophenylarsane was synthesized by reaction of phenyl arsonic acid with PCl_3 [8], Chloromethylphenylarsane was made by chlorination of dimethylphenylarsane [9]. A treatment of a suspension of this chloro derivative in acetone with KBr and KI, respectively, afforded bromo- and iodomethylphenylarsane.

2.2. Mass spectrometry

EI mass spectra, mass analyzed kinetic energy (MIKE) spectra, and collision induced dissociation (CID) mass spectra were measured with a Micromass double focusing VG ZAB 2F mass spectrometer of B/E geometry. Sample introduction was performed by absorbing the liquid samples to powdered Na_2SO_4 and by inserting the impregnated powder with a sample probe with controlled temperature into the ion source. Standard EI mass spectra were obtained at an electron energy of 70 eV, an acceleration voltage of 8 kV, and an ion source temperature of about 200 °C. MIKE spectra were measured by focusing the selected ion into the second field free region after the magnetic sector by the appropriate setting of the magnet field and by scanning the electric sector field. Thirty to forty scans were accumulated to increase the signal-to-noise ratio. CID mass spectra were obtained in the same manner but by additionally introducing He as collision gas into the collision cell of the second field free region until the intensity of the precursor ion was reduced to about 50% of its original value.

2.3. FT-ICR spectrometry

All FT-ICR experiments were performed using a Spectrospin Bruker CMS 47× FT-ICR instrument [10] equipped with an infinity^{TM} cell [11], a 4.7 T superconducting magnet, a 24 bit/128 kword Aspect 3000 computer and an external ion source [12]. For kinetic measurements, ions were generated by 20 eV EI from diiodophenylarsane in the ion source of the FT-ICR spectrometer, and the mixture of the ions was focused into the FT-ICR cell by means of the transfer optic. The trapping voltages of the back and front plates were set to 1 ± 0.1 V and the voltages of the excitation plates were set to 0.0 ± 0.1 V. The phenylarsandiyl radical cation, m/z 152, was isolated by broad band (frequency sweep) ejection of 88 V_{p-p} and by rf pulses of 14 V_{p-p} fixed frequency ("single shots") ejections of all other ions. The ejection process was finished after 15–20 ms. To remove any excess kinetic energy prior to reaction, the ions were thermalized by collisions with argon added by a pulsed valve which was opened for 8–15 ms. The argon was removed after a delay time of 0.5 s. Fragment ions and product ions formed during this period were again ejected by irradiation with appropriate "single shots" of 14 V_{p-p}. This method of reactant-ion generation has been described in detail previously [13]. The methyl halogenide as the neutral reactant was introduced into the FT-ICR cell continuously by a leak valve resulting in a constant pressure of 3×10^{-8} mbar to 8×10^{-8} mbar. The pressure readings of the ionization gauge were corrected for the sensitivity of the neutral gas used [14] and were calibrated by rate measurements of the reaction $NH_3^{\bullet +} + NH_3 \rightarrow NH_4^+ + NH_2^\bullet$ ($k_{bi} = 21 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) [15]. The reaction time delay was varied from 1.5 ms to about 30 s. At the end of each reaction time, all ions were excited by a frequency sweep of 88 V_{p-p} with a step width of 7.8 kHz and an excitation pulse of 8 µs. FT-ICR spectra were averaged by eight data acquisition cycles and recorded by 32 k data points for up to 30 different reaction times. Intensities of peaks were obtained by exponential multiplication and Fourier transformation of the time domain signal. For kinetic evaluation, intensities of the peaks of the magnitude spectra were normalized to the sum of all ions detected at each reaction time. Then, the relative intensity of the ions was plotted against the reaction time to create a "kinetic plot". By fitting these data to an exponential decay function using the Microcal Origin 4.5 program, [16] the pseudo-first order reaction rate constant k_{exp} was obtained. The bimolecular rate constant k_{bi} was determined from k_{exp} by using the number density of the neutral reactant derived from the corrected pressure of the neutral reactant in the FT-ICR cell. For convenience, reaction efficiencies $\text{eff}[\%] = 100 \times k_{bi}/k_{cpt}$ are used in the discussions. The collision rate constant k_c was calculated using the method of Su and Chesnavich [17] .The reproducibility of k_{exp} is very good, but due to uncertainty of the measurement of the pressure of the neutral reactant, the error in k_{bi} (and of eff) is about 30%.

2.4. Computational details

Theoretical calculations were performed by using the program GAUSSIAN 03W [18] and choosing UBHLYP/6–311 + G(2d,p)//UBHLYP/6–31 + G(d)) as the level of theory for CH_3Cl and CH_3Br as reactants. Total energy at 0 K, E_{tot}, calculated at this level was combined with zero point energy (ZPE) and thermochemical corrections to the enthalpy H^0_{298} at 298 K, respectively, which were based on the BHLYP/6–31 + G(d) harmonic vibrational analysis. This afforded total energy differences at 0 K denoted as ΔE_0 and differences of the standard enthalpy at 298 K designated as ΔH^0_r to characterize the thermochemistry of the ion/molecule reactions. The basis set 6–31 does not include data for I. Hence, all theoretical calculations for the reactions system phenylarsandiyl radical cation/CH_3I were carried but with the smaller basis set 3–21 at the level UBHLYP/3–21g(d,p).

3. Results and discussion

A significant peak at *m*/*z* 152 of the phenylarsandiyl radical cation $C_6H_5As^{\bullet+}$. $\mathbf{1}^{\bullet+}$, is usually observed in the EI mass spectra of phenylarsanes. However, in most 70e V EI mass spectra, this peak is accompanied by a peak at *m*/*z* 151 of $C_6H_4As^+$ ions of similar intensity. This latter ion is especially abundant if difluoro- or dichlorophenylarsane is used as the precursor since the molecular ions $C_6H_5AsX_2{}^{\bullet+}$ (X = F, Cl), have a strong tendency to fragment by elimination of HX instead of $X^\bullet$ [19]. Since the satellite ions $^{13}C^{12}C_5H_4As^+$, *m*/*z* 152, interferes with $\mathbf{1}^{\bullet+}$ during the ion selection procedure of the FT-ICR experiment, diiodophenylarsane $C_6H_5AsI_2$ is the most appropriate precursor to prepare $\mathbf{1}^{\bullet+}$. This compound fragments only by subsequent losses of two I atoms [19]. Unfortunately, the MIKE spectrum of $\mathbf{1}^{\bullet+}$ reveals that $\mathbf{1}^{\bullet+}$ decomposes also by loss of H to generate an ion at *m*/*z* 151. This process is energetically favored likely because of the special stability of a 1,2-phenylenearsanyl cation, *m*/*z* 151, in which the large and empty 4p AO of As overlaps in the plane of the benzene ring with the singly occupied 2p arine orbitals of the 1,2-didehydrobenzene moiety. Nonetheless, besides a small fraction of non-reactive ions *m*/*z* 152, other interferences by the even-electron ion $^{13}C^{12}C_5H_4As^+$ are not observed in the kinetic experiments.

No reaction is observed between $\mathbf{1}^{\bullet+}$ and methylchloride under the experimental conditions used. Therefore, the rate constant k_bi of this reaction system is below 0.5×10^{-11} cm^3 molecule^{-1} s^{-1} or the reaction efficiency is below 0.1%. The reactions of $\mathbf{1}^{\bullet+}$ with methylbromide and methyliodide are faster yielding total rate constants $k_\mathrm{bi} = 1.35 \times 10^{-11}$ cm^3/molecule^{-1}/s^{-1} and 22.2×10^{-11} cm^3/molecule^{-1}/s^{-1} and reaction efficiency 1.2 and 21.6%, respectively. The kinetic plots of these reactions are shown in Figs. 1 and 2. The main reaction product, which accounts for about 80% of the product ions at the end of the reaction, is the halogenophenylarsenium ion $C_6H_5As^+X$, X = Br or I. A second product ion corresponds to the rnethylphenylarsenium ion $C_6H_5As^+CH_3$. Interestingly, the $C_7H_7{}^+$ ion, either benzyl cation or tropylium ion, is generated as a third product ion of considerable abundance in the reaction system $\mathbf{1}^{\bullet+}/CH_3Br$, but not in the system $\mathbf{1}^{\bullet+}/CH_3I$.

The enthalpy of formation of relevant arsenic compounds and ions is not available for an estimation of the enthalpy ΔH^0_r of these ion/molecule reactions. Therefore, the reaction enthalpies were obtained by theoretical studies. The results are collected in Table 1. It has to be noted that only the small vasis set 3–21 was available for the calculations of iodo species. Although some of the imperfections of these low level calculations should have canceled in the relative reaction enthalpies $\Delta H^{298}_\mathrm{r}$, the calculated thermochemical values for the reaction system $\mathbf{1}^{\bullet+}/CH_3I$ must be taken with cation. The most plausible mechanism for the formation of the main product ion $C_6H_5As^+X$ is a radical substitution or halogen atom abstraction [20] of $\mathbf{1}^{\bullet+}$ from CH_3X. The theoretical calculations show that $\mathbf{1}^{\bullet+}$ forms a stable encounter complex with CH_3X in which electrophilic $\mathbf{1}^{\bullet+}$ is attached to the halogen X (Scheme 1). The exothermicity of the addition increases with the nucleophilicity of X, so that in particular the addition complex of CH_3I is formed with a large amount of excess energy. The excited complex dissociates either back to reactants or by loss of the methyl radical. Thus, the formation of the halogenophenylarsenium ion can be viewed as an electrophilically assisted radical substitution process. Note that the addition complex corresponds to a distonic halonium ion and that the loss of $CH_3{}^\bullet$ by a simple homolytic cleavage of the C–X bond would result in the excited triplet state of the product ion $C_6H_5As^+X$. Generation of this ion in its ground state requires a considerable structural change and a reorganization

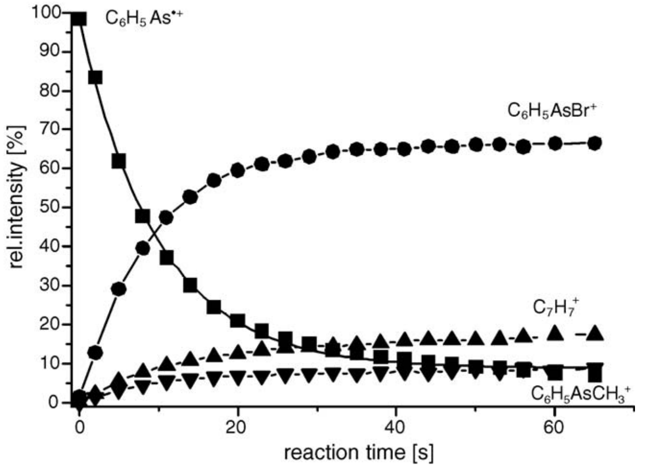


Fig. 1. Reaction of phenylarsenium ion $\mathbf{1}^{\bullet+}$ with CH_3Br ($p_{CH_3Br} = 3.6 \times 10^{-7}$ mbar).

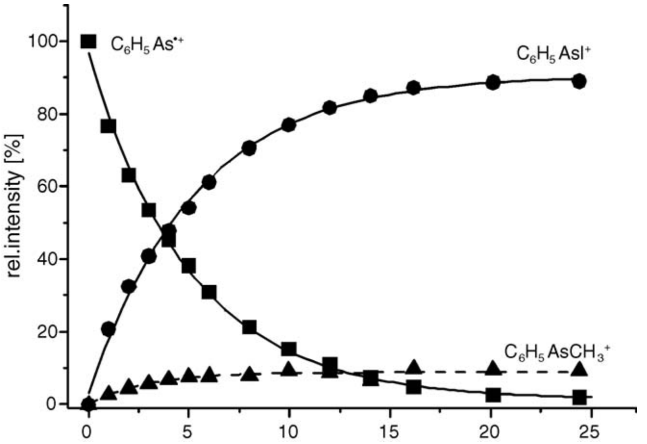
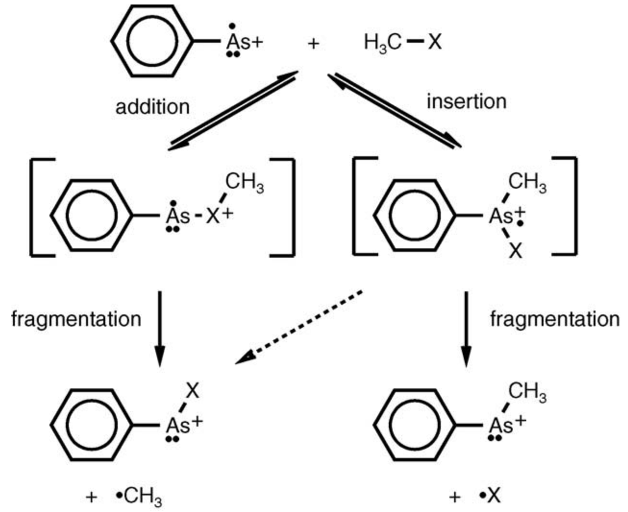


Fig. 2. Reaction of phenylarsenium ion $\mathbf{1}^{\bullet+}$ with CH_3I ($p_{CH_3I} = 7.6 \times 10^{-8}$ mbar).



Scheme 1.

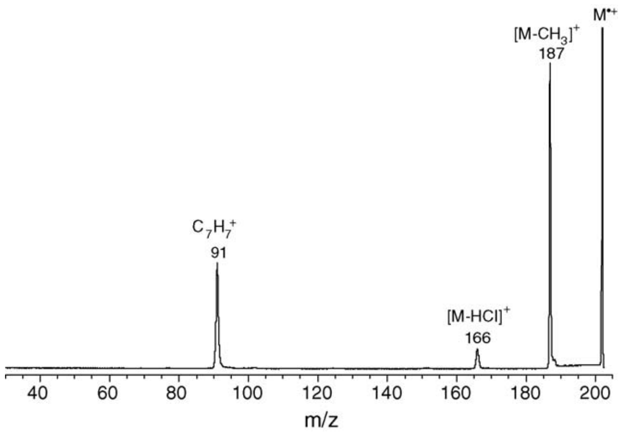


Fig. 3. MIKE spectrum of molecular ions of $C_6H_5As(CH_3)^{35}Cl$, $\mathbf{2}^{\bullet+}$.

of the valence electrons of the $C_6H_5As^+X$ moiety. Therefore, likely some extra activation enthalpy is involved in this substitution [20].

In the case of methylchloride as neutral reactant, Cl abstraction is only slightly exothermic, and because of the expected activation barrier, this reaction is not observed. The reactions of $\mathbf{1}^{\bullet+}$ with CH_3Br and CH_3I are calculated to be increasingly more exothermic, and the main reaction is abstraction of the Br- or I-atom resulting in formation of the halogenophenylarsenium ion. Nonetheless the reaction of $\mathbf{1}^{\bullet+}$ with CH_3Br is slow with eff = 1.2%, typically of a thermoneutral or weakly endotherrnic process. The obvious explanation is that the reaction enthalpy of $-31.4\,\mathrm{kJ\,mol^{-1}}$ for the radical substitution is counterbalanced by an activation enthalpy of similar size. Thus, only the I atom abstraction with a calculated ΔH_r^0 of $-101.7\,\mathrm{kJ\,mol^{-1}}$ leads to a fast reaction of $\mathbf{1}^{\bullet+}$ and CH_3I.

The formation of the less abundant product ion, methylphenylarsenium ion $G_6H_5As^+CH_3$, is calculated to be more exothermic than halogen atom abstraction for X = Br and I (see Table 1). Clearly, the branching between the reaction channels is determined by activation barriers $\Delta H_r^{\#}$ along the reaction path and not by ΔH_r^0. A likely mechanism for the generation of the methylphenylarsenium ion is the insertion of $\mathbf{1}^{\bullet+}$ into the C–X bond of CH_3X which is analogous to the reaction of an electrophilic carbene. The initial product of the insertion reaction is the corresponding halogenomethylphenylarsane radical cation $C_6H_5As(CH_3)\mathbf{X}^{\bullet+}$ ($\mathbf{2}^{\bullet+}$ X = Cl, $\mathbf{3}^{\bullet+}$ X = Br, $\mathbf{4}^{\bullet+}$ X = I; see Scheme 1). The theoretical calculations show that the formation of the insertion products $\mathbf{2}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ is quite exothermic (see Table 1). In the diluted gas phase of the FT-ICR cell, ΔH_r^0 remains with the insertion product ion and induces subsequent decompositions. The fragmentation of excited $\mathbf{2}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ can be investigated by MIKE spectra of these ions which are shown in Figs. 3–5.

Metastable ions $\mathbf{2}^{\bullet+}$ decompose mainly by loss of a $^{\bullet}CH_3$ radical while loss of the Cl ligand is not observed. An interesting feature is the formation of the $C_7H_7^+$ ion, and it is shown elsewhere that this ion arises by a rearrangement which is typical of CH_3 ligands at the As atom of phenylarsanes [21]. However, none of the fragmentation products of $\mathbf{2}^{\bullet+}$ is observed as a product ion of an ion/molecule reaction. Therefore, $\mathbf{2}^{\bullet+}$ is possibly not generated by an ion/molecule of $\mathbf{1}^{\bullet+}$ because of a considerable activation barrier of the insertion process. The

Table 1

Total energy at 0 K, E_{tot}, [hartree] and enthalpies at 298.15 K, ΔH^{298} [hartree], of reactants and possible products of the ion/molecule reactions of phenylarsanediyl radical cation and halomethanes, and the relative reaction enthalpy, ΔH_r^{298} [$\mathrm{kJ\,mol^{-1}}$] (X = Cl, Br: calculated by UBHLYP/6–31 1 + G(2d,p)//UBHLYP/6–31 + G(d); X = I: UBHLYP/3–21lG(d,p))

Species	X = Cl			X = Br			X = I		
	E_{tot}	ΔH^{298}	ΔH_r^{298}	E_{tot}	ΔH^{298}	ΔH_r^{298}	E_{tot}	ΔH^{298}	ΔH_r^{298}
$C_6H_5As^{\bullet+}$	−2467.04486	−2466.94463	–	−2467.04486	−2466.94463	–	−2455.21532	−2455.11417	–
CH_3X	−500.10661	−500.06327	–	−2613.99547	−2613.95268	–	−6930.29350	−6930.25106	–
$C_6H_5As^{\bullet+}$+CH_3X	−2967.15147	−2967.00790	0.0	−5081.04033	−5080.89731	0.0	−9385.50882	−9385.36523	0.0
$C_6H_5As(X)CH3^{\bullet+}$	−2967.22339	−2967.07854	−187.9	−5081.11583	−5080.97106	−196.1	−9385.62397	−9385.47790	−298.3
$C_6H_5AsCl^+$	−2927.32970	−2927.22523	–	−5041.22230	−5041.11789	–	−9345.93549	−9345.83038	–
$CH_3^{\bullet}$	−39.82616	−39.79139	–	−39.82616	−39.79139	–	−39.60867	−39.57360	–
$C_6H_5AsX^+ + CH_3^{\bullet}$	−2967.15586	−2967.01662	−22.9	−5081.04846	−5080.90928	−31.4	−9385.54416	−9385.40398	−101.7
$C_6H_5AsCH_3^+$	−2506.99510	−2506.85340	–	−2506.99509	−2506.85340	–	−2494.97313	−2494.83020	–
$X^{\bullet}$	−460.15567	−460.15331	–	−2574.06239	−2574.06003	–	−6890.58856	−6890.58620	–
$C_6H_5AsCH_3^+ + X^{\bullet}$	−2967.15077	−2967.00671	3.1	−5081.05748	−5080.91343	−42.3	−9385.56169	9385.41640	−134.4
$(C_6H_5As^{\bullet+} + CH_3X)$	−2967.19542	−2967.04900	−105.4	−5081.08935	−5080.94346	−119.0	−9385.59575	−9385.44943	−223.5

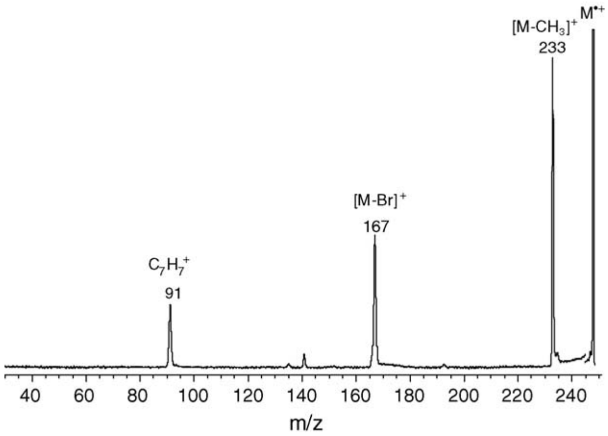


Fig. 4. MIKE spectrum of molecular ions of $C_6H_5As(CH_3)^{79}Br$ **2**$^{\bullet+}$.

MIKE spectrum of the bromo derivative **3**$^{\bullet+}$ (Fig. 4) exhibits signals for the bromophenylarsenium ion (loss of CH_3, *m/z* 233), the methylphenylarseniurn ion (loss of Br, *m/z* 167), and for the $C_7H_7^+$ cation (*m/z* 91). Interestingly, these three ions correspond to the product ions of the ion/molecule reaction of **1**$^{\bullet+}$ with CH_3Br (see Fig. 1). The relative intensities of the ions are different in the MIKE spectrum and in the product ion spectrum at the end of the reaction, but of course the internal energy of the precursor ion **3**$^{\bullet+}$ is different in both experiments. Increasing the internal energy of **3**$^{\bullet+}$ by collision with He results in a CID spectrum, which contains a series of small peaks of fragment ions none of which are observed as product ions of the ion/molecule reaction besides the phenylarsanyl radical cation, *m/z* 152. A second effect is a considerable increase of the relative intensity of the bromophenylarsenium ion. This would be in agreement with the intensity distribution of the product ions of the reaction of **1**$^{\bullet+}$ and CH_3Br. However, it remains dubious whether insertion of **1**$^{\bullet+}$ into the C–Br bond of CH_3Br and fragmentation of the resulting **3**$^{\bullet+}$ is the only source of the product ions. More likely, a combination of the insertion/fragmentation mechanism and of the halogen atom abstraction mechanism occurs.

This is also the outcome of a comparison of the product ions of the ion/molecule reaction of **1**$^{\bullet+}$ with CH_3I and of the fragment ions of metastable **4**$^{\bullet+}$ The MIKE spectrum of **4**$^{\bullet+}$ (Fig. 5) displays only a single signal for the methylphenylarsenium ion (loss of I, *m/z* 167). Neither the iodophenylarsenium ion, *m/z* 279, nor the $C_7H_7^+$ ion, *m/z* 91, is observed. Obviously the loss of I is energetically so favorable that other process cannot compete. Even in the CID mass spectrum of **4**$^{\bullet+}$, only small amounts of ions *m/z* 279 and *m/z* 91 are found. The absence of $C_7H_7^+$ ions in the MIKE spectrum of **4**$^{\bullet+}$ agrees with the absence of this ion among the product ions of the ion/molecule reactions of **1**$^{\bullet+}$ with CH_3I. Note that the main product ion, the iodophenylarsenium ion, is not observed in the MIKE spectrum and only weakly in the CID spectrum of **4**$^{\bullet+}$. Hence, on the one hand, all of the iodophenylarsenium ions of the product ion spectrum of the ion/molecule reaction have to be generated by iodo atom abstraction, and on the other hand, all of the methylphenylarsenium ions are produced by the insertion/fragmentation mechanism. In this case, the branching ratio abstraction/insertion of the two reaction mechanisms is simply reflected by the intensity ratio 9/1 of the two product ions at the end of the reaction. Therefore, the electrophylically assisted radical substitution of the halogen by **1**$^{\bullet+}$ is by far the main reaction for CH_3I and likely also for CH_3Br, while the oxidative insertion of the eletrophilic carbenoid **1**$^{\bullet+}$ into the C-halogen bond is of less importance.

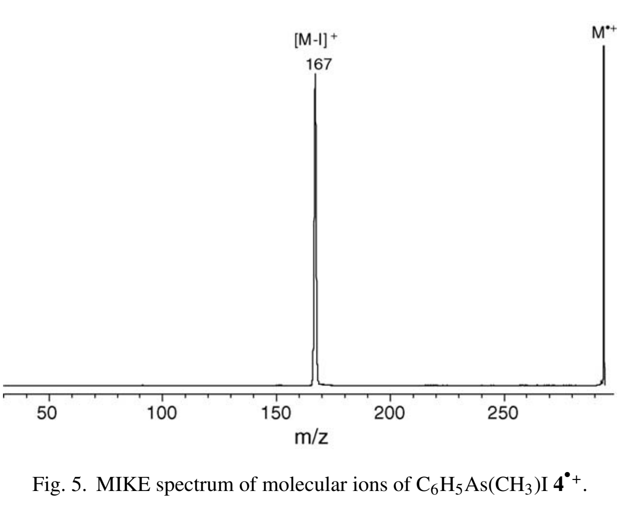


Fig. 5. MIKE spectrum of molecular ions of $C_6H_5As(CH_3)I$ **4**$^{\bullet+}$.

4. Conclusion

The phenylarsandiyl radical cation $C_6H_5As^{\bullet+}$, **1**$^{\bullet+}$, undergoes a slow ion/molecule reaction with CH_3Br and a fast one with CH_3I yielding in both cases the halogenophenylarsenium ion $C_6H_5As^+X$ as the main product ion. A second reaction product ion is the methylphenylarsenium ion $C_6H_5As^+CH_3$, and, in the case of CH_3Br as reactant, $C_7H_7^+$ ions. No reaction is observed with CH_3Cl. The assumption, that this order of reactivity is a consequence of the corresponding reaction enthalpy, was verified by theoretical calculations. These calculations show that the electrophilic **1**$^{\bullet+}$ may experience exothermic addition to the halogen atom of CH_3X, but a subsequent fragmentation of this energetically excited intermediate by the loss of a $CH_3^\bullet$ radical is sufficiently exothermic only for X = Br and I. Thus, mechanism of the transfer of the X atom from CH_3X to the radical cation **1**$^{\bullet+}$ can be viewed as an electrophilically assisted radical substitution process. Remarkably, the formation of the methylphenylarsenium ion by loss of the halogen atom from the collision complex of the reactants is the more exothermic reaction pathway. In spite of this, the methylphenylarsenium ion is only a minor reaction product. Clearly the reaction pathway for generation of this product ion includes a substantial activation barrier. A clue for the mechanism of this reaction is the observation, that the product spectra of the ion/molecule reaction and of the fragment ions observed in the MIKE spectra of the corresponding molecular ions of $C_6H_5As(X)CH_3^{\bullet+}$ are identical. In particular, $C_7H_7^+$ ions are only observed in both types of spectra for X = Br. It is suggested that the second reaction mode of the ion/molecule reactions of **1**$^{\bullet+}$ with CH_3X corresponds to an insertion of the carbenoid **1**$^{\bullet+}$ into the C–X bond. The insertion product is energetically excited $C_6H_5As(X)CH_3^{\bullet+}$ which may fragment by loss of $^\bullet X$. However, this insertion process requires very likely a considerable activation enthalpy.

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References

[1] (a) R.A. Moss, Acc. Chem. Res. 22 (1988) 15;
(b) M.S. Platz, Acc. Chem. Res. 28 (1995) 487.

[2] W.T. Borden, N.P. Gritsan, C.M. Hadad, W.L. Karner, C.R. Kemnitz, M.S. Platz, Ace. Chem. Res. 33 (2000) 765.

[3] (a) M. Driess, H. Grützmacher, Angew. Chem. Int. Ed. Engl. 35 (1996) 827;
(b) A.H. Cowley, Acc. Chem. Res. 30 (1997) 445;
(c) K. Lammertsma, Top. Curr. Chem. 229 (2003) 95.

[4] M.R. Litzow, T.R. Spalding, Mass spectrometry of inorganic and organometallic compounds series inorganic physical chemistry, in: M.F. Lappert (Ed.), Monograph 3, Elsevier Scientific Publ. Co., Amsterdam, London, New York, 1973.

[5] M. Letzel, D. Kirchhoff, H.-F. Grützmacher, D. Stein, H. Grützmacher, Dalton Trans., submitted for publication.

[6] V.I. Minkin, M.N. Glujhovtsev, B.Y. Simkin, Atomaticity and Antiaromaticity, Wiley, New York, 1994.

[7] W. Steinkopf, D. Schwen, Chem. Ber. 54 (1921) 1437.

[8] R.J. Garascia, G.W. Batzis, J.O. Kroeger, J. Org. Chem. 23 (1960) 1271.

[9] W. Steinkopf, W. Mieg, Chem. Ber. 53 (1920) 1017.

[10] M. Allemann, H.P. Kellerhals, K.P. Wanczek, Int. J. Mass Spectrom. Ion Processes 46 (1983) 139.

[11] P. Caravatti, M. Allemann, Org. Mass Spectrom. 26 (1991) 514.

[12] P. Kofel, M. Allemann, H. Kellerhals, K.P. Wanczek, Int. J. Mass Spectrom. Ion Phys. 65 (1985) 97.

[13] D. Thölmann, H.-F. Grützmacher, J. Am. Chem. Soc. 113 (1991) 3281.

[14] J.E. Bartmess, R.M. Georgiadis, Vacuum 33 (1983) 149.

[15] (a) V.G. Anicich, J. Phys. Chem. Ref. Data 22 (1993) 1506;
(b) V.G. Anicich, An Index of the Literature for Bimolecular Gas Phase Cation-molecule Reaction Kinetics, JPL Publication, 2003.

[16] Microcal Origin 4.1, Microcal Software Inc., Northampton, MA 01060 USA, 1996.

[17] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.

[18] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Gross, G. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, I. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Pittsburgh, PA (2003), Gaussian 03, Revision B.04.

[19] D. Kirchhoff, H.-F. Grützmacher, H. Grützmacher, H. Eur. J. Mass Spectrom. 10 (2005) 857.

[20] (a) J.M. Tedder, Angew. Chem. Int. Ed. Engl. 21 (1982) 433;
(b) S. Shail, A. Shueki, Angew. Chem. Int. Ed. Engl. 38 (1999) 586;
(c) H. Fischer, L. Radom, Angew. Chem. 113 (2001) 1380.

[21] (a) D; Kirchhoff, H.-F. Grützmacher, H. Grützmacher, submitted for publication;
(b) D. Kirchhoff, Tandem-massenspektrometrische Untersuchungen-Struktur und Redktivität von ionisierten Arylelementverbindungen der 5. Hauptgruppe, PhD-Dissertation, Universität Bielefeld, 1999.