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Atmospheric pressure ionization and gas phase ion mobility studies of isomeric dihalogenated benzenes using different ionization techniques

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Abstract

Ion mobility spectrometry (IMS) featuring different ionization techniques was used to analyze isomeric *ortho-*, *meta-* and *para-*dihalogenated benzenes in order to assess how structural features affect ion formation and drift behavior. The structure of the product ions formed was investigated by atmospheric pressure chemical ionization (APCI) mass spectrometry (MS) and IMS-MS coupling. Photoionization provided $[M]^+$ ions for chlorinated and fluorinated compounds while bromine was cleaved from isomers of dibromobenzene and bromofluorobenzene. This ionization technique does not permit the different isomers to be distinguished. Comparable ions and additional clustered ions were obtained using ^{63}Ni ionization. Depending on the chemical constitution, different clustered ions were observed in ion mobility spectra for the separate isomers of dichlorobenzene and dibromobenzene. Corona discharge ionization permits the most sensitive detection of dihalogenated compounds. Only clustered product ions were obtained. Corona discharge ionization enables the classification of different structural isomers of dichlorobenzene, dibromobenzene and bromofluorobenzene.

Keywords: Ion mobility spectrometry; Atmospheric pressure ionization; Mass spectrometry; Dihalogenated benzenes

1. Introduction

Ion mobility spectrometry (IMS) permits the simple, rapid determination of organic compounds by fieldable and transportable devices [1,2]. The IMS technique is successfully used in a number of different fields including security [3], military [4], petrochemical [5] and environmental analysis [6] as well as diagnostics [7,8], process control [9] and air pollution control [10]. We applied the IMS technique for the determination of halogenated benzenes in environmental samples [6]. Ion mobility spectrometers can be used as individual units or coupled with separation techniques (GC [11] or HPLC [12]) for the analysis of complex mixtures or as a separation technique for mass spectrometry [13].

The principle of IMS is based on determining the drift velocities (v_d) attained by ionized sample molecules in the weak electric field of a drift tube at atmospheric pressure.

Different techniques can be used for ion formation in gas phase at atmospheric pressure. ^{63}Ni ionization sources are commonly used in IMS for the ionization of neutral sample molecules [14,15]. Positive product ions are formed mainly via proton-transfer reactions [16] depending on the gas-phase basicities of the compounds investigated as well as on the temperature and drift gas used [17,18]. Photoionization (PI) and corona discharge (CD) ionization were developed as non-radioactive ionization sources in IMS. PI enables compounds to be determined with an ionization energy below the energy emitted by the radiation source used. According to the literature, the most likely ionization pathway provides $[M]^+$ product ions [19]. Using CD ionization, positive product ions may be formed via different processes due to the varying strength of the electric field around the corona needle. Electron impact, photoionization and proton-transfer reactions can all initiate the formation of product ions [20]. However, the formation of product ions can generally be affected by subsequent ion–molecule reactions for all the aforementioned techniques [21].

After being ionized, the ions formed are separated within the drift tube and the drift velocities are determined, which

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are proportional to the mobility (K) of ions. Ion mobility is influenced by the operational parameters used as well as the mass of analytes (m) and their collisional cross section. The collisional cross section (Ω_D) includes structural parameters (physical size and shape) and the resultant electronic factors describing the ion-neutral interaction forces [22,23]. The theory of ion mobility has been extensively described elsewhere [24,25].

The influence of ionic mass on ion mobility can be described by mass-to-mobility correlation curves, which are known for a large number of substances. By contrast, the effect of structural differences on the ionization pathways and drift behavior is not completely understood.

Our aim was to determine what structural features affect ion formation or drift behavior in ion mobility spectrometry depending on the ionization technique used. Therefore, we investigated sets of isomeric dihalogenated benzenes using ^{63}Ni ionization, CD ionization and PI to estimate the influence of molecular structure on ionization pathways and drift behavior. In order to limit the number of variables influencing the ion mobilities of various compounds to ionic mass (m) and structure (Ω_D), we applied identical instrumentation and operational parameters (drift gas, gas flows, temperature). The investigation of isomers enables mass effects to be neglected.

Previously, studies of isomeric compounds were only performed using ^{63}Ni ionization [26] and include branched and unbranched ketones, thiocyanates, isothiocyanates [27], phthalic acids [28], halogenated nitrobenzenes [29], amines [30], anilines [31], E/Z isomers [32], diamines [33] and nitrogenous heterocycles as well as aromatics substituted by functional groups [34]. Isomeric dihalogenated benzenes were investigated by Carr [35] using ^{63}Ni ionization. Different ion mobility spectra were obtained for 1,2- and 1,3-disubstituted compounds. Separate isomers were assumed to display different drift behavior.

However, investigations of non-polar constitutional isomers of hydrocarbons [36,37] showed that differences in isomers' ion mobility spectra primarily result from the formation of different ions. We wanted to establish whether these results can be transferred to more polar substances. Therefore our study included the application of different ionization techniques in IMS, the structure elucidation of product ions formed by mass spectrometric (MS) investigations and IMS/MS measurements, as well as the calculation of molecular properties in order to assess their influence on ion mobility spectra.

2. Experimental

2.1. Ion mobility measurements

The substances used in this study had a purity of about 99% and were obtained from Fluka, Sigma-Aldrich and Merck. Their purity was verified by gas chromatography.

The details of the sample introduction system used for IMS and its function were described previously [38]. Liquid samples of about 300 μl of the compounds investigated were sealed in polyethylene permeation tubes. The permeation tubes, which had a volume of 1 ml and a wall thickness of 0.5 mm, were placed inside a temperature-controlled glass column. The solid samples of 1,4-dichlorobenzene and 1,4-dibromobenzene were put into an open vessel and also placed inside the glass column.

Purified and dried ambient air was pumped through the glass column containing the permeation tube at a constant flow of 25 l/h at temperatures of 30 °C (liquid samples) or 70 °C (solid samples). The sample gas stream was split using flow controllers. A defined amount of sample gas stream was rarefied with purified and dried ambient air. The flow rate of this total gas stream into the IMS was kept constant (25 l/h). The concentration of the compounds in the sample gas stream was calculated using the weight loss of the permeation vessels over a certain time. The moisture content of the gas streams was controlled by a moisture sensor AMX1 (Panametrics). Gas-drying by silica gel and purification by charcoal yielded a relative humidity of about 2.4% (−25 °C dew point ±3 °C).

The measurements were performed with BRUKER RAID 1 ion mobility spectrometers [20]. With the exception of ionization, all the measuring parameters were kept constant to ensure identical operational parameters (membrane inlet, gas flow, temperatures in inlet system, ionization region and drift tube) were used for all the measurements. The standard operating characteristics used for the ion mobility spectrometers are listed in Table 1.

Series of measurements with increasing concentrations were carried out for each compound in order to estimate any concentration correlation of ion mobility spectra. The reduced mobility values (K_0 values) were calculated according to the conventional equation [39]:

$$K_0\,(\mathrm{cm^2/Vs}) = \left(\frac{d}{t \times E}\right)\left(\frac{p}{760}\right)\left(\frac{273}{T}\right) \qquad (1)$$

where d is the drift length (cm), t is the drift time (s), E is the field strength (V/cm), p is the pressure (Torr) and T is the temperature (K).

2.2. Mass-spectrometric measurements

Two different techniques were used to identify the product ions formed. The photoionization source was directly used as the ion source of an API-III tandem mass spectrometer from PE-SCIEX (Toronto, Canada). A 10 eV krypton lamp served as the radiation source. The samples were introduced gaseously via permeation tubes as described above. The ionization source works at ambient temperature and ambient moisture. Ambient air was used as carrier gas.

To analyze product ions formed by ^{63}Ni ionization, ion mobility spectrometry–mass spectrometer coupling was used. Coupling these techniques usually entails adjusting

Table 1
Standard operating characteristics for BRUKER RAID 1 ion mobility spectrometers

	^{63}Ni ionization	Photoionization	Corona discharge
Ionization	555 MBq	10 eV (Kr lamp)	10^6 V/cm
Identical features for all spectrometers used			
Inlet system	Membrane inlet		
Membrane	Dimethylsilicone		
Inlet temperature	80 °C		
Flow system	Bidirectional flow system		
Carrier flow rate	25 l/h (air)		
Drift flow rate	25 l/h (air)		
Shutter opening time	30 μs		
Temperature of drift tube	50 °C		
Electric field	Approximately 245 V/cm		

the operational parameters of the ion mobility spectrometer due to the small sample amount which can be transferred to the mass spectrometer and the necessary compatibility of the electric fields between the two devices. For these reasons, the measurements were taken with a longer shutter pulse (2.2 ms) and a modified electric field design within a higher concentration range of compounds. Although the ion mobility spectra obtained using common spectrometers cannot be completely reproduced with this coupling, the general structures of product ions formed can still be assigned. IMS-MS couplings are currently only available using ^{63}Ni ionization. The experimental and technical details of the IMS-MS coupling were described previously [37]. The mass spectra were all obtained with 1000 accumulations due to the low concentration within a mass range of 10–300 amu.

2.3. Calculation of molecular surfaces and volumes

The Connolly surfaces [40] and volumes of the molecules were calculated on the basis of optimized molecular geometries with the CERIUS^2 software suite (Accelrys Inc., San Diego, USA). Geometry optimization was performed using the semi-empirical AM1 method [41] integrated into the SPARTAN 5.0 suite (Wavefunction, Inc., Irvine, USA).

3. Results and discussion

A detailed list of the compounds investigated and their physicochemical properties is given in Table 2. The ionization energies of compounds are below 10 eV and permit direct ionization using PI with the krypton lamp (10 eV).

3.1. Ion mobility spectra

The positive ion mobility spectra of dihalogenated compounds investigated reveal significant differences depending on the ionization technique used. The positive spectra were detected using CD and ^{63}Ni ionization as well as photoionization (PI). PI and ^{63}Ni ionization were used to capture the negative spectra. The ion mobility spectrometer equipped

Table 2
Physicochemical properties of the compounds investigated

	m/z	IE (eV)	AE (eV)	Surface (Å^2)	Volume (Å^3)
1,2-Dichlorobenzene	146	9.06	12.92 (−Cl)	141.344	117.955
1,3-Dichlorobenzene	146	9.10	13.3 (−Cl)	137.372	115.336
1,4-Dichlorobenzene	146	8.92	13.2 (−Cl)	142.982	118.154
1,2-Dibromobenzene	234	8.98	12.16 (−Br)	149.124	126.794
1,3-Dibromobenzene	234	9.01	12.15 (−Br)	146.275	124.734
1,4-Dibromobenzene	234	8.82	12.17 (−Br)	150.968	127.398
1,2-Difluorobenzene	114	9.29	n.a.	126.324	100.772
1,3-Difluorobenzene	114	9.33	n.a.	121.965	98.830
1,4-Difluorobenzene	114	9.16	15.5 (−F)	123.954	99.528
1,2-Chlorofluorobenzene	130	9.17	13.94 (−Cl)	126.539	104.765
1,3-Chlorofluorobenzene	130	9.22	13.40 (−Cl)	129.385	106.893
1,4-Chlorofluorobenzene	130	9.10	13.30 (−Cl)	130.728	107.364
1,2-Bromofluorobenzene	174	9.12	n.a.	132.163	110.396
1,3-Bromofluorobenzene	174	9.18	n.a.	132.830	110.832
1,4-Bromofluorobenzene	174	9.01	n.a.	133.610	111.195

IE: ionization energy (http://webbook.nist.gov/). AE: appearance energy of fragment ions (http://webbook.nist.gov/) (n.a.: not available). Surfaces and volumes of molecules were calculated using CERIUS^2.

with CD ionization used cannot work in negative mode. Such a device was recently introduced by Khayamian et al. [42]. The results of all the measurements are summarized in Table 3. The drift times detected exhibit deviation of 0.06 ms using the experimental conditions described above. This variation provides differences in the reduced mobility values calculated of about 0.01 cm^2/Vs. These differences evidently arise from small differences in air constitution and moisture.

CD ionization permits the most sensitive detection of the substances investigated. An average concentration range between 0.5 and 20 $\mu g/l$ was detected. The measurements were started with the visual formation of product ions up to a decrease in reactant ion intensity of about 80%. The use of PI and ^{63}Ni ionization requires concentrations between 20 and 300 $\mu g/l$. However, the concentrations determined are very specific for the introduction system described above due to the different adsorptive capacities of connecting tubes as well as for the spectrometers used due to the specific permeability of compounds transferring the membrane inlet. However, all spectrometers were equipped with a comparable membrane inlet system. No correlation was found

Table 3
Reduced mobility values and mass-spectrometric data for the compounds investigated

	Product ion peaks detected					*m/z*	
	^{63}Ni (+)	^{63}Ni (−)	PI (+)	PI (−)	CD	^{63}Ni MS	UV MS
1,2-Dichlorobenzene	1.83 1.71 [S]	RIN	1.84 [1.55]	PE	1.70	146 (100) 148 (60)	146 (100) 148 (60)
1,3-Dichlorobenzene	1.84 1.74 [S] 1.67	RIN	1.83	PE	1.67	($M^{\bullet+}$)	($M^{\bullet+}$)
1,4-Dichlorobenzene	1.82 1.79 [S]	RIN	1.82	PE	1.71		
1,2-Dibromobenzene	1.72 1.61 [S]	RIN 2.49 [S]	1.72	PE	1.61	171 (100) 173 (100) 136 (40)	234 (70) 236 (100) 238 (70)
1,3-Dibromobenzene	1.71 1.56 [S]	RIN 2.50 [S]	1.70	PE	1.57	47 (40) $[MBr]^{\bullet+}H_2O$	($M^{\bullet+}$)
1,4-Dibromobenzene	1.84 [1.70]	RIN 2.50 [S]	1.70	PE	1.70		
1,2-Difluorobenzene	1.99 1.76	RIN	1.99	PE	1.79	111 (100) 93 (25)	114 (100)
1,3-Difluorobenzene	2.00 1.75	RIN	2.00	PE	1.78	($M^{\bullet+}$)	($M^{\bullet+}$)
1,4-Difluorobenzene	2.00 1.76	RIN	2.00	PE	1.79		
1,2-Chlorofluorobenzene	1.92 1.76	RIN	1.92 [1.46]	PE	1.74	130 (100) 128 (40) 132 (35)	130 (100) 132 (35)
1,3-Chlorofluorobenzene	1.92 1.74	RIN	1.91	PE	1.73	($M^{\bullet+}$)	($M^{\bullet+}$)
1,4-Chlorofluorobenzene	1.92 1.75	RIN	1.91	PE	1.74		
1,2-Bromofluorobenzene	1.85 1.69 [S]	[2.44] RIN 2.03 [S]	1.84	PE	1.69	114 (100) 112 (65) 136 (45) 208 (30)	174 (100) 176 (100)
1,3-Bromofluorobenzene	1.84 1.68 [S]	[2.45] RIN 2.04 [S]	1.84	PE	1.67	($?^{\bullet+}$)	($M^{\bullet+}$)
1,4-Bromofluorobenzene	1.85 1.69 [S]	RIN 2.05 [S]	1.85	PE	1.69		

Reduced mobility values (cm^2/Vs). RIN (rectant ions negative): no product ion peaks detectable. PE (photoelectrons): no product ion peaks detectable. Peaks in ion mobility spectra detectable as shoulder of main peak [S] or in very low intensities [ ]. ( ): Relative intensity of peaks in mass spectra (%).

between the specific variation in ion mobility spectra and the concentrations used.

PI provides one product ion peak for nearly all compounds in positive mode. The product ion peaks exhibit a sharp, symmetric peak profile. A significant shift in reduced mobilities was observed for these peaks depending on the molecular mass of the substances measured. Additional product ions were only observed for 1,2-dichlorobenzene (1.55 cm^2/Vs) and 1,2-chlorofluorobenzene (1.46 cm^2/Vs) with very low intensities. No significant differences in ion mobility spectra were established for the separate *ortho*-, *meta*- and *para*-disubstituted isomers of each compound.

The positive ion mobility spectra obtained by ^{63}Ni ionization consist of two product ion peaks for nearly all compounds. One product ion peak with the same reduced mobility value in comparison to PI was observed for all substances as the main peak in positive ion mobility spectra. Exceptional behavior was observed for 1,4-dibromobenzene where the peak obtained by PI (1.70 cm^2/Vs) appears as a shoulder of the main peak (1.84 cm^2/Vs). The second peak in the ion mobility spectra of all the other substances appears at lower reduced mobility values. This shift to higher drift times indicates the higher ionic mass of these product ions. In contrast to the main peak of spectra, different reduced mobility values were observed for these additional product ion peaks depending on the position of substituents. A lower reduced mobility value was observed for the *meta*-disubstituted compounds of dichlorobenzene (1.67 cm^2/Vs) and dibromobenzene (1.56 cm^2/Vs) in comparison to the *ortho*- and *para*-disubstituted isomers. Differences in reduced mobility values of 0.01 cm^2/Vs between these isomers were observed for bromofluorobenzene, difluorobenzene and chlorofluorobenzene. However, these differences may arise from the specific variation of the spectrometers used. Differentiation was ascertained between the reduced mobility values of *ortho*- and *para*-isomers of dichlorobenzene (1.71 and 1.79 cm^2/Vs) and dibromobenzene (1.61 and 1.70 cm^2/Vs) while the *ortho*- and *para*-disubstituted isomers of difluorobenzene, chlorofluorobenzene and bromofluorobenzene provide comparable ion mobilities.

CD ionization provides ion mobility spectra consisting of one product ion peak. The reduced mobility values are comparable with those obtained for additional product ions formed by ^{63}Ni ionization for nearly all substances. The deviating drift behavior of *meta*-disubstituted isomers can be established for dichlorobenzene (*ortho*/*para*: 1.70/1 cm^2/Vs, *meta*: 1.67 cm^2/Vs), dibromobenzene (*ortho*: 1.61 cm^2/Vs, *meta*: 1.57 cm^2/Vs, *para*: 1.70 cm^2/Vs) and bromofluorobenzene (*ortho*/*para*: 1.69 cm^2/Vs, *meta*: 1.67 cm^2/Vs). Difluorobenzene (1.78/9 cm^2/Vs) and chlorofluorobenzene (1.73/4 cm^2/Vs) provide differences of 0.01 cm^2/Vs and cannot be clearly attributed to structural effects.

In Fig. 1, a comparison of ion mobilities from two sources is shown by graphing reduced mobility values for ions formed in the PI source versus reduced mobility values for ions created in the CD source for each substance investigated. ^{63}Ni ionization provides identical ions compared with PI and CD ionization (clustered ions). Since PI of these chemicals will lead evidently to M^+ ions, this comparison was intended to disclose the degree of clustering expected from protonated (MH^+) or cluster ions and their hydrates. In the plot, ions from dihalogenated benzenes created by CD were uniformly larger (lower K_0 value) than ions created in the PI source, with one exception of *para*-dibromobenzene. This shift of reduced mobility values and the different dependence of K_0 values on the ionic mass indicate the occurrence of clustered product ions. The formation of clustered ions results evidently from

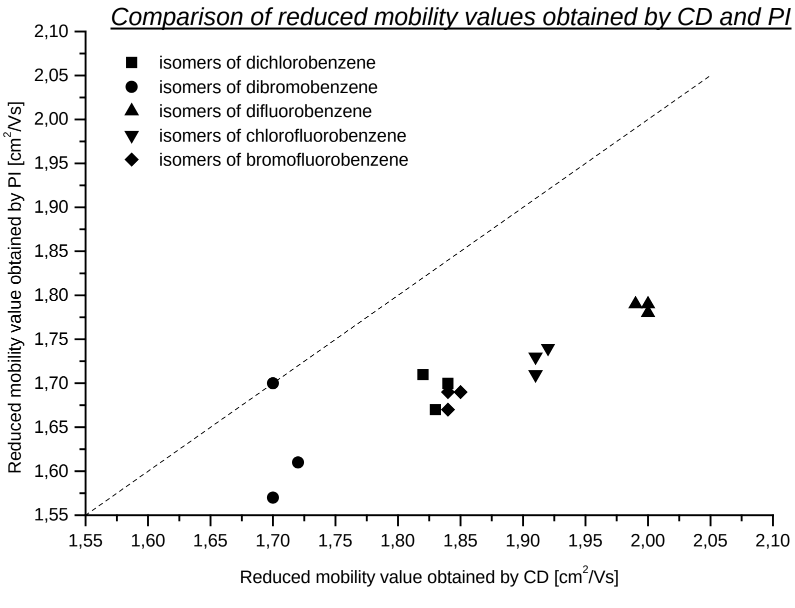

Fig. 1. Comparison of reduced mobility values obtained by PI and CD ionization.

ion–molecule interaction or associations of ions formed with the supporting atmosphere. Therefore, a complex mixture of ions can be observed for ^{63}Ni ionization. These product ions are formed by proton attachments as well as by the aforementioned reaction with the supporting atmosphere (NO^+, H_2O^+, $NH_4{}^+$). These reactions at atmospheric pressure evidently provide clustered ions. Whether ions with a different degree of clustering or comparable ions with a different drift behavior due to changes in collision surface are formed cannot be determined from the comparison of reduced mobility values shown in Fig. 1. A similar behavior of separate *ortho*-, *meta*- and *para*-isomers of difluorobenzene, chlorofluorobenzene and bromofluorobenzene can be observed regarding the general ionization pathways. As can be seen from Fig. 1, a deviating behavior was established for the isomers of dichlorobenzene and dibromobenzene. The ionization reactions provide different clustered ions depending on the chemical constitution.

Negative product ions were only observed for dibromobenzene using ^{63}Ni ionization. The peak detected at 2.50 cm^2/Vs can evidently be attributed to bromide cleaved from dibromobenzene due to dissociative electron attachment. The preferred elimination of halogens from brominated aromatics in comparison to chlorinated or fluorinated benzenes is explained by the lower bond strengths. The bond strength of C_6H_5–Br (81 kcal/mol) is lower than C_6H_5–Cl (96 kcal/mol) or C_6H_5–F (126 kcal/mol) [43]. Apart from dibromobenzene [44], the values for dihalogenated isomers are not known from the literature, although a similar behavior can be anticipated.

The negative ions obtained by PI are not characteristic for the substances investigated. The photoelectrons detected are almost the same. The formation mechanism of these ions is not yet clearly understood.

Fig. 2 illustrates by way of example the results of all the ion mobility measurements performed for the isomers

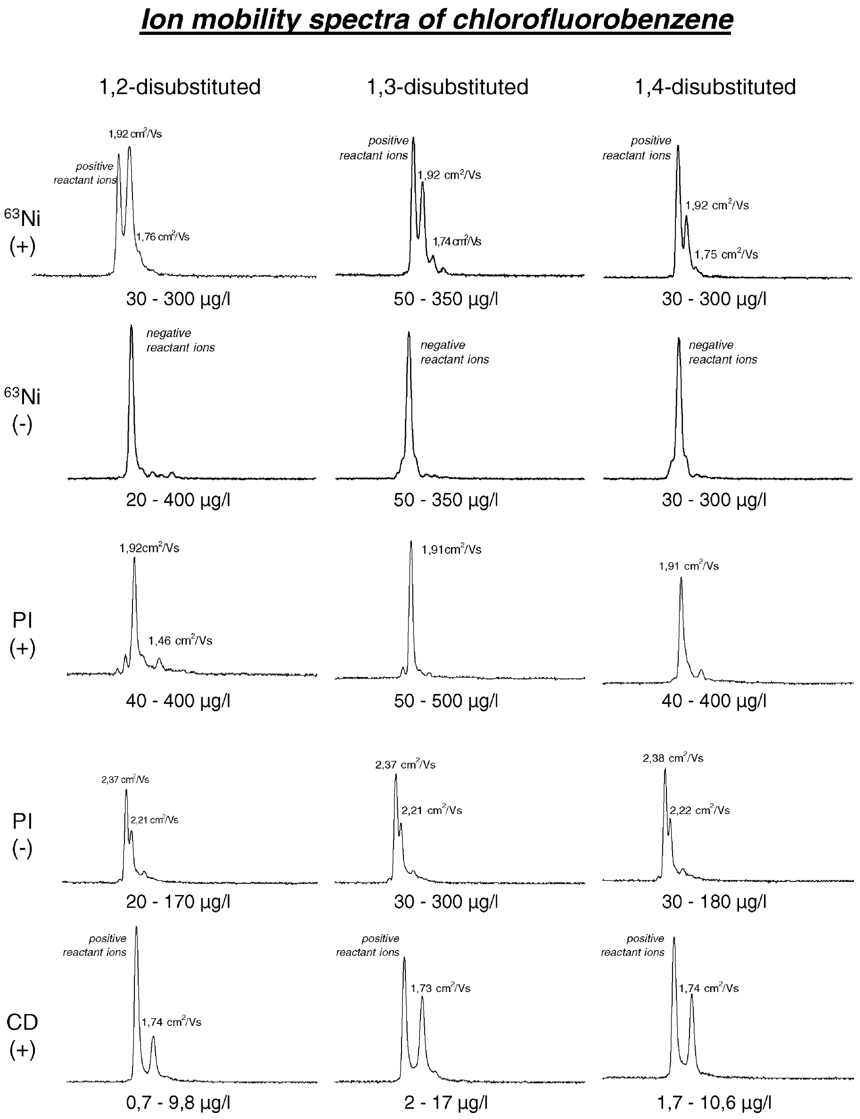

Fig. 2. Product ions of chlorofluorobenzene obtained by ion mobility spectrometry using different ionization techniques.

of chlorofluorobenzene. A series of spectra was captured within the concentration range shown in Fig. 2 using each ionization technique. The reduced mobility values of product ions shown were unchanged through the whole concentration range.

The results established using ^{63}Ni ionization are comparable with those obtained by Carr [35]. Although different experimental conditions were used (temperatures of IMS: approximately 220 °C, N_2 as carrier and drift gas), differences in drift times of 1,2- and 1,3-dichlorobenzene ($\Delta = 0.18$ ms) and dibromobenzene ($\Delta = 0.30$ ms) were found in positive spectra. No differences were established for 1,2- and 1,3-difluorobenzene. In contrast to our investigations, only single peaks were observed for these compounds. The different drift velocities were attributed to differences in the average collisional cross section of $[M]^+$ product ions.

3.2. Peak assignment

Different techniques were used to elucidate the structures of product ions formed. Mass-to-mobility correlation curves were derived on the basis of the reduced mobility values calculated. The mass-spectrometric measurements were performed to determine the structure of product ions formed under the conditions of APCI. Only this combination of ion mobility measurements using different ionization techniques and mass spectrometry enables the processes of ion formation to be understood. The mass-spectrometric measurements by themselves do not permit structural elucidation due to the different concentration ranges and different experimental conditions. Furthermore, the stability of clustered ions in the transition from the ambient pressure region of ion mobility spectrometer to the high vacuum of mass spectrometer is not known from the literature.

The most likely ionization pathway using PI provides $[M]^+$ product ions. As can be seen from Table 2, the krypton lamp (10 eV) used in our experiments permits direct ionization while the formation of fragment ions requires higher energies. Therefore, a mass-to-mobility correlation curve was derived on the assumption that $[M]^+$ ions are formed (Fig. 3).

As can be seen from Fig. 3, a linear relationship between molecular masses and reduced mobility values can be observed for dichlorobenzene, difluorobenzene and chlorofluorobenzene. The formation of $[M]^+$ product ions can be assumed for these substances. The small peak obtained for chlorofluorobenzene at 1.46 cm^2/Vs can be assigned to a dimer product ion ($[M_2H]^+$) using this curve. Deviating behavior is observed for bromine-containing substances. The position of these points in the diagram indicates a lower ionic mass than expected for $[M]^+$ ions. A different drift behavior can be concluded from the different slope of the mass-to-mobility function for these substances. However, the comparison of the ion mobility spectrum of dibromobenzene (1.70 cm^2/Vs) with the spectrum obtained for bromobenzene (1.89 cm^2/Vs) [45] shows that the product ions of dibromobenzene do not result from the elimination of bromine. Obviously, the product ions of brominated aromatics are formed via substitution reactions. However, these ions cannot be clearly attributed to certain structures. This peak assignment can be used for the main peaks in ion mobility spectra obtained by ^{63}Ni ionization, too. $[M]^+$ or $[MH]^+$ ions are formed. The additional product ions detected at lower reduced mobilities can be attributed to cluster ions due to their higher ionic mass.

The mass-spectrometric investigations confirm the deviating behavior of brominated compounds. These measurements were performed with the 1,2-disubstituted isomers of

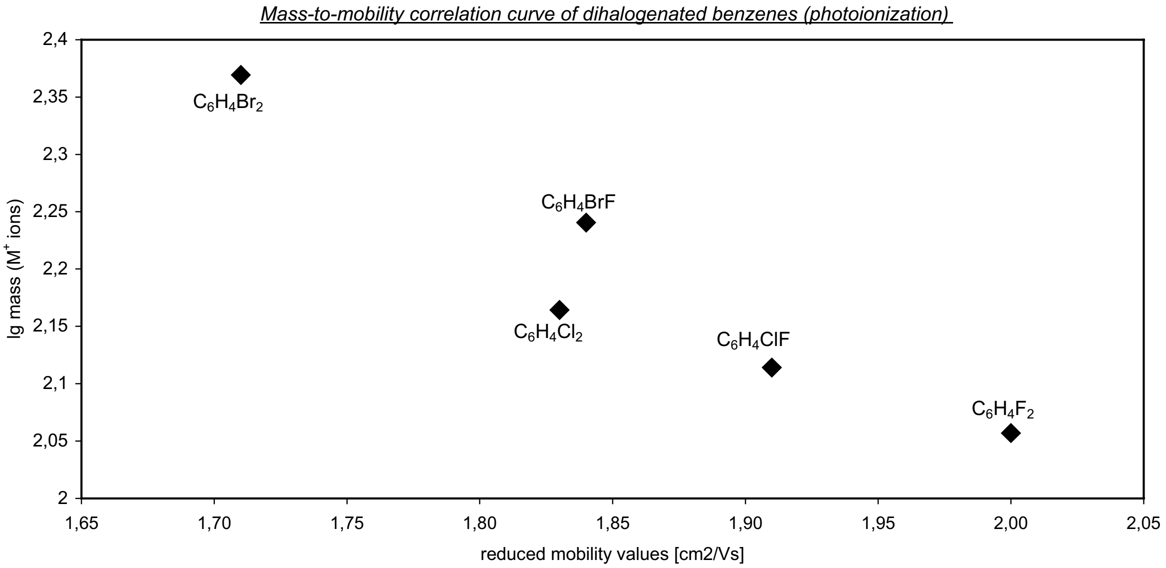

Fig. 3. Mass-to-mobility correlation curve for dihalogenated benzenes.

each compound. The summarized results for isomers investigated are shown in Table 3. Molecular ion peaks $[M]^+$ were detected for *ortho*-difluorobenzene, *ortho*-dichlorobenzene and *ortho*-chlorofluorobenzene with both ionization techniques used. The typical isotopic pattern was detected for chlorine containing substances. Therefore, the main peaks in ion mobility spectra obtained by PI and ^{63}Ni ionization can be clearly attributed to $[M]^+$ or $[MH]^+$ ions for these compounds. Molecular ions were detected for brominated aromatics using PI-MS coupling. In contrast to this technique, IMS-MS coupling provides main peaks at $m/z = 171$ and $m/z = 173$ for 1,2-dibromobenzene ($m/z = 234$) and a main peak at $m/z = 114$ for 1,2-bromofluorobenzene ($m/z = 174$). These mass numbers indicate the replacement of bromine and the formation of clustered product ions. The peak intensities of main peaks detected for 1,2-dibromobenzene (1:1) indicate the presence of bromine in the fragment ion. The formation of $[(M\text{-}Br)^+H_2O]$ can be supposed for 1,2-dibromobenzene. A single peak was detected for 1,2-bromofluorobenzene. Therefore, the elimination of bromine can be supposed. The exact structure for the ions of bromofluorobenzene cannot be determined. The mass spectra obtained do not indicate typical mass differences between the molecular ions and ions detected.

Although the ion mobility spectra after ^{63}Ni ionization detected at the front of the mass spectrometer exhibit the additional product ions, these ions could not be detected in mass spectrum. The higher concentrations evidently suppress the detectability of clustered ions, which compared to $[M]^+$ ions only occur in small concentrations.

Fig. 4 illustrates the results of the mass-spectrometric measurements performed for the isomers of chlorofluorobenzene by way of example.

3.3. Molecular surfaces and volumes

Using constant operational parameters, ion mobility is determined by the masses of molecules investigated and their collisional cross section. A correlation between the collisional cross section and ion mobility can be expected for each set of isomers in our investigation due to their identical mass.

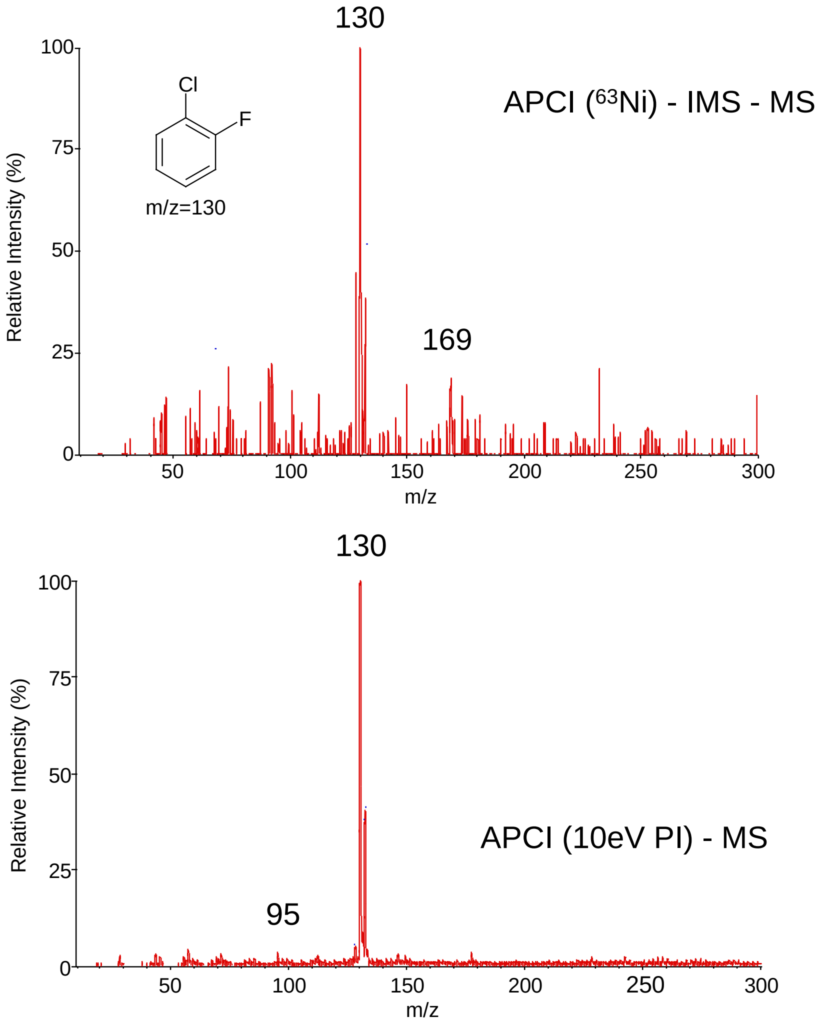

Fig. 4. Product ions of chlorofluorobenzene obtained by APCI-MS.

The surfaces and volumes of neutral sample molecules were calculated as a rough approximation of the collisional cross section. We assumed that the geometry of benzene rings only alters insignificantly if $[M]^+$ ions are formed or that all the molecules investigated change in a comparable manner. The data calculated are summarized in Table 2 for the compounds analyzed.

For difluorobenzene, dichlorobenzene and dibromobenzene, the calculation of surfaces and volumes of molecules provides the smallest molecular size for 1,3-disubstituted compounds while 1,2- and 1,4-dihalogenated compounds exhibit comparable values. However, a maximum deviation of 4% was established for the surfaces calculated, while the differences in the volumes of molecules do not exceed 2.5% for the individual isomers of each substance.

As can be seen from the ion mobility spectra obtained by PI, no differences in drift behavior were established for the different isomers of these compounds—a finding which tallies with aforementioned results.

However, the formation of clustered ions causes differences in ion mobility spectra obtained by ^{63}Ni ionization and CD ionization. Whether different product ions are formed depending on the position of halogens or the chemical ionization reaction provides ions with different physicochemical properties which affect the drift behavior cannot be unambiguously determined from the investigations here.

4. Conclusion

$[M]^+$ ions are formed using PI and ^{63}Ni ionization for the isomers of dichlorobenzene, difluorobenzene and chlorofluorobenzene. The structural differences of *ortho*-, *meta*- and *para*-isomers are not sufficient to cause differences in the drift behavior of $[M]^+$ or $[MH]^+$ ions. Product ions of brominated compounds are formed by cleavage of bromine via substitution reactions. However, comparable drift times can be detected for the isomers of these compounds. Therefore, a comparable ionization pathway can be supposed.

Clustered ions are formed by ^{63}Ni ionization and CD ionization. The drift times detected for clustered ions using these techniques vary for the isomers of dichlorobenzene, dibromobenzene and partly for bromofluorobenzene.

The differences in collisional cross section of isomeric compounds are not sufficient to provide different drift times if $[M]^+$ ions are formed. However, ionization reactions at atmospheric pressure form clustered ions with different drift behavior depending on the position of substituents. The most deviating behavior was observed for 1,3-dihalogenated compound.

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