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Response of halogenated compounds in ion mobility spectrometry depending on their structural features

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ABSTRACT

Ion mobility spectrometry (IMS) with handheld and transportable devices permits the sensitive detection of chlorinated compounds which are important in environmental monitoring. The ion mobility spectra in negative measuring modus mostly show one product ion peak [$(H_2O)_nCl^-$] due to dissociative electron attachments. In this paper, we investigated relevant chlorinated compounds (R–Cl) where R represents allyl-, benzyl-, phenyl-, alkyl- and vinyl-groups. These groups cause differences in the R–Cl bond strength and differences in the cleavage of chlorine can therefore be expected. All chlorinated substances investigated provide the same product ion peak at 2.75 $cm^2\,Vs^{-1}$ independent on the different C–Cl bond strength. However, distinct influences of structural features on the peak intensities of the $(H_2O)_nCl^-$ product ion peak were established. Generally, increasing sensitivities were obtained in the order chlorobenzenes < vinyl- < allyl- < alkyl compounds < benzylchlorides. Sensitivities and limits of detection (LODs) of aromatic compounds depend on the nature and position of second substituent. Electron-withdrawing substituents (chlorine, fluorine, nitrile) enhance sensitivity while electron-repelling substituents decrease it. A dependence of sensitivity on the chain length or ring size can be observed for alkyl compounds. Additional influences of intramolecular interactions on the sensitivity were found for di-halogenated compounds. Therefore, the quantification of negative product ion peaks of chlorinated compounds requires a consideration of structural features of analytes.

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1. Introduction

Ion mobility spectrometry (IMS) has been developed as an analytical technique for detecting and identifying volatile and semi-volatile organic compounds. IMS was originally used for the detection of warfare agents. However, this method becomes more and more popular in field analytical chemistry and process control due to the features of ion mobility spectrometers. The devices are configured as transportable and handheld units which work with batteries or accumulators. Furthermore, no additional gas supply is necessary if the spectrometer is equipped with a closed drift gas circuit. In contrast to other field screening techniques, ion mobility measurements provide characteristic spectra for substances investigated and do not only provide a sum signal [1].

Ion mobility spectrometers are today commonly used for different applications including homeland security [2], military [3], petrochemical analysis [4] and environmental monitoring [5] as well as medical diagnostics [6,7], process control in industry [8] and air pollution control [9]. An estimated number of 90,000 spectrometers are in use worldwide.

Ion mobility measurements base on the determination of drift velocities which ionized sample molecules attain in a weak electric field of a drift tube at atmospheric pressure. The ions are gated into the drift tube as an ion swarm via an electronic shutter grid which is briefly opened at a given time interval of few microseconds. In the drift tube, the ions move as a swarm toward a detector down a voltage gradient through a gas atmosphere provided by a flow of purified air or nitrogen, usually in a direction opposite that of ion motion. The ions traverse the drift region of ~5–15 cm in a few milliseconds. The drift time of an ion swarm can be associated with the ions through mass, charge and collision cross-section, which includes structural parameters (physical size and shape) and the electronic factors describing the ion-neutral interaction forces. Therefore, ions with different mass and/or structure attain different drift velocities providing a basis for separation of ions in IMS analyzers [10].

Determining ion mobilities initially requires the formation of ions from neutral sample molecules. The method of ionization most commonly used in IMS analyzers today is chemical ionization initiated with a radioactive source, typically 100 or 300 MBq of Nickel (^{63}Ni) or Tritium (^{3}H).

In addition to positive reactant ions, negative ions are also being formed in an ion source principally through the attachment of thermalized electrons to molecular oxygen. The dominant reaction

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pathway provides $(H_2O)_nO_2^-$ as reactant ions in addition to various adducts such as $(H_2O)_nO_2O_2^-$ or $(H_2O)_n(CO)_2O_2^-$. Negative product ions are mainly formed from neutral sample molecules (MX) due to charge transfer reactions and include dissociative electron attachments (Eq. (1)):

$$(MX) + (H_2O)nO_2^- \rightarrow M + X^- + nH_2O + O_2 \qquad (1)$$

and associative electron attachments according to Eq. (2):

$$(MX) + (H_2O)nO_2^- \rightarrow (MX)O_2^- + nH_2O \qquad (2)$$

Negative product ions from chlorinated compounds are mainly formed via dissociative charge transfer. Chlorinated compounds therefore provide well-defined spectra consisting of one major peak which can be attributed to $(H_2O)_nCl^-$ ions.

As known from previous investigations, ion mobility based techniques permit the sensitive detection of chlorinated compounds in negative polarity [11]. Halogenated substances belong to the most widespread pollutants in the environment [12]. For this reason, IMS became an effective field screening technique in environmental chemistry and process control. However, a variety of halogenated substances from different chemical classes with different physicochemical properties occurs in the environment and must be analyzed. As known, different substances with varying properties can cause different detector's responses [10]. Therefore, one aim of our study was to determine the response of negative ions formed from chlorinated compounds depending on their structural features. Furthermore, we wanted to investigate whether calibration curves are applicable for classes of substances or each substance requires an individual calibration.

For this purpose, we investigated substances from different chemical classes with importance in environmental monitoring including chlorobenzenes ($R–C_6H_4–Cl$), chlorinated vinyl- ($R–CH{=}CH–R$), allyl- ($CH_2{=}CH–CH_2–R$), alkyl ($CH_3–(CH_2)_n–CH_3$) compounds and benzylchlorides ($R–C_6H_4–CH_2–Cl$).

Although the first investigations of chlorinated compounds with IMS were performed in the early seventies of the last century by Karasek et al. and Carr [13–16], no systematic investigations of different classes of halogenated compounds are known to our knowledge. In these investigations mono-halogenated, di-halogenated benzenes and halogenated nitrobenzenes were determined using IMS in negative polarity. Related studies were done by DePuy et al. using mass spectrometry where gas-phase S_N2 and E2 reactions of alkyl halides were investigated [17]. A further work was published by Karpas et al. who determined the responses of halogenated alkanes and alkenes with a gas-chromatography (GC)-IMS coupling [11]. Baim et al. [18] investigated the possible improvement of LODs (limits of detection) using dopants for chlorinated compounds and suggested the use of oxygen dopants for GC-IMS. Furthermore, different studies were performed for understanding ion formation processes of halogenated compounds in positive measuring modus [19].

In addition to ion mobility spectrometry, the mechanisms of ionization were investigated using electron capture detectors (ECDs) where comparable ionization reactions take place as described above [20,21]. For different chemical classes, the ECD response was correlated with structural features and considerable differences in the response were found [22–24]. In contrast to ion mobility measurements, ECDs work at elevated temperatures (commonly ≥150 °C) in a pure inert gas atmosphere. However, it is known from literature that the ECD response strongly depends on the operating temperature [25] and the composition of carrier gas used [26,27]. Therefore it was the question whether this knowledge can be reflected in IMS.

Although the chloride fragmentation from chlorinated organic compounds belongs to the well investigated reactions in organic chemistry in solutions, there are much less systematic studies about this reaction in the gas-phase. Therefore, it was another aim to investigate whether the same parameters (e.g. bond distances, bond energies, intramolecular interactions) are responsible for the cleavage of chlorine as known from organic chemistry.

Table 1
Operating parameters of ion mobility spectrometers used in this study.

	RAID M – Bruker Daltonik	IMS Portable - G.A.S.
Characteristic	Handheld unit	Transportable unit
Carrier gas	Nitrogen	Nitrogen
Carrier gas flow rate [mL min^{-1}]	600	100
Inlet system	Silicon rubber membrane	Direct inlet
Temperature of inlet system [°C]	60	45
Ion source	63Ni (100 MBq)	3H (300 MBq)
Flow system	Closed circuit	Open system
Grid pulse width [μs]	200	300
Length of drift tube [cm]	6.1	6.0
Drift tube temperature [°C]	40	45
Electric field [V cm^{-1}]	295	410
Flow system	Bi-directional	Uni-directional
Drift gas	Air	Nitrogen
Drift gas flow [mL min^{-1}]	660	500
Residual moisture of drift gas	approx. 1 ppm	approx. 2 ppm

2. Experimental

Two different types of ion mobility spectrometers were used in this study. Their basic features and operating parameters are summarized in Table 1.

A handheld analyzer (RAIDM, Bruker-Daltonic, Leipzig, Germany) was applied which is equipped with a silicone rubber membrane inlet. Membrane inlets are particularly valuable in such analyzers by preventing excessive excursions with moisture from ambient air and by excluding other contaminants such as dust or aerosols. In a membrane inlet, sample is directed against the membrane where organic substances dissolve and permeate through the membrane. Other substances such as water vapor have lessened solubility in the membrane and are passed into the analyzer at a decreased efficiency, preserving purity internal atmosphere. An unwelcome consequence of the membrane inlet is that vapor sample concentrations in the source are known only at a semi-quantitative level. However, we use such analyzers for field screening measurements routinely and we therefore involved these analyzers in our investigation.

Furthermore, we used a transportable spectrometer with a direct inlet (IMS Portable, G.A.S., Dortmund, Germany) in order to ensure the reproducibility of possible differences between the substances investigated.

For calculation of peak position in ion mobility spectra, the drift velocity (v_d) was calculated from the drift time (t_d) and the length of the drift tube and is proportional to the strength of electric field (E) and the mobility coefficient (K). Mobility coefficients were converted to reduced mobilities, K_o, in which temperature and pressure of the gas atmosphere is corrected to 273 K and 760 Torr (mm Hg). Reduced mobility values are given in $cm^2\,Vs^{-1}$.

The chemicals were introduced via permeation tubes. Three hundred μL of neat sample were sealed in polyethylene permeation tubes with a length of 35 mm, an inside diameter of 4 mm and an outside diameter of 6 mm which were in a temperature-controlled glass column. Chemicals were obtained in 99% or better purity from Sigma–Aldrich (Taufkirchen, Germany), and Merck (Darmstadt, Germany). Nitrogen with a quality of 5.0, scrubbed over charcoal, was passed through the glass column with a constant flow, split, and diluted using scrubbed nitrogen in a special mixing chamber to provide a range of concentrations. The geometry and flow rates of this system were optimized for avoiding an over pressurization. The sample gas was primed into the ion mobility spectrometers either by the spectrometer's internal pump with 600 mL min^{-1} along the membrane inlet (RAIDM) or with 100 mL min^{-1} by an external micro membrane pump (Fürgut GmbH, Tannheim, Germany) in front of the direct inlet. All gas flows were adjusted and controlled using mass flow controllers (measuring range: 0–500 mL min^{-1}; Analyt, Mühlheim, Germany) which were calibrated with a soap-bubble meter before use. Details of this sample introduction system were described previously [28]. The concentration of the compounds in the sample gas stream was calculated using the weight loss of the permeation tube over a certain time. The weight loss was determined using a microbalance. Using the weight loss, the total amount of gas flow through the permeation vessel and the additional rarefaction of gas streams, the concentration in the sample gas stream into the ion mobility spectrometer was calculated.

In order to ensure the comparability of calibrations regarding the cleavage of chlorine, the concentrations are given in $\mu mol\,L^{-1}$ instead of $\mu g\,L^{-1}$. The concentrations were calculated according to Eq. (3).

$$c_{\mathrm{mol}}\quad[\mu\mathrm{mol/L}] = \frac{c_{\mathrm{mass}}\,[\mu\mathrm{g/L}]}{M\,[\mu\mathrm{g}/\mu\mathrm{mol}]} \qquad (3)$$

At least three calibration curves were obtained for each substance. The measurement uncertainty was determined by repeat series of measurements. The intensities of product ions vary in average in a range of ±10% related to the mean value. The slope of calibration graphs is defined as sensitivity. A good sensitivity therefore means a large degree of response to a change in concentration of analytes being measured. Limits of detection were determined with the Excel sheet DINTEST (university hospital of Heidelberg) based on the German standard procedure DIN32643 [29].

3. Results and discussion

The initial measurements were performed with the RAID M spectrometrs equipped with a membrane inlet unless otherwise stated. All substances investigated provided spectra consisting of one major product ion peak which appears at 6.39 ms (t_d (reactant ions)/t_d (product ions): 1.20) in negative measuring modus. According to literature, this product ion peak results from the formation of $(H_2O)_nCl^-$ product ions due to dissociative electron attachments [10]. Because all substances investigated provide peaks with the same reduced mobility value, this ionization pathway with the heterolysis of chlorine seems to be the most probable and the formation of identical product ions for all substances can be assumed. These mechanisms of ion formation were extensively investigated using IMS-MS in previous studies [30]. Due to the same structure of product ions formed, we only considered the relative abundance of product ions formed in the following investigations. Fig. 1 shows the calibration curves of substances from each chemical class investigated including chlorinated vinyl-, allyl-, alkyl compounds and benzylchlorides. In vinyl chlorides, the chlorine is directly bonded to sp^2 hybridized carbon atom of the double bond while an additional $-CH_2-$ group is positioned between double bond and the chlorine atom in the case of allyl chlorides. The same principle is given for chlorobenzenes with a direct bond of chlorine to the aromatic ring while a $-CH_2-$ group is located between the aromatic ring and the chlorine atom in the case of benzylchlorides. In alkyl chlorides, the chlorine atom is bonded to the aliphatic chain.

Chlorinated benzenes are not stated in Fig. 1 due to their low sensitivity of detection. The calibration curves of chlorobenzenes are far outside from the concentration range shown. Although Fig. 1 shows only mono-halogenated substances by the way of example, the general differences in LODs and sensitivity can also be reproduced for other compounds from these chemical classes.

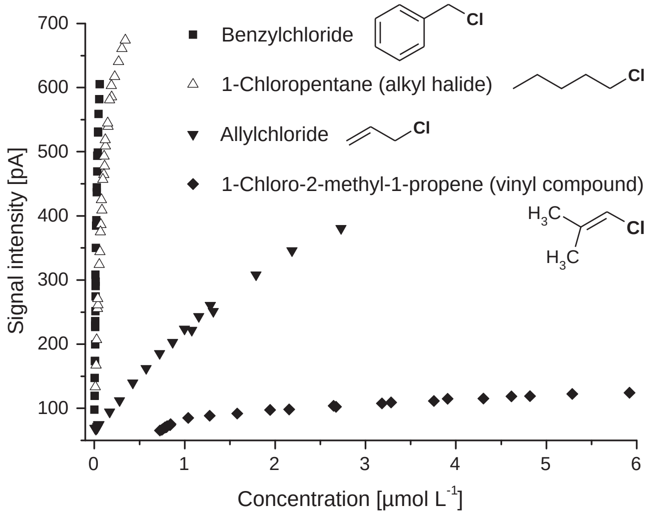

Fig. 1. Calibration curves of chlorinated compounds with different structural features.

Considerable differences in sensitivity and LODs can be observed. Increasing sensitivities in the order chlorobenzenes < vinyl- < allyl- < alkyl compounds < benzylchlorides were established. Obviously, the heterolysis of chlorine from the sp^2 hybridized carbon atom in the case of vinyl compounds and chlorobenzenes is limited. In contrast, alkyl chlorides and benzylchlorides with a C–Cl bond to a sp^3 hybridized carbon atom show excellent sensitivities and LODs. Although allyl compounds have the same bonding state, they are more insensitive detectable in comparison to the afore-mentioned compounds.

As known from organic chemistry, the chemical properties of halogenated compounds and the trend to the heterolysis of chlorine are determined by the polarizability of carbon-halogen bond. The polarity decrease in the order (with Ar: aryl): $R{-}CH{=}CH{-}CH_2{-}X > Ar{-}CH_2{-}X > R{-}X > Ar{-}X > R{-}CH{=}CH{-}X$ [31]. This goes along with decreasing bond lengths and increasing bond energies. With exception of allyl chlorides, this general order can be reproduced in ion mobility spectra. Benzylchlorides and alkyl chlorides are more sensitive detectable in comparison with chlorobenzenes and vinyl chlorides. Furthermore, the constitution of ions formed due to the cleavage of chlorine has an influence of possible heterolysis of carbon-chlorine bond. In this case, the cleavage of chlorine is facilitated for allyl- and benzyl- compounds due to the formation of resonance-stabilized carbenium ions. In contrast, halogenated benzenes and vinyl compounds have a low trend to the heterolysis of chlorine due to the enhanced electronegativity of sp^2 hybridized C atoms and the +M (mesomeric) effect of halogens.

3.1. Mono-halogenated compounds

For a further characterization of structural features influencing the ion formation, more substances of chemical classes were investigated. The measuring results of mono-halogenated compounds are summarized in Fig. 2 for selected substances by the way of example. The comparison of a saturated (2-chloropropane) and unsaturated (2-chloro-1-propene) compound is shown in Fig. 2a and the comparison of isomeric compounds (1-chloro-2-methyl-1-propene and 3-chloro-2-methyl-1-propene) in Fig. 2b. The chlorine atom is bonded to the sp^2 hybridized carbon atom of the double bond in one of these compounds while the chlorine atom is bonded to sp^3 hybridized carbon of the single bond in the other one. A general difference in sensitivity and LODs can be seen as discussed above. The higher bond energy of sp^2 hybridized car-

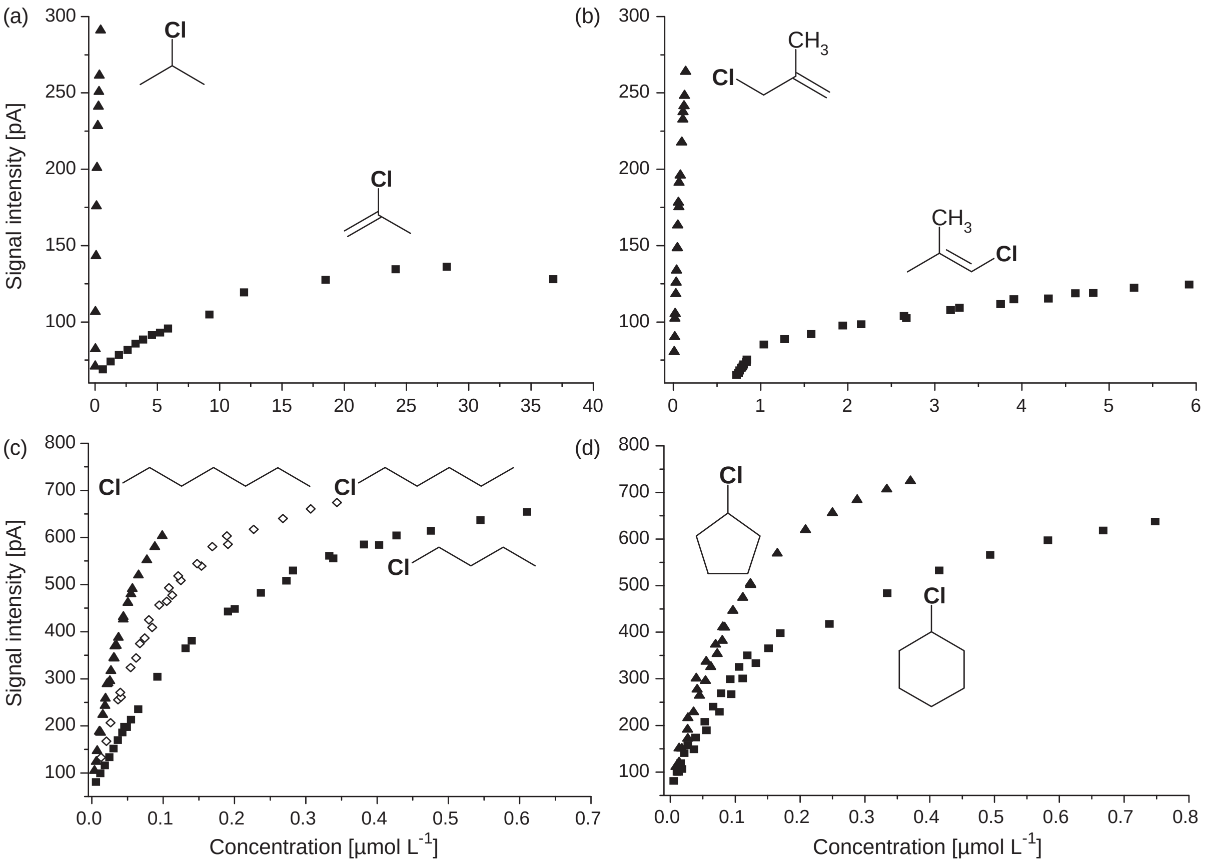

Fig. 2. Comparison of calibration curves of mono-halogenated compounds with different bonding states ((a) 2-chloropropane and 2-chloro-1-propene; (b) 3-chloro-2-methyl-1-propene and 1-chloro-2-methyl-1-propene) and influence of chain length (c) 1-chlorohexane, 1-chloropentane and 1-chlorobutane) and ring size ((d) chlorocyclopentane and chlorocyclohexane) on calibration curves.

bon in comparison with sp^3 hybridized carbon generally provides a lower sensitivity and enhanced LODs. Fig. 2c and d shows the influence of chain length and ring size on the calibration curves of mono-halogenated aliphatic and alicyclic compounds. As shown in Fig. 2c, a clear dependence of sensitivity can be observed for aliphatic compounds depending on their chain length. Although all compounds shown have roughly comparable LODs (e.g. n-C_4H_9Cl: 3.6 nmol L^{-1}; n-$C_6H_{13}Cl$: 3.8 nmol L^{-1}), an increasing chain length provides enhanced sensitivities. The possible reason for these differences is an unanswered question at the moment. Possible substituent effects should be of minor importance in terminal halogenated n-alkyl compounds with 4 and more carbon atoms. As a rough approximation of possible differences in bond energies, we calculated the bond distances of C–Cl bond. The geometry optimization for this calculation was performed using the semi-empirical AM1 method [32] integrated into the SPARTAN 5.0 suite (Wavefunction, Inc., Irvine, USA). However, each distance of C–Cl bonds of 1-chlorbutane, 1-chloropentane and 1-chlorohexane was calculated with 1.757 Å (1 Å = 10^{-10} m). Therefore, different bond energies do not seem to be the responsible parameter for these differences.

Although the calculated bond length of chlorocyclopentane (1.764 Å) and chlorocyclohexane (1.772 Å) indicate an enhanced sensitivity of chlorocyclohexane, the calibration curves (Fig. 2d) are contrary to the expected behaviour. Both substances have comparable LODs (chlorocyclypentane: 6 nmol L^{-1}; chlorocyclohexane: 2 nmol L^{-1}). However, chlorocyclopentane is more sensitive detectable. As known from textbooks of organic chemistry [31], the heterolysis of chlorine is also influenced by the ring strain of alicyclic systems. Obviously, the slightly higher ring strain of cyclopentane in comparison to cyclohexane causes the improved heterolysis of chlorine.

3.2. Di-halogenated compounds

Fig. 3 shows the calibration curve of the di-halogented 2,3-dichloro-1-propene ($CH_2{=}CCl{-}CH_2Cl$). The bonding types of chlorine and structural elements correspond with those of 2-chloro-1-propene ($CH_2{=}CCl{-}CH_3$) and 3-chloro-1-propene

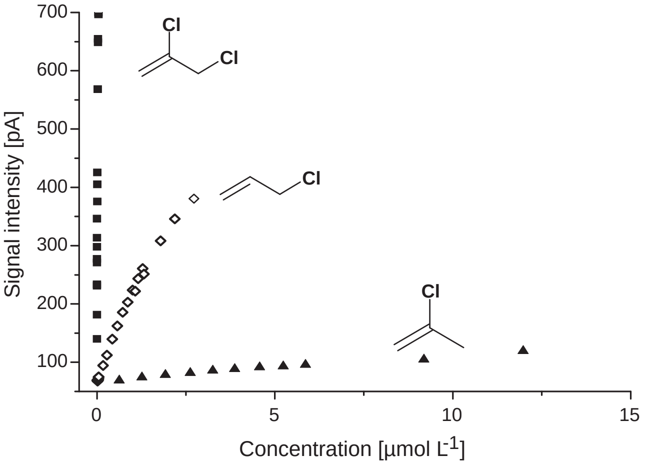

Fig. 3. Heterolysis of chlorine from a di-halogenated compound (2,3-dichloro-1-propene) in comparison to mono-halogenated substances (3-chloro-1-propene and 2-chloro-1-propene) with similar structural features.

($CH_2{=}CH{-}CH_2Cl$). If no additional influencing parameters affect the heterolysis of chlorine, the calibration curve of 2,3-dichloro-1-propene should result from the addition of the calibration curves of the corresponding mono-halogenated compounds. However, it can be seen from Fig. 3 that the di-halogenated substance is more sensitive detectable. The enhanced sensitivity of di-halogenated compounds evidently results from additional intramolecular interactions. That intramolecular interactions exist can be deduced from the different bond distances in mono- and di-halogenated compounds. Although the bond distances of the di-halogenated are shorter (sp^2C-Cl: 1.700 Å; sp^3C-Cl: 1.747 Å) in comparison with mono-halogenated compounds (sp^2C-Cl of 2-chloro-1-propene: 1.710 Å and sp^3C-Cl of 3-chloro-1-propene: 1.756 Å), the additional interaction forces promote the heterolysis of chlorine. It can be concluded from this comparison that intramolecular interaction can also affect the detectability of chlorine. Intramolecular interactions evidently enhance the sensitivity of measurements.

The more detailed investigations of di-halogenated compounds are summarized in Fig. 4. Fig. 4a shows the calibration curves of 1,4-dichloro-2-butene with 2 chlorine atoms bonded to sp^3 hybridized carbons and 1,3-dichloropropene with one sp^3 C–Cl bond and one sp^2 C–Cl bond. The enhanced sensitivity of 1,4-dichloro-2-butene confirms our observations for mono-halogenated compounds. Compounds where the chlorine atom is bonded to sp^3 hybridized carbon of a single bond are more sensitive detectable. The bonding type affects also the sensitivity of di-halogenated compounds in the same manner as discussed for mono-halogenated substances.

The influence of possible intramolecular interactions is shown in Fig. 4b by comparing the calibration curves of 1,3- and 2,3-dichloropropene where the distance between the chlorine atoms is different. The slightly more sensitive detectability of 2,3-dichloropropene with a closer distance of chlorine atoms indicates that intramolecular interactions provide an enhanced sensitivity.

The dependence of chain length of di-halogenated alkyl compounds is shown in Fig. 4c. With increasing chain length, an increasing sensitivity can be observed ($ClCH_2{-}CH_2Cl < ClCH_2{-}CH_2{-}CH_2Cl < ClCH_2{-}(CH_2)_2{-}CH_2Cl$). Although the differences are not as obvious as determined for mono-halogenated compounds, the established tendency is the same. Generally, the observed influencing parameters determining the heterolysis of chlorine are the same for mono- and di-halogenated compounds. However, additional intramolecular interactions affect the formation of negative product ions in the case of di-halogenated compounds.

3.3. Halogenated aromatic compounds

In addition to aliphatic and alicyclic compounds, the heterolysis of chlorine from two chemical classes of aromatic compounds (chlorobenzenes and benzylchlorides) was studied. The results are summarized in Figs. 5 and 6.

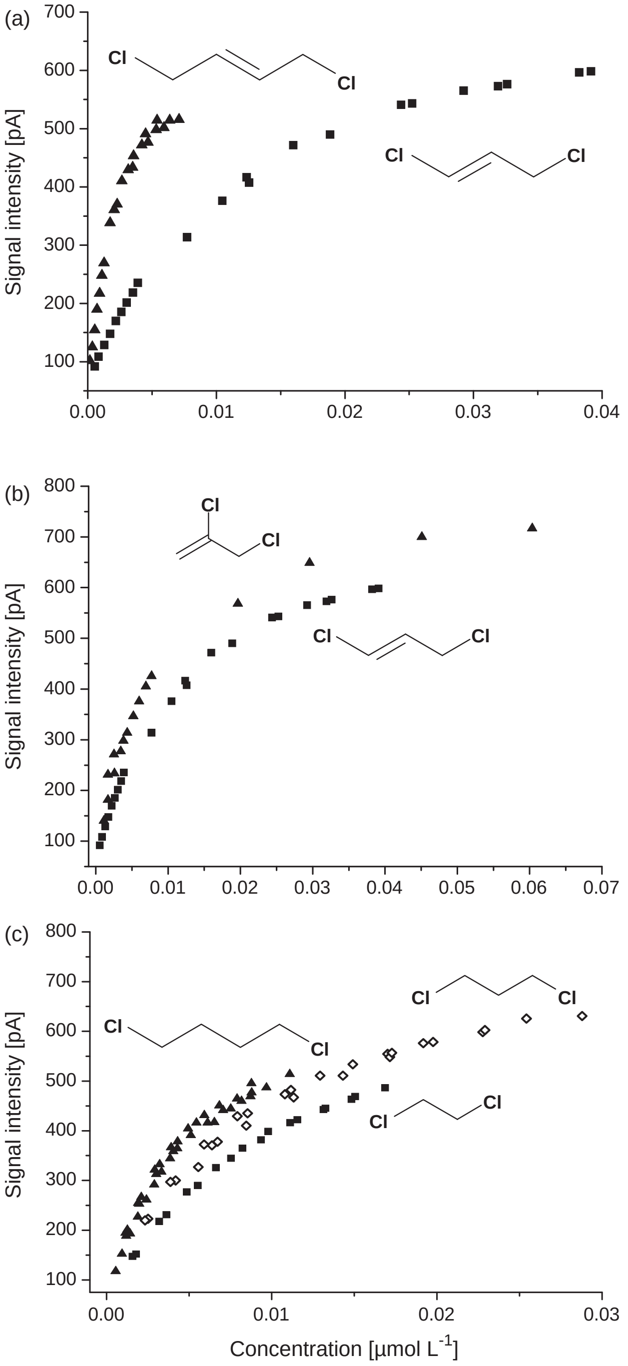

Fig. 4. Calibration curves of di-halogenated compounds with different bonding type (a), different position of chlorine (b) and different chain length (c).

As discussed above, chlorinated benzenes are insensitively detectable using IMS. However, it can be seen from the negative ion mobility spectra of selected chlorobenzenes in Fig. 5 that the signal intensity of chloride peaks depends on the nature of the second substituent. The spectra of 1,2-chlorobenzonitrile, 1,2-chlorofluorobenzene and 2-chlorotoluene are shown as well as benzylchloride as reference substance. Benzylchloride and chlorobenzonitrile were injected with comparable concentrations (0.5 $\mu g\,L^{-1}$; 4 $nmol\,L^{-1}$). However, the signal intensity of the chlorine peak in the ion mobility spectrum of chlorobenzonitrile is lower in comparison to benzylchloride. Although the concentration of 2-chlorotoluene was 220 fold higher (110 $\mu g\,L^{-1}$; 900 $nmol\,L^{-1}$) in comparison with chlorobenzonitrile, the intensity of chloride peak is near the detection limit. A similar peak intensity was observed for 1,2-chlorofluorobenzene which was injected with 65 $\mu g\,L^{-1}$ (500 $nmol\,L^{-1}$). Generally, the detectability of chlorobenzenes depends on the nature of second substituent. Electron-withdrawing substituents (chlorine, fluorine, nitrile) enhance the sensitivity while electron-repelling substituents (methyl) decrease it.

An influence of second substituent can also be observed for benzylchlorides. Fig. 6 shows the calibration curves of ortho- (Fig. 6a) and para- (Fig. 6b) chloro-, fluoro- and methyl-benzylchlorides. Additionally, benzylchloride is depicted as reference substance. Generally, chloro- and fluorobenzylchloride are more sensitive detectable in comparison with methylbenzylchloride and benzylchloride. The substituent effects are identical with those described for chlorobenzenes. The calibration curves of chloro-

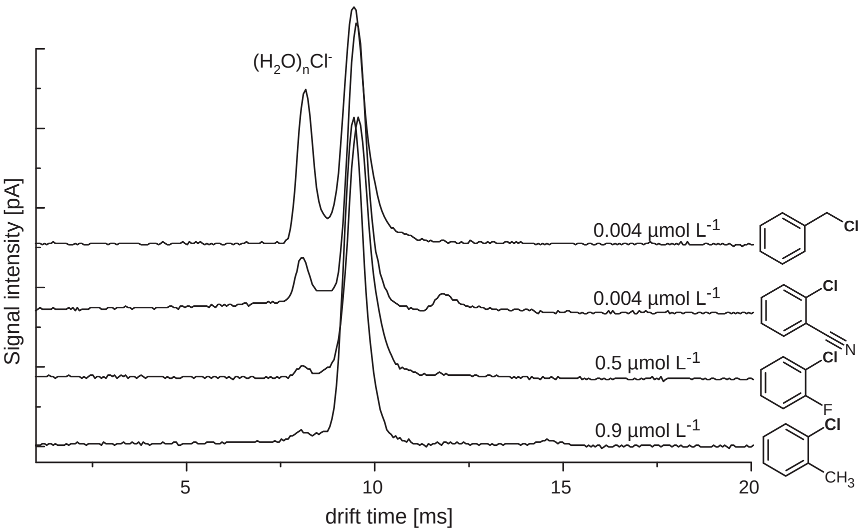

Fig. 5. Peak intensities in ion mobility spectra of benzyl chloride (0.5 µg L^{-1}), 2-chlorobenzonitrile (0.5 µg L^{-1}), 2-chlorofluorbenzene (65 µg L^{-1}) and 2-chlorotoluene (110 µg L^{-1}) depending on the concentration.

and fluorobenzylchloride are closed. Obviously, the second chlorine atom of chlorobenzylchloride which is directly bonded to the aromatic ring does not provide any contribution to the signal intensity of chloride peak. As described for chlorobenzenes, the heterolysis from the chlorine bonded to the aromatic ring is limited due to the higher bond energy. The calibration curves of 4-methylbenzylchloride and benzylchloride are nearly identical. If the methyl group is located in para-position to the $-CH_2-Cl$ group of benzylchloride, no effect of the methyl group is detectable. In the case of 2-methylbenzylchloride with a consecutive position of the $-CH_3$ group to the $-CH_2-Cl$ group of benzylchloride, an enhanced sensitivity can be established which is probably caused by intramolecular interactions. In contrast to chlorobenzenes, benzylchlorides have excellent detection limits. The LODs of chlorobenzylchloride and fluorobenzylchloride are below 100 ng L^{-1} while 120 ng L^{-1} are required for the detection of benzylchloride.

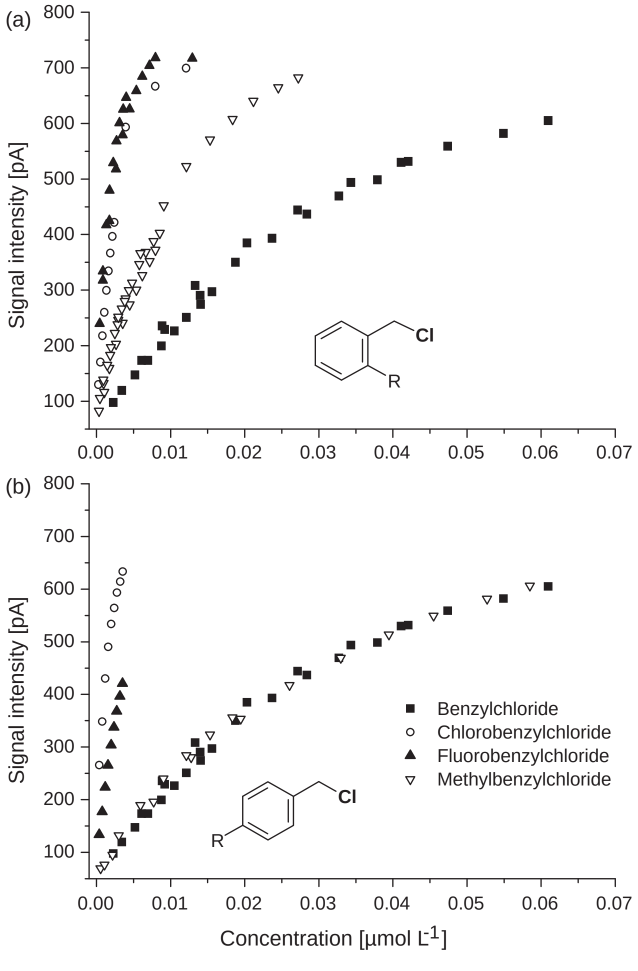

Fig. 6. Calibration curves of benzylchloride and ortho- (a) and para- (b) substituted benzylchlorides.

3.4. Measurements using direct inlet

All the above-mentioned investigations were performed with an ion mobility spectrometer equipped with a membrane inlet. In order to reproduce the patterns discussed above, comparison measurements were carried out with an ion mobility spectrometer equipped with a direct inlet. It is noteworthy that both ion mobility spectrometers with different inlet configuration work with different operational parameters. The use of different drift gases with different flow rates can cause different ionization pathways. This can subsequently result in the formation of product ions with different structure. Nevertheless, the essential parameters influencing the structure of ions formed (moisture of gases and temperature) are comparable for both drift and carrier gases. Using the direct inlet spectrometer, all substances also provide identical product ions which appear at 5.67 ms ((t_d (reactant ions)/t_d (product ions): 1.09).

Some examples are summarized in Fig. 7. As known, each ion mobility spectrometer requires a separate calibration due to the optimized gas flow system used. It was therefore not the aim of these measurements to compare the LODs. The aim was to verify the discussed differences in calibration curves. These studies can be summarized in the following manner: we observed the same patterns of calibration curves for all mono- and dihalogenated substances discussed above. The different slopes of calibration curves can evidently be reproduced. Fig. 7a and b shows the calibration graphs of alkyl halides and alicyclic compounds by the way of example. Although the direct inlet permits the 10 times more sensitive detection of these compounds, the general order of sensitivity is the same. This holds true for all com-

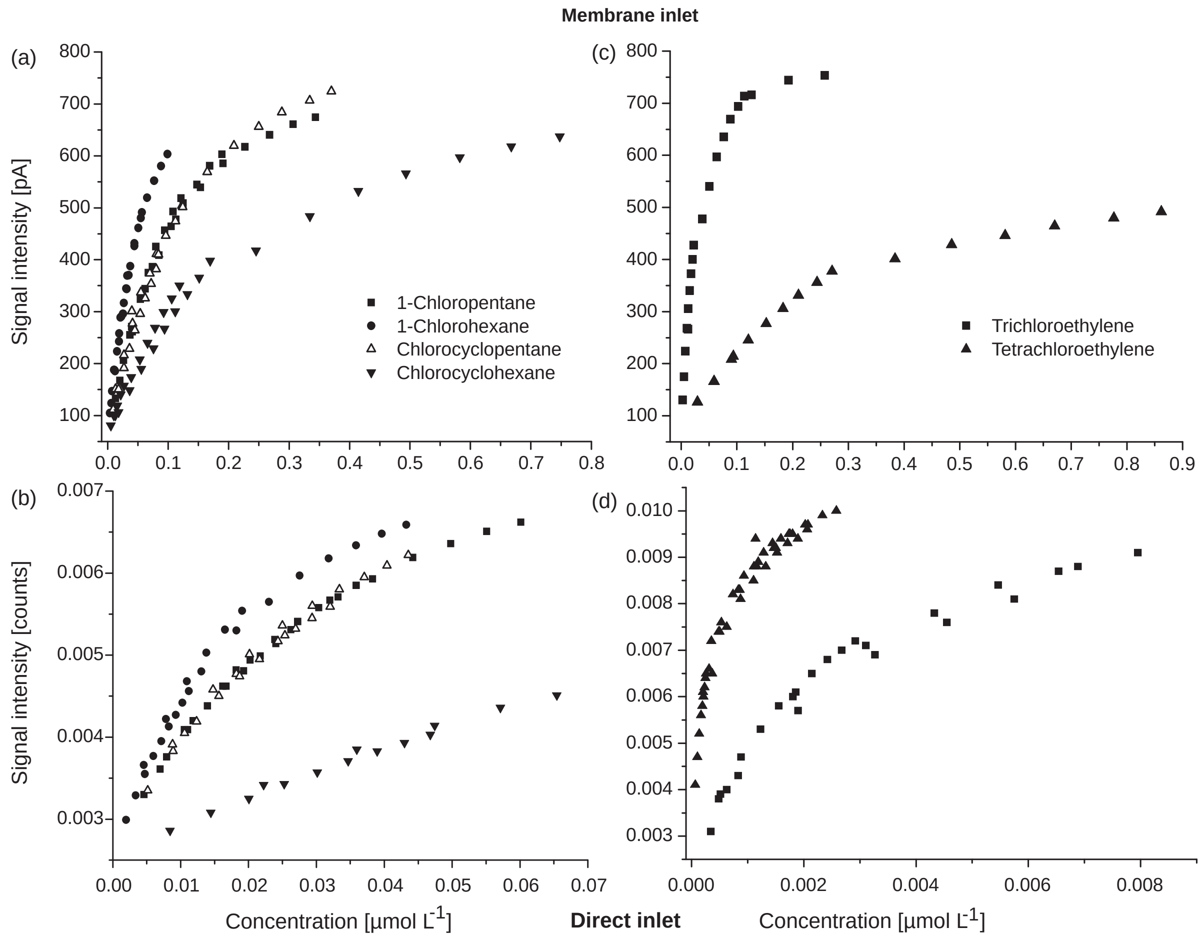

Fig. 7. Calibration curves of alkyl halides and alicyclic compounds (a, b) and chlorinated substances (c, d) determined using membrane inlet (a, c) and direct inlet (b, d).

pounds mentioned above. However, differences can be observed for compounds with lessened solubility in the membrane such as substances with 3 and more chlorine atoms. Fig. 7c and d shows this effect for trichloroethylene and tetrachlorethylene. Although the use of a direct inlet permits the 100-fold better detectability, the different rates of diffusion through the membrane leads to different order in sensitivity. Therefore, we included in the investigations presented here mono- and di-halogenated compounds.

4. Conclusion

Different classes of substances were systematically and comparatively investigated regarding the signal intensity of chlorine peak which results from the heterolysis of chlorine from the analytes. A clear correlation between the structural features of halogenated substances and the relative abundance of product ions formed was observed while the peak position of product ions are generally the same for all substances using consistent experimental conditions. The structural parameters influencing the gas-phase ionization reactions and the order of sensitivity are partly comparable with those which are known from organic chemistry in solutions. However, additional investigations regarding the possible parameters influencing the signal intensity are necessary (e.g. moisture and temperature of drift gases) in order to verify the results obtained. The order of reactivity determined in IMS in the presented study can be associated with that which is known for nucleophilic substitution reactions. A similar mechanism in the gas-phase ionization was suggested by Karasek et al. [15] for halogenated nitrobenzenes with OH^- ions as nucleophiles. Due to the considerable number of influencing parameters, the chloride peak cannot be used as possible sum signal for chlorinated compounds and each substance requires an individual calibration in IMS.

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