International Journal of Mass Spectrometry 286 (2009) 32–38

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

An online ultra-high sensitivity Proton-transfer-reaction mass-spectrometer combined with switchable reagent ion capability (PTR + SRI – MS)

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ARTICLE INFO

Article history:
Received 7 May 2009
Received in revised form 10 June 2009
Accepted 10 June 2009
Available online 18 June 2009

Keywords:
PTR-MS
Proton transfer ionization
Proton transfer reaction
Switchable reagent ions
PTR+SRI-MS
Isomer separation

ABSTRACT

Proton-transfer-reaction mass-spectrometry (PTR-MS) developed in the 1990s is used today in a wide range of scientific and technical fields. PTR-MS allows for real-time, online determination of absolute concentrations of volatile (organic) compounds (VOCs) in air with high sensitivity (into the low pptv range) and a fast response time (in the 40–100 ms time regime). Most PTR-MS instruments employed so far use an ion source consisting of a hollow cathode (HC) discharge in water vapour which provides an intense source of proton donor H_3O^+ ions. As the use of other ions, e.g. NO^+ and $O_2{}^+$, can be useful for the identification of VOCs and for the detection of VOCs with proton affinities (PA) below that of H_2O, selected ion flow tube mass spectrometry (SIFT-MS) with mass selected ions has been applied in these instances. SIFT-MS suffers, however, from at least two orders lower reagent ion counts rates and therefore SIFT-MS suffers from lower sensitivity than PTR-MS.

Here we report the development of a PTR-MS instrument using a modified HC ion source and drift tube design, which allows for the easy and fast switching between H_3O^+, NO^+ and $O_2{}^+$ ions produced in high purity and in large quantities in this source. This instrument is capable of measuring low concentrations (with detection limits approaching the ppqv regime) of VOCs using any of the three reagent ions investigated in this study. Therefore this instrument combines the advantages of the PTR-MS technology (the superior sensitivity) with those of SIFT-MS (detection of VOCs with PAs smaller than that of the water molecule and the capability to distinguish between isomeric compounds).

We will first discuss the setup of this new PTR+SRI-MS mass spectrometer instrument, its performance for aromates, aldehydes and ketones (with a sensitivity of up to nearly 1000 cps/ppbv and a detection limit of about several 100 ppqv) and finally give some examples concerning the ability to distinguish structural isomeric compounds.

1. Introduction

Proton-transfer-reaction mass-spectrometry (PTR-MS) was developed over a decade ago for the detection of gaseous organic compounds in air [1,2]. Today this technique is used in a wide range of scientific and technical fields allowing real-time, online, determination of absolute concentrations of volatile organic compounds (VOCs) in air with high sensitivity (into the low pptv range) and a fast response time (in the 40–100 ms time regime). The major driving force behind the fast spread of these instruments (today there are currently more than 150 commercial instruments in use worldwide [3]) was the desire by scientists to be able to accurately monitor volatile organic compounds (VOCs) in the atmosphere which are emitted from different biogenic and anthropogenic sources. The production, storage and use of fossil fuel products as well as intensive agriculture and biomass burning leads to an increasing change of the atmospheric composition. Deposition processes and important photochemical reactions remove and change the VOC composition in the atmosphere. Photochemical reactions are dominated by reactions involving the hydroxyl radical (OH) produced via the photolysis of water during daytime. The monitoring of reactions of VOCs with the OH radical requires different time scales from minutes to months. For many established analyzers a sample preparation and accumulation over some time is necessary and therefore they do not allow for real-time applications. Proton-transfer-reaction mass-spectrometry (PTR-MS) has overcome some of the disadvantages of traditional GC measurements and is by now a well established mass spectrometric technique used in a wide variety of fields including besides atmospheric science, medical and

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doi:10.1016/j.ijms.2009.06.006

biotechnological applications, food and flavour science, detection of illicit substances and industrial monitoring (see recent reviews [4–6] and conference reports [7,8]).

Besides the many advantages when compared to other methods (high sensitivity, real-time online monitoring, absolute quantification) one of the drawbacks of PTR-MS is the fact that only those compounds can be detected whose proton affinity is larger than that of H_2O (used for good reasons in the majority of commercial PTR-MS instruments [6], although in certain instances also NH_4^+ has been used as proton donor). Moreover, as in classic PTR-MS only the mass-to-charge ratio of the protonated parent ion (or product ion) can be determined, the presence of several different species on the same nominal mass, or even cluster ion formation and parent ion fragmentation may lead to complications in the interpretation of measured mass spectra. Various ways have been developed to overcome these complications concerning identification and interpretation including specially designed drift tubes [9,10], ion traps [11–15], triple quadrupoles [16], coupling with GC [17], and recently quite successfully the use of high resolution time of flight (TOF) mass spectrometers [18–25] where isobaric ions can be separated due to the high mass resolving power. In contrast, the disadvantage of not being able to ionize compounds whose proton affinity is smaller than that of H_2O is nicely avoided in the selected ion flow technique (SIFT), where mass pre-selection of a variety of reagent ions is employed. Detection sensitivity for SIFT-MS is, however, about two orders of magnitude lower than that for PTR-MS [6]. The use of SIFT-MS for chemical analysis has been early on explored by Spanel and co-workers [26–28] including extensive work on the ion-molecule chemistry in SIFT reactors with chemical ionization agents like H_3O^+, NO^+ and O_2^+ ions. Although Spanel et al. come to the conclusion that H_3O^+ is ideal for many applications, NO^+ and O_2^+ ions have been demonstrated to have their benefits. NO^+ is like H_3O^+ a soft ionizer, and ionization occurs mainly through charge transfer or hydride ion transfer and depending on the reactor conditions by termolecular association reactions. On the other hand O_2^+ is found to be a less soft chemical ionization agent and can be used where proton transfer does not work. Moreover, these SIFT studies have demonstrated that like H_3O^+ these alternative ions tend to react rapidly with most organic molecules with reaction rate coefficients, k, being close to the collisional rate coefficient, k_c, for bimolecular reactions.

Ellis, Monks and co-workers [29,30] have recently overcome these drawbacks by successfully combining chemical ionization mass spectrometry with Proton-transfer-reaction mass spectrometry (called CIRMS). Clean sources of reagent ions, such as H_3O^+, NH_4^+, NO^+ and O_2^+ ions, have been obtained without any mass preselection by switching the gas supply of a low intensity radioactive source. Obviously the ability to switch to other types of chemical ionization reagents which is achieved within a minute in this CIRMS instrument described in Ref. [29], provides a powerful extra dimension to this technique including the differentiation of isomeric compounds as demonstrated already by Spanel and co-workers [26–28].

In following up this pioneering work (see also another recent report on the possibility to use CI agents others than H_3O^+ and NH_4^+ in PTR-MS [31]) we report here the development of a new version of an IONICON PTR-MS instrument [3] using a novel and modified HC ion source plus drift tube design, which (i) allows for the easy and fast switching (within less than 10 s as compared to the 1 min by [29]) between H_3O^+, NO^+ and O_2^+ ions. This switchable reagent ion (SRI) instrument (called PTR + SRI-MS) is capable of measuring VOCs with all three ions at ultra-high sensitivity (nearly 1000 cps/ppbv) and at ultra-low concentrations (with detection limits in the ppqv regime) and (ii) features much higher primary ion count rates than in the previous studies [29–31]. It thus not only features the major advantage of PTR-MS technology (the superior sensitivity) but also the possibility to detect VOCs with PAs smaller than that of the water molecule and the capability to distinguish between isomeric compounds.

This paper has three aims. First we will show that HC driven PTR-MS can be adapted to exploit with high efficiency chemical ionization reagents other than the standard proton donor ions H_3O^+ and NH_4^+. Moreover, we will demonstrate that it is not only possible to cleanly generate the chemical reagent ions NO^+ and O_2^+ in our novel HC discharge ion source, but with primary ion intensities matching or in case of NO^+ even surpassing those of the H_3O^+ ions thus enabling ultra-high sensitivity and ultra-low detection limits also for this added dimension of PTR-MS technology. Finally, we will present measurements showing that by using this switchable reagent ion capability, PTR-MS becomes able to differentiate between isomeric aldehyde/ketone pairs, in particular when also considering the details of the corresponding reaction rates as a function of E/N in the drift tube reactor.

2. Instrument description and characteristics

The present Proton-transfer-reaction *plus* Switchable Reagent Ion Mass Spectrometer (PTR + SRI-MS) is an instrument based on the design of the commercially available High-Sensitivity PTR-Quad-MS system from IONICON [3]. The present instrument was constructed by interfacing an improved IONICON hollow cathode ion source plus drift tube section with a high end Inficon quadrupole mass spectrometer. The PTR + SRI-MS in its current commercially available version is mounted in a single mobile rack, where the mass spectrometer, the ion source plus drift tube system, the vacuum system (three turbomolecular pumps and one foreline backing pump) and all electronics are integrated. The rack dimensions are 55 × 86 × 78 cm (W × H × D) and the whole instrument weighs approximately 140 kg. The data acquisition and analysis system is situated in an external laptop computer and display system.

In the hollow cathode ion source H_3O^+ reagent ions are normally produced from water vapour (with less than 1% impurity ions) and introduced as reagent gas from a water tank. One of the advantages of the improved high performance HC ion source (based on extensive studies on the characteristics of hollow cathode discharge operation [32–34]) is that it requires less than 10 s to switch between reagent ions. This includes switching of the corresponding inlet lines to air and the O_2 gas reservoir, respectively. The source gas for the NO^+ ions was ambient air which is passed through a Supelco charcoal filter, whereas a cylinder of pure O_2 (Air Liquide) was used to produce O_2^+ ions. The production of both, the NO^+ and the O_2^+ chemical ionization agents is exceptionally clean in our combination of hollow cathode ion source coupled to the drift reactor. The only significant contaminant ions are O_2^+ and NO_2^+ in case of NO^+ reagent ions and NO^+, NO_2^+ and H_3O^+ in case of O_2^+ reagent ions with abundances of less than 1% for the NO^+ CI agent and less than 4% in case of the O_2^+ CI agent. We are able to extract from our HC source very intense ion currents, i.e., reagent ions with typical intensities of 40×10^6 cps for H_3O^+, 60×10^6 cps for NO^+ and 50×10^6 cps for O_2^+ (measured at the detector after drift tube and mass filter). It is interesting to note that so far typical count rates used in most of the available PTR-MS devices are according to [6] in the 1×10^6 cps range. In comparison IONICON has for the last few years routinely reached 10×10^6 cps for the high-sensitivity HS-PTR-MS. It is clear that the present ion source constitutes a major improvement also in intensity and thus sensitivity.

After production the reagent ions enter via a transfer section the adjacent drift tube, where the sample to be analyzed is continuously injected via a sample line system with an adjustable flow between 50 and 1000 sccm and adjustable temperature between 40–150 °C. The pressures maintained in the drift tube are between

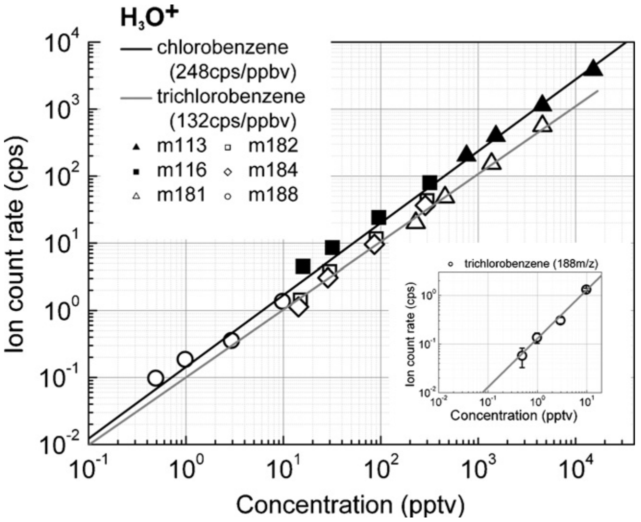

Fig. 1. Correlation plot (measured ion count rates versus absolute concentration) for chlorobenzene and tricholorobenze for H_3O^+ reagent ions measured at 130 Td and with integration times between 7 and 180 s. Chlorobenzene designated with open symbols at mass 113 and 116, and tricholorobenzene designated with filled symbols at mass 181, 182, 184 and 188. Insert shows the trichlorobenzene data close to the detection threshold after subtraction of background signal.

2.2 and 2.4 mbar. In this drift tube (adjustable temperature between 40–120 °C) Proton-transfer-reactions occur between hydronium ions and VOCs or chemical ionization reactions of NO^+ and $O_2{}^+$ with VOCs. The outgoing product VOCs ions then enter via a specially designed transfer lens system the quadrupole mass spectrometer. As with earlier PTR-MS instruments the measurement response time is less than 100 ms. Finally, it is interesting to note that the new HC discharge design, the optimized ion transfer situation and the improved background signal are responsible for the high sensitivity and the low detection limit (see below) achieved for this PTR + SRI – MS apparatus.

3. Studies with aromates, aldehydes and ketones

We will discuss the present measurements in two major subsections: the first deals with aromates including correlation plots, sensitivity tables and mass spectra and the second with aldehydes and ketones. Within each of these subsections, we will discuss separately the results obtained with the different reagent ions H_3O^+, NO^+ and $O_2{}^+$. In particular we compare the sensitivities/detection limits reached, their different reaction behaviour and the added value derived from using a PTR + SRI – MS instrument in multiple ion mode. The analytes employed in this study (using premixed calibration gas mixtures of aromates, aldehydes and ketones from Ionimed Analytik GmbH and from Restek) were mixed at different flow rates, e.g., 1, 3, 10 and 20 sccm with synthetic air at a flow rate of 1000 sccm (see [35]) and then continuously flowed into the upstream section of the drift tube reactor at a flow rate of 300 sccm, from which 25 sccm are finally introduced into the drift tube. The gas inlet lines and the drift tube were kept at a temperature of 60 °C to minimize gas adhesion on the inner walls and to maintain constant reaction conditions for the chemical ionization.

3.1. Aromates

Figs. 1–3 show examples of correlation plots for measured ion count rates versus absolute concentration demonstrating the superior response for VOCs detection of this PTR + SRI – MS instrument in the case of aromatic hydrocarbons. The sensitivity response for the three different reagent ions H_3O^+, NO^+ and $O_2{}^+$ has been assessed for a number of typical aromatic analytes at $E/N = 130$ Td using a known standard gas mixture (see Table 1) by carrying out a series of step-wise dilutions. Measuring not only the major isotope of the product ion but also minor isotope product ions allows us to obtain data points over several orders of magnitude.

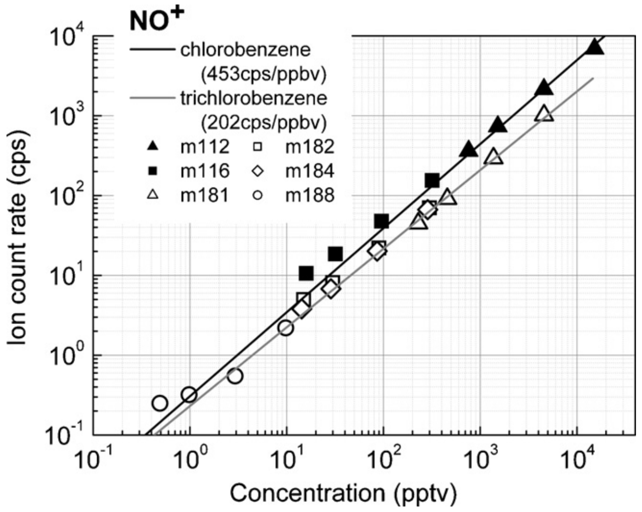

Fig. 2. Correlation plot (measured ion count rates versus absolute concentration) for chlorobenzene and trichlorobenzene for NO^+ reagent ions measured at 130 Td and with integration times between 7 and 180 s. Symbols as in Fig. 1.

Figs. 1 and 2 show a correlation plot for chlorobenzene and tricholorobenzene over five orders of magnitude. Here the linearity of response of the instrument across this large concentration range (from the ppbv to the ppqv range) for both the H_3O^+ and NO^+ reagent ions is clearly demonstrated. Derived sensitivities with values up to about 750 cps/ppbv for these two and also other aromatic analytes are given in Table 1. It can be seen that highest sensitivities are found for the NO^+ ions (approx. 30–40% higher than that for the H_3O^+ ions) because of the higher intensity in the reagent ion current, whereas for the $O_2{}^+$ ions the sensitivities are on average appr. 30% lower than that for the H_3O^+ ions (because of lower reagent ion current and lower rate coefficients). These sensitivities are on par with the good sensitivities (∼1 Hz/pptv) reported recently by Hanson et al. [36] using Proton-transfer-reaction mass spectrometry at 11 hPa (approximately four times higher pressure than here) with a circular glow discharge ion source.

The insert in Fig. 1 also gives a close-up of the correlation plot for trichlorobenzene measured with the H_3O^+ reagent ions close to

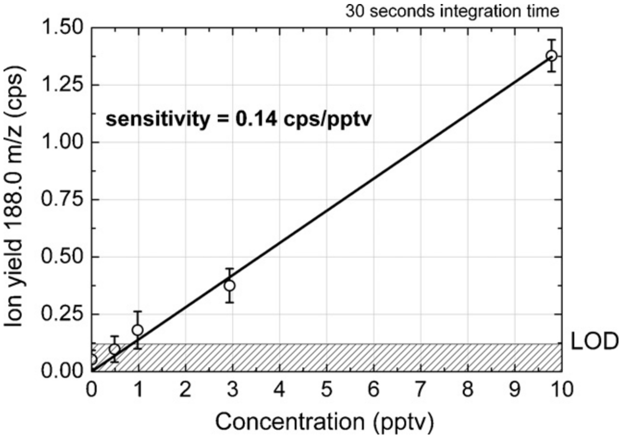

Fig. 3. Correlation plot (ion count rate versus absolute concentration) for trichlorobenzene measured with H_3O^+ reagent ions at 130 Td and with a 30 s integration time. Determination of limit-of-detection (LOD) and error bars see text.

Table 1
Sensitivities in cps/ppbv of nine aromatic hydrocarbons for H_3O^+, NO^+ and O_2^+ reagent ions measured at 130 Td and with a 500 ms accumulation/integration time (that is five scans with 100 ms per mass). In brackets the corresponding product ions are given. For a discussion of the sensitivities of the two isomers xylene and ethylbenzene see text. The molecular mass number and the concentration in the calibration gas sample are also presented.

Compound	Molecular mass (amu)	Concentration of this compound in the calibration gas (ppbv)	H_3O^+ mass (cps/ppbv)	NO^+ mass (cps/ppbv)	O_2^+ mass (cps/ppbv)
Benzene	78	91.8	405 (M79)	495 (M78)	307 (M78)
Toluene	92	89.9	449 (M93)	685 (M92)	350 (M92)
Chlorobenzene	112	55.4	533 (M113)	732 (M112)	437 (M112)
Xylene	106	267.6	447 (M107)	598 (M106)	357 (M106)
Ethylbenzene	106	88.9			301 (M91)
Styrene	104	88.0	470 (M105)	610 (M104)	315 (M104)
Trimethylbenzene	120	177.7	404 (M121)	567 (M120)	292 (M120)
Dichlorobenzene	146	96.1	570 (M147)	719 (M146)	498 (M146)
Trichlorobenzene	180	39.2	214 (M181)	270 (M180)	201 (M180)

the detection limit. Besides showing (after deduction of background signal) linearity of response also in this range, it demonstrates the ultra-low detection limit of the present setup. With an integration time of 180 s, we are able to observe concentrations of several 100 ppqv. This is the first time that such low sample concentrations have been detected with PTR-MS. Finally, we show H_3O^+ results in Fig. 3 for trichlorobenzene where several data points with an integration time of 30 s each have been measured at different calibration steps. From these data points we determine the average and the standard deviation and plot these values in Fig. 3 versus the measured concentration. From this plot we derive the sensitivity by a linear fit to be (135 ± 1) cps/ppbv. Moreover, this plot also demonstrates the limit-of-detection (LOD) achieved. The LOD is the concentration which can be reliably distinguished from the background noise. Using a signal-to-noise (S/N) ratio of 3 results in a LOD of $3 \times \sigma_0 = 0.12$ cps (see hatched area in Fig. 3) where σ_0 is the standard deviation of the background noise level of measurements at 0 pptv. Using the sensitivity to calculate the corresponding volume-mixing-ratio, gives for this case a LOD of 890 ppqv.

Moreover, it is interesting to note that the two isomeric compounds, xylene and ethylbenzene (with a molecular mass of 106 amu), cannot be distinguished by ordinary PTR-MS as both compounds share the same protonated parent mass of $m/z = 107$. As already pointed out by Spanel et al. [28] based on SIFT studies of these two analytes also product ions with the NO^+ agent show the same complication, i.e. both isobaric compounds are present after charge transfer reactions on the parent ion mass $m/z = 106$. Nevertheless, using O_2^+ as a CI agent allows us to distinguish these two isobars due to the different reaction routes and different ratios for product ions. Whereas charge transfer leads in the majority (80%) of the O_2^+/xylene collisions to parent ion production detected at mass 106, in the remainder of cases (20%) an adduct ion $C_7H_7^+$ via dissociative charge transfer at mass 91 is produced. In case of ethylbenzene, the ratios are quite opposite, i.e., 30% parent ion and 70% fragment ion production. It is clear that this different behaviour between H_3O^+ and NO^+ on the one hand and O_2^+ on the other hand can be used to derive the corresponding amounts of xylene and ethylbenzene in an unknown sample. This is only possible, however, if there are no other interfering compounds at these masses. We have checked this here by using an IONICON PTR-TOF-MS instrument (time of flight based PTR-MS system) described in Refs. [23–25] which allows to separate and identify isobaric contaminants (see Fig. 4). In doing so we were able to obtain the respective sensitivities for the O_2^+ ionizing agent given in Table 1. It is noteworthy that these reaction ratio values have been reported by Spanel et al. [28] on the basis of SIFT-MS investigations and that these values have been used in further applications. Nevertheless, as can be seen from the present study, see Fig. 5, this ratio strongly depends on the kinetic energy in the reaction, i.e., in case of xylene the percentage of fragment ions decreases from about 20% at an E/N of 135 Td to less than 10% at an E/N of 75 Td. This fact has to be taken into account when accurate concentration determinations are to be made. This is particularly important in environmental applications because ethylbenzene and xylene isomers are often targeted during environmental monitoring exercises due to their widespread presence in fuels and paints.

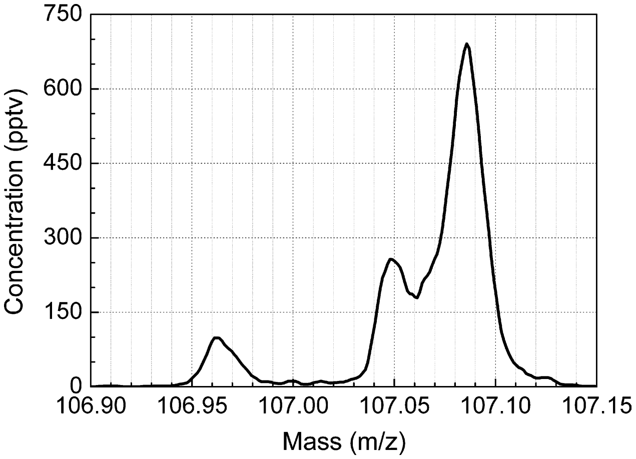

Fig. 4. High resolution mass spectrum measured with an IONICON PTR-TOF-MS [23–25] at around m/z 107 Th. Besides the compound under study (xylene) detected after reaction with H_3O^+ at the protonated mass 107.0861 we also observe two additional background peaks, one at 107.0497 (protonated parent ion peak of benzaldehyde) and one at 106.9634.

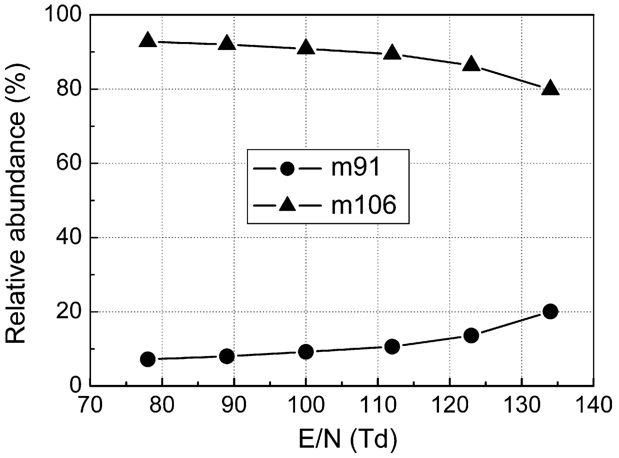

Fig. 5. Branching ratios versus the reduced field strength E/N for xylene detected with O_2^+ reagent ions at the parent ion mass 106 and a fragment ion mass 91, see text.

Table 2
Sensitivities in cps/ppbv of 8 aldehydes for H_3O^+ reagent ions measured at 112 Td and NO^+ reagent ions measured at 90 Td (values were found to be an ideal compromise between strong association/clustering at low *E*/*N* and strong fragmentation at high *E*/*N* ratios), with a 2 s accumulation/integration time (that is 20 scans with 100 ms per mass). In brackets the corresponding product ions are given. The molecular mass number and the concentration in the calibration gas sample are also presented.

Compound	Molecular mass (amu)	Concentration of this compound in the sample gas (ppbv)	H_3O^+ mass (cps/ppbv) at 112 Td	H_3O^+ mass (cps/ppbv) at 112 Td	NO^+ mass (cps/ppbv) at 90 Td
Acetaldehyde	44	21.4	544 (M45)		163 (M43)
Acrolein	56	18.9	604 (M57)		703 (M55)
Propanal	58	20.4	580 (M59)		461 (M57)
Butanal	72	19.0	100 (M73)	483 (M55)	602 (M71)
Crotonaldehyde	70	18.7	640 (M71)		771 (M69)
Valeraldehyde	86	18.1	71 (M87)	520 (M69)	602 (M85)
Hexanal	100	18.4	78 (M101)	462 (M83)	557 (M99)
Heptanal	114	16.8	101 (M115)	360 (M97)	460 (M113)

Finally, Fig. 6 gives as an example mass spectral data obtained using the H_3O^+, NO^+ and $O_2{}^+$ reagent ions to ionize the aromate-gas mixture. It immediately becomes apparent that as expected from the earlier mentioned SIFT studies [28] ionization routes are quite different for these three reagent ions. H_3O^+ mostly leads to the production of the protonated parent ion (including isotopes). NO^+ mainly yields the pure parent ion after charge transfer, whereas $O_2{}^+$ leads to extensive fragmentation via charge transfer due to the large excess energy deposited in the ensuing parent ion after charge transfer. Whereas the ionization energy of NO with 9.6 eV is just above the energies of most of the aromates (lying between 8.27 and 9.25 eV [28]), the ionization energy of O_2 with 12.06 eV is several eV above the energies of these aromates.

3.2. Aldehydes and ketones

The aldehyde mixture (see Table 2) also yields quite different mass spectra for the three reagent ions. As seen in Fig. 7 on a first glance, NO^+ reactions yield the simplest spectrum, mainly giving dehydrogenated cations $(M\text{-}H)^+$ plus HNO produced via hydride ion (H^-) transfer (see also earlier SIFT studies by Spanel et al. [26]). However, $O_2{}^+$ reactions mostly proceed by charge transfer which is again sufficiently exothermic to produce strong fragmentation of the excited parent ion M^{+*} resulting in several fragment ions. The Proton-transfer-reaction from H_3O^+ for the smaller aldehydes produces only the protonated MH^+ plus H_2O. In contrast for the larger aldehydes another reaction process occurs in which varying fractions of the MH^+ ion dissociate via the ejection of a water molecule yielding hydrocarbon ions of the type $(M\text{-}H_2O)H^+$.

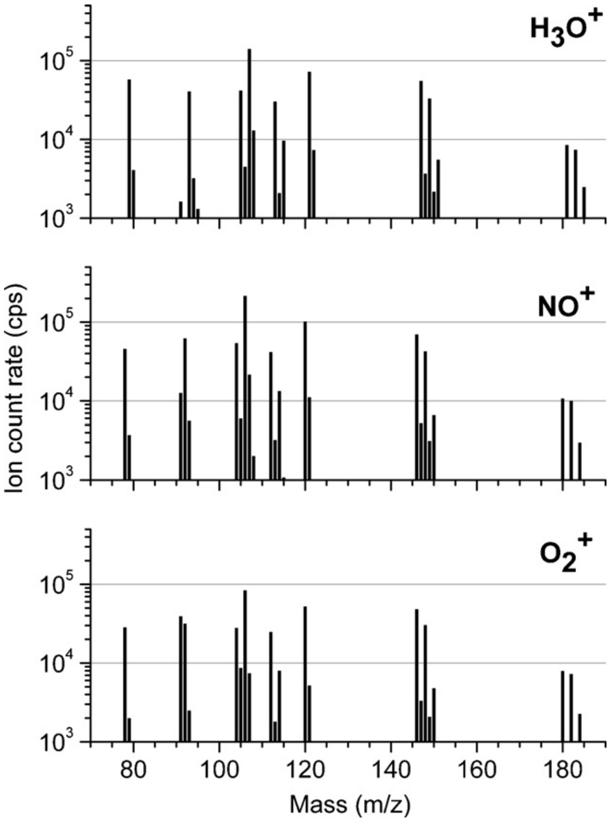

Fig. 6. Mass spectra from reaction with nine aromatic hydrocarbons (see Table 1) for H_3O^+ (top panel), NO^+ (middle panel) and $O_2{}^+$ (bottom panel) reagent ions measured at 130 Td and with 500 ms integration time (that is five scans with 100 ms per mass).

Table 2 gives sensitivities determined via correlation plots for both ionization routes for H_3O^+ (where applicable) and for the dehydrogenated parent ion in case of NO^+ ionization. The sensitivities have the same order of magnitude as for the aromatic hydrocarbons.

An especially interesting situation arises in case of NO^+ reactions with ketones. According to Spanel et al. [26] these reactions proceed via termolecular association reactions (at effective bimolecular rate coefficients that are close to the collisonal one) yielding in their detailed investigations predominantly ions of the kind $M.NO^+$. In contrast Blake et al. [30] using NO^+ reagent ions in their PTR-MS study have reported an almost complete lack of any association complexes with NO^+. Blake et al. attributed these differences to the higher collision energy (typically at an *E*/*N* of 165 Td yielding center of mass energies of about several tenth of an eV) used in their own study as compared to the SIFT-MS study (where reagent ions are thermalized in an inert buffer gas). They argue that any complexes formed in the drift-tube are fragmented subsequently through collisions with the buffer gas thus recovering the free NO^+ cations in their study. In order to elaborate on this question we have studied here reactions of both, H_3O^+ and NO^+, with ketones and aldehydes as a function of E/N in the drift tube.

Fig. 8 shows as an example the measured count rates for NO^+ reactions for the two ketones: acetone (propanone) and butanone and the data for the corresponding two structural aldehyde isomers: propanal and butanal, respectively. The overriding conclusion from these data is firstly that indeed association complexes $M.NO^+$ of the ketones (acetone and butanone) are produced at mass 88 and 102, respectively. At low *E*/*N* these association complexes are produced in comparable abundances to the protonated species produced via H_3O^+ at the protonated parent masses 59 and 73, respectively (not shown in this figure for the sake of clarity). Moreover, these association complexes $M.NO^+$ of acetone and butanone at mass 88 and 102, respectively, are (in contrast to the protonated species produced via H_3O^+ at masses 59 and 73 which stay independent from *E*/*N*) decreasing strongly in intensity with increasing *E*/*N*, i.e. by almost three orders of magnitude when going from 70 Td to 130 Td. Moreover, in contrast to earlier studies (e.g. Ref. [26]) we observe with NO^+ reagent ions also the presence of parent ions of acetone and butanone at mass 58 and 72, respectively, albeit

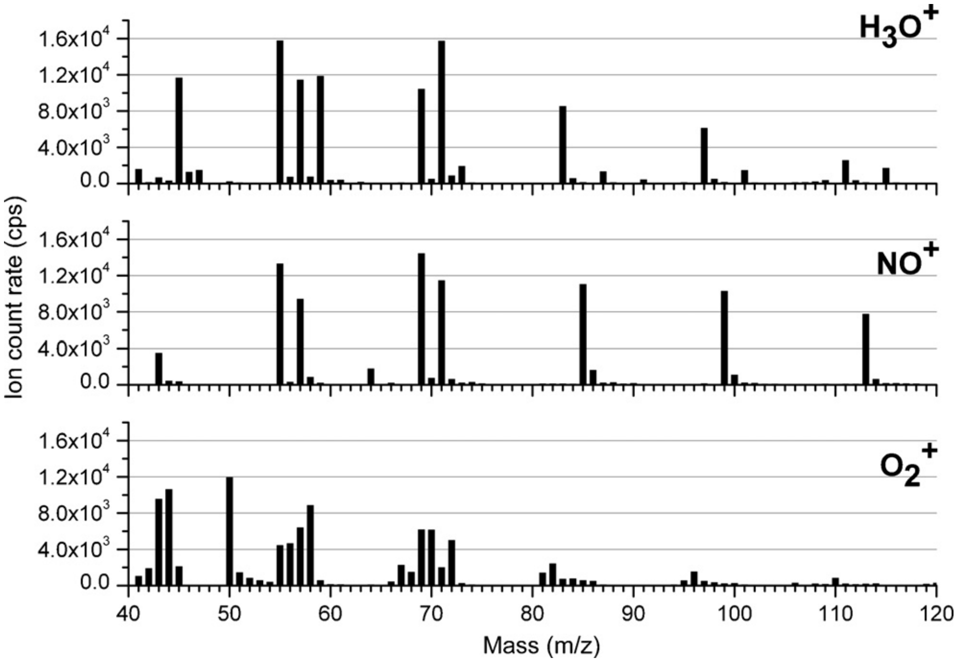

Fig. 7. Mass spectra from reactions with eight aldehydes (see Table 2) for H_3O^+ (top panel), NO^+ (middle panel) and $O_2{}^+$ (bottom panel) reagent ions measured at 112, 90 and 112 Td, respectively and with 2 s integration time (that is 20 scans with 100 ms per mass).

at much smaller abundance than the complex ions and they also show a much smaller dependence on *E*/*N*. In contrast, the respective isomeric aldehydes (propanal and butanal) are reacting with NO^+ exclusively to give dehydrogenated product ions at mass 57 and 71 with only a weak energy dependence at very high *E*/*N*.

It is clear that these differences in reaction probabilities between ketones and aldehydes (here demonstrated for the pairs acetone/propanal and butanone/butanal at the molecular masses 58 and 72, respectively) for NO^+ reagent ions can in a similar fashion as described above for the isomeric pair xylene and ethylbenzene be used to separate contributions for these isomeric aldehyde/ketone pairs, i.e., acetone (propanone) from propanal and butanone from butanal. Again, taking the reaction ratios given in the SIFT studies by Spanel et al. [26] will not be sufficient in all cases (see also discussion in [30]) as reaction ratios are strongly depending on *E*/*N*. Because for H_3O^+ reactions both, ketones and aldehydes, only show up at the protonated parent mass the analytical value and implications of these observations given here for NO^+ reactions in Fig. 8 are quite evident.

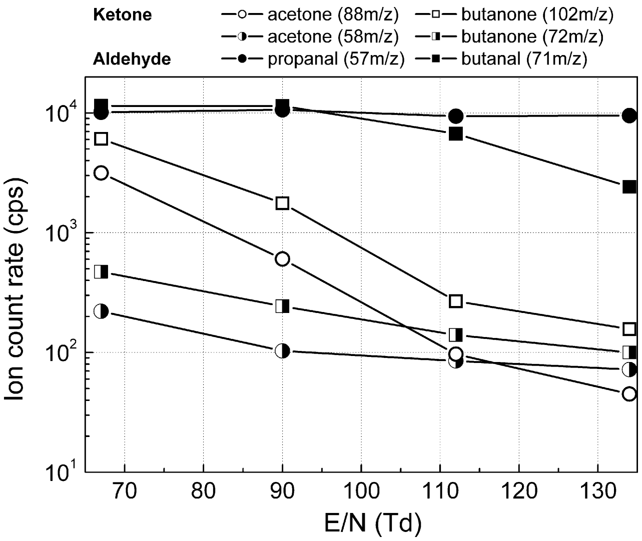

Fig. 8. Ion count rates versus the reduced field strength *E*/*N* for two ketones acetone (propanone) and butanone and for the corresponding two structural aldehyde isomers propanal and butanal. The ketones are measured at the association complex mass 88 for acetone (designated open circle) and 102 for butanone (designated open square) and at parent mass 58 of acetone (designated half filled circle) and parent mass 72 of butanone (designated half filled square). In contrast, the respective isomeric aldehydes propanal and butanal react with NO^+ exclusively to dehydrogenated product ions at mass 57 (designated filled circle) and 71 (designated filled square), respectively.

4. Conclusions

The main differences between SIFT-MS and PTR-MS are that there is (i) no initial mass selection of reagents ions and (ii) no dilution of the analyte sample in a carrier gas in PTR-MS. The net result of these two features is according to Ref. [6] a detection sensitivity for PTR-MS which is two orders of magnitude better than that of SIFT-MS. To allow condition (i) in PTR-MS the ion source must be carefully chosen and constructed to avoid any impurity ions. So far this was achieved by using a hollow cathode running with water vapour producing paramount intensities of H_3O^+ ions, this source being the staple ion source for the majority of PTR-MS studies and instruments. Here we have extended this hollow cathode gas discharge ion source concept (see also the earlier radioactive variant by Ellis, Monks and co-workers [22–24]) to allow also the production of NO^+ and $O_2{}^+$ ions in the very same manner and with the same high efficiencies as previously used to produce H_3O^+ in PTR-MS instruments. Here the advantages of both methods have been married, i.e. the high sensitivity of PTR-MS and the versatility of multiple reagent ion capability of SIFT-MS. We call this new variant a PTR + SRI – MS instrument, that is a PTR-MS instrument capable of working in switchable reagent ion (SRI) mode, with an unparalleled sensitivity, detection limit and versatility.

In a next step we will extend this capability to our recently developed time of flight PTR-MS instruments (IONICON PTR-TOF-MS [23–25]) allowing an even greater analytic value for the many applications pursued by this technique, including its widespread use as a tool for detecting and quantifying in real-time online trace gas compounds in atmospheric studies, aroma analysis, illicit substance detection and medical science.

Acknowledgements

Work partially supported by the Leopold Franzens University, Innsbruck, the IONICON Analytik GmbH, Innsbruck, the IONIMED Analytik GmbH, Innsbruck, the FWF and FFG, Wien, Austria and the European Commission, Brussels. We also would like to gratefully acknowledge valuable discussions with Dr. Nancy Hecker-Denschlag, IONIMED Analytik GmbH, Innsbruck.

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