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Gas-phase ion mobility studies of constitutional isomeric hydrocarbons using different ionization techniques

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Abstract

We have investigated the influence of structural differences on the ionization pathways and drift behavior in ion mobility spectrometry for constitutional isomeric hydrocarbons. The ion mobility spectra of isomeric alkylated benzenes (C_9H_{12} and $C_{10}H_{14}$) were recorded using photoionization, ^{63}Ni ionization and corona discharge ionization. Defined spectra for almost all isomeric compounds were observed using photoionization. When using this technique, no differences in ion mobility spectra of isomers can be observed. However, the methods of atmospheric-pressure chemical ionization (^{63}Ni and corona discharge ionization) produce differences in ion mobility spectra or in the detectable concentration ranges of isomeric compounds depending on the number and position of aliphatic side chains. (Int J Mass Spectrom 208 (2001) 67–72) © 2001 Elsevier Science B.V.

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1. Introduction

Ion mobility spectrometry (IMS) permits the simple, rapid on-site determination of gaseous compounds by fieldable and hand-held devices [1,2]. IMS is based on determining the drift velocities (v_d) which ionized sample molecules attain in the weak electric field of a drift tube at atmospheric pressure. The drift velocity is proportional to the strength of the electric field (E) and the mobility (K) of ions. Therefore, ion mobility can be derived using

$$K = \frac{v_d}{E} \tag{1}$$

The general theory for the mobility of ions in a weak electric field can be expressed as

$$K = \left(\frac{3q}{16N}\right)\left(\frac{2\pi}{\mu kT}\right)^{1/2}\left(\frac{(1+\alpha)}{\Omega_D}\right) \tag{2}$$

where q is the charge of the ion, N is the density of drift gas molecules, $\mu = (m \times M)/(m + M)$ is the reduced mass of the ion (m) and drift gas molecule (M), k is the Boltzmann constant, T is the temperature, α is the correction factor ($\alpha < 0.02$ for $m > M$), Ω_D is the average ionic collision cross section. Considering Eq. (2), ion mobility is considerably influenced by the

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temperature, drift gas used and ionic charge, as well as the mass of analytes and their collisional cross sector. The term (Ω_D) includes geometrical parameters (physical size and shape) and electronic factors describing the ion–neutral interaction forces [3–6]. When comparing ion mobility spectra, the application of identical instrumentation and operational parameters (drift gas, gas flows, temperature) limits the number of variables influencing the ion mobilities of different compounds to ionic mass (m) and structure (Ω_D). The influence of ionic mass on ion mobility can be described by mass-to-mobility correlation curves. These relationships 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. The objective of our article is to shed light on this relationship.

To eliminate mass effects, constitutional isomeric hydrocarbons with identical molecular weight (alkylated benzenes with three and four carbon atoms in aliphatic side chains) were examined. For the hydrocarbons investigated, polar effects can be minimized in contrast to substances containing functional groups. All the aforementioned compounds were measured using ^{63}Ni, corona discharge, and photoionization in positive mode to estimate the influence of molecular structure on the ion mobility and ionization pathway. ^{63}Ni ionization sources are commonly used in IMS for the ionization of neutral sample molecules [7,8]. Positive product ions are formed mainly by way of proton-transfer reactions [9]. The relative abundances of the products largely depend on the gas-phase basicities of the compounds investigated as well as on the temperature and composition of the carrier gas [10,11]. Photoionization (PI) and corona discharge (CD) ionization were developed as alternative nonradioactive ionization sources in IMS. The application of PI is restricted to the determination of unsaturated and aromatic compounds. The most probable ionization pathway provides $[M]^+$ product ions [12]. Using CD ionization, positive product ions may be formed by way of different processes due to the varying strength of the electric field around the corona needle. Electron impact, photoionization, and proton-transfer reactions can initiate the formation of product ions depending on the distance of sample molecules from corona needle [13]. However, the formation of product ions can generally be affected by subsequent ion–molecule reactions [14].

Using ^{63}Ni and PI, nonpolar hydrocarbons are insensitively detectable [15,16]. Therefore, only few measuring results and investigations regarding the ionization pathways are available for these compounds [17–20]. Investigations with CD-IMS have recently shown that the ionization processes described above permit the sensitive determination of these compounds in the low ppm range [15,21].

Previously, studies of isomeric compounds were only performed using ^{63}Ni ionization and only included substances containing polar functional groups (branched and unbranched ketones, thiocyanates, isothiocyanates [22], phthalic acids [23], dihalogenated benzenes [24], halogenated nitrobenzenes [25], amines [26], anilines [27], E/Z isomers [28], diamines [29], and nitrogenous heterocycles as well as aromatic compounds substituted by functional groups [30]).

2. Experimental

The details of the sample introduction system used and its function are described elsewhere [31]. Liquid samples containing about 300 μL of the hydrocarbons examined were sealed in permeation tubes made of polyethylene. The permeation tubes had a volume of 1 mL and a wall thickness of 0.5 mm, and were placed in a glass column. The substances used in this study had a purity of about 99% and were obtained from Fluka. Purified and dried ambient air was pumped through the glass column containing the permeation tube at a constant rate of 25 L/h. The sample gas stream was split using flow controllers. A defined amount of the 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 contents of the gas streams were controlled by 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).

The measurements were performed with ion mobility spectrometers manufactured by BRUKER. With the exception of ionization, all the measuring parameters were kept constant. The PI source was equipped with a krypton lamp (10 eV). The basic features of the CD ionization source used in this study are described in detail elsewhere [13]. For β ionization, a 555MBq ^{63}Ni source was used as the electron source.

The spectrometers are equipped with a membrane inlet and operate with a bi-directional flow system. The operational parameters used to obtain the spectra were: temperature of inlet system: 80 °C; carrier gas flow rate: 25 L/h; drift gas flow rate: 25 L/h; electric field: about 245 V/cm; temperature of drift tube: 80 °C; pressure: atmospheric pressure. Air was used as the carrier gas and drift gas.

The reduced mobility values (K_0 values) were calculated using the conventional equation [32]:

$$K_0 = \left(\frac{d}{tE}\right)\left(\frac{p}{760}\right)\left(\frac{273}{T}\right) = (\mathrm{cm}^2/\mathrm{V\ s}) \qquad (3)$$

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).

3. Results and discussion

The measured ion mobility spectra are depicted in Figs. 1 and 2. The substances in Fig. 1 include the constitutional isomers with the formula C_9H_{12}, Fig. 2 shows substances with the formula $C_{10}H_{14}$. Using ^{63}Ni ionization, the ion mobility spectra are influenced by the concentration range detected as well as the moisture content of the carrier gas. Therefore, the detection of reproducible spectra by ^{63}Ni ionization requires the application of identical measuring conditions. The reduced mobility values obtained by PI and CD ionization are nearly unaffected by these operational parameters.

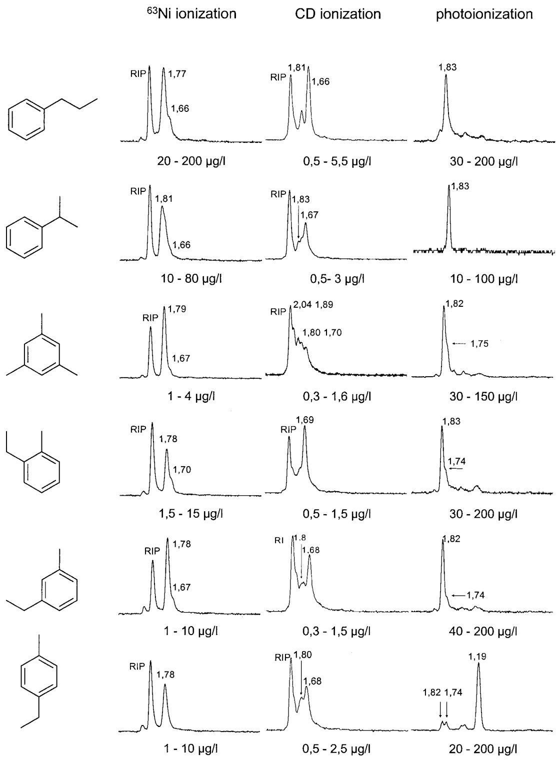

Fig. 1. Ion mobility spectra of C_3 benzenes (RIP: positive reactant ion; reduced mobility values: cm^2/V s).

Using PI, most of the constitutional isomeric compounds provide comparable spectra consisting of one major peak with identical reduced mobility values (1.83 cm^2/V s for C_3 benzenes and 1.74 cm^2/V s for C_4 benzenes). These peaks obviously result from the formation of $[M]^+$ product ions. These ions are created due to the most probable ionization pathway using PI [12]. Consequently, $[M]^+$ ions with different structures and ionic collision cross sections are formed from the isomeric compounds. The ion formation by way of following isomerization including the migration of alkyl groups can be excluded. However, the structural differences of $[M]^+$ product ions are not sufficient to provide different drift velocities for isomeric ions investigated. The detection of comparable reduced mobility values for the $[M]^+$ product ions of all isomeric compounds indicates that the drift behavior of the product ions formed is unaffected by steric differences for alkylated benzenes investigated using PI. Additional peaks with a very low intensity in some spectra can be attributed to the formation of clustered ions.

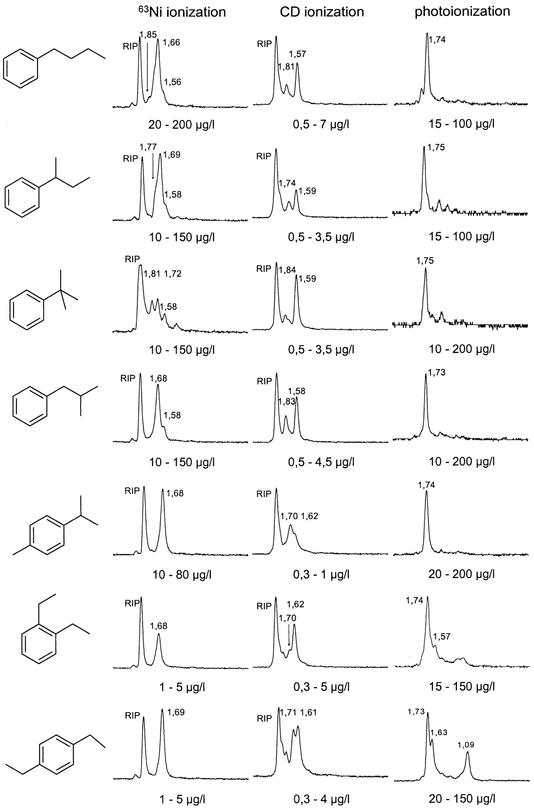

Fig. 2. Ion mobility spectra of C_4 benzenes (RIP: positive reactant ion; reduced mobility values: $cm^2/V\ s$).

Deviating behavior can be observed for *p*-disubstituted substances (1,4-diethylbenzene, 4-ethyltoluene). Additional peaks with reduced mobility values of 1.63 and 1.09 $cm^2/V\ s$ are observed for 1,4-diethylbenzene. For 4-ethyltoluene, an exceptional peak with a reduced mobility value of 1.19 $cm^2/V\ s$ is detected. This K_0 value can evidently be assigned to dimer ions. A mass-to-mobility correlation curve ($\lg m = -0.47K_0 + 2.94$) can be derived from the data obtained (1.83 $cm^2/V\ s$: M^+ C_3 benzenes; 1.74 $cm^2/V\ s$: M^+ C_4 benzenes; 1.19 $cm^2/V\ s$: dimer ion M_2H^+ for 4-ethyltoluene). Using this function, the ionic masses for additional peaks in the spectrum of 1,4-diethylbenzene were calculated. Ionic masses of 150 and 269 can be assigned to these peaks (1.63 and 1.09 $cm^2/V\ s$). These structures clearly result from the formation of water-ion clusters and from dimerization.

Using CD ionization, considerable differences in ion mobility spectra of the isomeric compounds are observed depending on the position and the structure of substituents. Two peaks appear in the spectra of the hydrocarbons investigated. However, the reduced mobility values calculated and the intensity ratio between the two peaks vary due to the structural differences.

For monosubstituted benzenes, the position of the peak with lower reduced mobility (1.66 $cm^2/V\ s$ for propylbenzenes and 1.58 $cm^2/V\ s$ for butylbenzenes) correlates with the ionic mass of the compounds. It can be seen from the spectra depicted that the peak with higher reduced mobility (1.80 $cm^2/V\ s$ for *n*-alkyl benzenes and 1.83 $cm^2/V\ s$ for benzenes with a branched aliphatic side chain) appear at identical K_0 values for both propyl- and butylbenzenes. Therefore, the formation of identical fragment ions from all the monosubstituted substances can be supposed.

Disubstituted C_3 benzenes provide similar spectra to monosubstituted compounds. The spectra of isomeric ethyltoluenes illustrate the dependence of the intensity ratio between the two peaks detected (1.80 and 1.68 $cm^2/V\ s$) on the position of the aliphatic side chain. An intensity decrease of the peak at 1.80 $cm^2/V\ s$ is observed in the order $p > m > o$-substituted isomer. 1,3,5-Trimethylbenzene provides a crowded spectrum with low resolution consisting of four peaks. All disubstituted C_4 benzenes (*p*-isopropyltoluene, 1,2- and 1,4-diethylbenzene) provide ion mobility spectra with identical reduced mobility values (1.70 and 1.62 $cm^2/V\ s$). These K_0 values clearly differ from the product ion peaks obtained for monosubstituted butylbenzenes. In accordance with disubstituted C_3 benzenes, the peak with higher reduced mobility (1.70 $cm^2/V\ s$) is found to be more intensive for *p*-disubstituted compounds compared to *o*-diethylbenzene.

Using ^{63}Ni ionization, the spectra consist of one major peak. The K_0 value of this major peak is detected at comparable reduced mobilities for isomeric compounds (1.78 $cm^2/V\ s$ for C_3 benzenes; 1.68 $cm^2/V\ s$ for C_4 benzenes). However, these reduced mobilities differ from the values of major peaks determined by PI. With the exception of disubstituted C_4 benzenes, an additional peak appears in spectra of investigated compounds as the shoulder of the major peak at higher concentrations. The reduced mobility values for this peak correspond to the K_0 values of the major peak obtained using CD ionization. In comparison to monosubstituted alkyl benzenes, disubstituted compounds provide a sharp peak profile. The congested spectrum of tert-butylbenzene results from the high concentrations due to the insensitive detection and the gradual slope of the calibration graph.

The mass-to-mobility correlation curve obtained by PI is not applicable to methods of atmospheric-pressure chemical ionization (^{63}Ni and CD ionization). Obviously, these ionization techniques provide product ions with deviating drift behavior due to the effect on ionization processes by fragmentation reactions and cluster formation. Ion formation through similar ionization mechanisms can be attributed to the appearance of peaks with identical reduced mobilities in the spectra of both methods.

The detectable concentration ranges vary depending on the ionization technique used. CD ionization permits the most sensitive detection of alkylated benzenes. Detection limits of 0.3–0.5 μg/L (g) were established (Figs. 1 and 2). Similar concentration ranges are detectable for all the compounds investigated using this ionization method. The use of PI also provides comparable measuring ranges for all the substances examined. However, enhanced detection limits are established as well as a restricted linear range of calibration curves. Differences in detectable concentration ranges are observed using ^{63}Ni ionization depending on the substitution rate. Monosubstituted compounds are insensitively measurable in comparison to polysubstituted substances. Obviously, the shift of electrons due to the positive inductive effect of aliphatic side chains permits the enhanced attachment of protons or protonated species for polysubstituted benzenes.

The experimental results are confirmed using methods of pattern recognition. The principal components analysis provides a significant correlation of ion energetic data (appearance potential and ionization energy) and the reduced mobility values obtained by CD ionization. Therefore, the different ion mobility spectra of mono- and disubstituted benzenes can be attributed to different ionization pathways. The reduced mobility values observed using ^{63}Ni ionization and PI are nearly unaffected by different structural features of compounds investigated.

4. Conclusion

Differences in the ion mobility spectra measured of isomeric alkyl benzenes with summation formulas of C_9H_{12} and $C_{10}H_{14}$ were established depending on the ionization technique used. The detection of identical reduced mobility values and comparable concentration ranges using PI indicates that the formation of product ions and their drift behavior are relatively unaffected by structural differences. CD ionization permits the most sensitive detection of the nonpolar hydrocarbons investigated. However, considerable differences in ion mobility spectra were ascertained depending on the structure of isomeric compounds. Therefore, differences in ionization pathways can be supposed due to the structural differences. The ^{63}Ni ionization provide similar reduced mobility values for all isomeric hydrocarbons. However, the detectable concentration ranges are influenced by structural differences. Therefore, different abundances of the product ions can be assumed.

The differences established in ion mobility spectra obtained by methods of atmospheric-pressure chemical ionization (CD ionization and ^{63}Ni ionization) clearly result from different ionization pathways or different relative abundances of the product ions. The formation of clustered ions can be supposed due to the deviating drift behavior in comparison to PI. For CD ionization, additional fragment ions can be observed. Contrary to these methods, the ionization pathways in PI are comparatively uninfluenced by structural effects.

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