Short communication

The effect of ozone in positive ion mode ion mobility spectrometry

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Abstract

An additional contributing factor to the spectral complexity in positive ion mode ion mobility spectrometry of unsaturated compounds using corona discharge ionization is disclosed. The cause is shown to be an ozonolysis-type reaction initiated by ozone produced by the corona ionization source.
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1. Introduction

A number of recent articles have compared ionization sources used in ion mobility spectrometry (IMS) [1–3]. In these articles it is stated that although the use of corona discharge (CD) ionization in IMS allows for sensitive detection of unsaturated compounds, the ions contributing to the mobility spectra cannot be completely identified due to the complexity of possible ionization pathways. Whilst the different possible ionization pathways arising from the use of a CD ionization source can increase the complexity of IMS spectra compared to ^{63}Ni ionization sources, it is suggested in this communication that another contributing factor to spectral congestion can also be present.

Previous work on corona discharge ion mobility spectrometry has shown that the production of ozone by a corona source can severely affect reactant and product ion distributions and sensitivity in the negative ion mode [4]. In this work it was shown that a continuous corona discharge source can generate concentrations of ozone and NO_x high enough to convert the constituents of the negative mode reactant ion peak (RIP) from O_2^- and CO_4^- -based ions to CO_3^- and NO_3^- ions. Such a conversion renders the negative ion mode unresponsive to sample vapours. However this could be overcome by the implementation of a reverse flow regime. In that correspondence it was also stated that positive mode responses to unsaturated and aromatic compounds could also

be affected by the presence of ozone. This letter illustrates the effect of ozonolysis-type reactions on the positive ion mode IMS spectra of aromatic compounds.

2. Experimental

The tandem IMS/mass spectrometry system used in these experiments (containing atmospheric pressure ionization, reaction and drift regions, coupled by a 50 μm diameter orifice to a reduced pressure chamber containing a mass spectrometer running in external ion mode) has been described previously [4]. The IMS ionization region was adapted so that in addition to the fixed ^{63}Ni source there was also a corona ionization source which could be switched on or off, i.e., experiments were performed with either;

- ^{63}Ni source alone, or
- ^{63}Ni source and continuous corona source.

The ions produced by the corona source were determined by comparison of the spectrum of the ^{63}Ni source alone with that obtained from the combined ^{63}Ni and continuous corona sources. A standard flow direction (with the flow (known as the carrier gas flow) through the ionization region towards the shutter grid) was used throughout the work.

For the positive ion mode experiments described here corona currents of 1 μA were used yielding ozone and NO_x concentrations of approximately 100 ppb. The concentrations were determined by chemiluminescence for NO_x (Model 200A, Advanced Pollution Instrumentation Inc., San Diego, CA) and UV absorption for ozone (Model

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400A, Advanced Pollution Instrumentation Inc., San Diego, CA) and were used as produced by the corona source—no other control was employed. Previous work has indicated that a ^{63}Ni source run under similar conditions produces ca. 8 ppb ozone and 3 ppb NO_x [5].

The results for benzene and 1,4-dimethyl benzene (*p*-xylene) are reported here. Analyte concentrations were produced using dilution techniques and the analytes were introduced into the carrier gas flow using a syringe drive (Harvard Apparatus, Natick, MA). All experiments were performed with a water-based RIP produced by a water concentration of ca. 100 ppm (created using an in-line diffusion source and measured using a calibrated hygrometer ("MCM Si-grometer")).

3. Results and discussion

3.1. Benzene

Fig. 1 shows the IMS spectra resulting from a concentration of 1.5 ppm benzene introduced into the system for ^{63}Ni and combined ^{63}Ni/continuous corona sources. The sensitivity of the system to benzene is considerably enhanced with the corona source (Fig. 1b) over that obtained with the ^{63}Ni source (Fig. 1a). This is in part due to the larger concentration of N_2^+ produced by the harsher ionising conditions of the corona source resulting in higher concentrations of NO^+ [6]. The use of NO as a reactant gas for chemical ionization in IMS has been previously demonstrated [7]. The increased production of $C_6H_6\cdot NO^+$ ($M\cdot NO^+$), added to other new product ions (m/z 85, 95 and 111 corresponding to $M + 7$, $M + 17$ and $M + 33$ respectively) with the same mobility, yields an increase in sensitivity. The ions from each source are assigned in Table 1.

3.2. Dimethyl benzene

Fig. 2 shows the IMS spectra resulting from a concentration of 0.8 ppm 1,4-dimethyl benzene introduced into the system. Although the spectra are similar for both the ^{63}Ni source and the corona there are notable differences. The ions are assigned in Table 2.

The identity of the ion with m/z value 79 (with its intensity spread over the tail of the RIP for both ^{63}Ni and combined ^{63}Ni/corona sources) remains unknown. The ions with m/z values of 121, 129, 133 and 155 are produced from the corona ionization. However, the ions with m/z values cor-
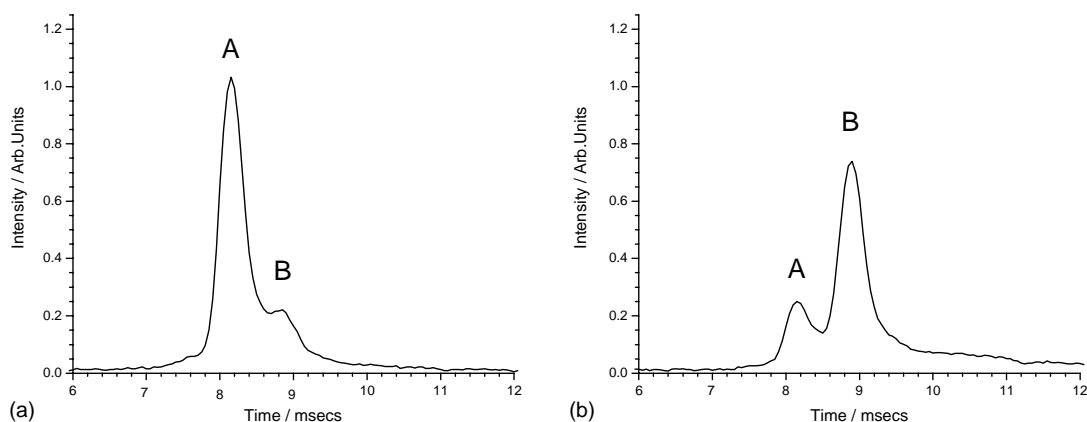

Fig. 1. IMS spectra of 1.5 ppm benzene using; (a) ^{63}Ni ionization source, (b) combined ^{63}Ni/corona discharge source. Ion assignments are given in Table 1. Labels A and B relate reactant ions and product ions respectively and are identified in Table 1.

Table 1
Ion assignments for the ^{63}Ni and continuous corona ion mobility spectra obtained from 1.5 ppm benzene

Source	Ions in peak A		Ions in peak B	
	m/z and assignment	Relative intensity	*m/z* and assignment	Relative intensity
^{63}Ni source	RIP	100	m/z 108: ($M\cdot NO^+$)	24[a]
	m/z 78 (M^+)	48		
Corona	RIP	42	m/z 85[b]: $(M + 7)^+$	14
			m/z 95: $(M + 17)^+$	21
			m/z 108: ($M\cdot NO^+$)	112[a]
			m/z 111: $(M + 33)^+$ + minor species	21

The ions produced by the ^{63}Ni source are also produced by the combination of the ^{63}Ni and corona sources. Intensities are relative to the most intense peak. The RIP intensity in both cases includes the typical ions $H_3O^+(H_2O)_x$, where $x = 1$–4. The additional ions observed with the combined ^{63}Ni/corona source are shown in bold.

[a] These intensities contain a contribution from M^+ ions at the same mobility, thought to be produced from dissociation of the $M\cdot NO^+$ ion at the interface to the mass spectrometer.

[b] This ion is actually found between the two peaks A and B, but cannot be observed as an independent peak in the IMS spectrum.

responding to (M + 7), (M + 17) and (M + 33), where M is the molecular weight of the neutral sample species, are the same as those seen for benzene and are produced in the presence of ozone.

Fig. 2. IMS spectra using ^{63}Ni and continuous corona ionisation sources for 0.8 ppm 1,4-dimethyl benzene in an IMS system using standard sample flow. Ion assignments are given in Table 2.
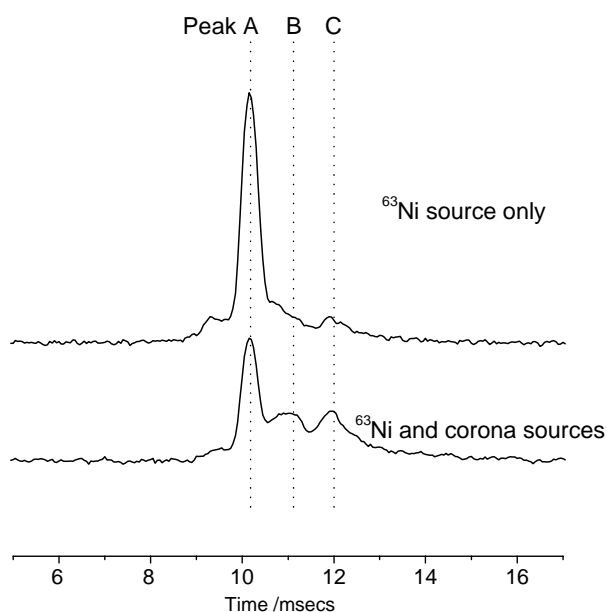
3.3. Product ion formation

The production of ions for both benzene and 1,4-dimethyl benzene can be understood by recourse to the example ozonolysis reaction below.
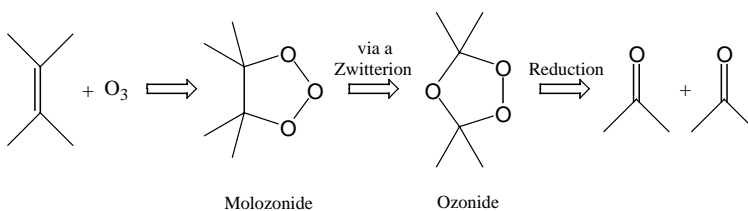
The formation of possible product ions for benzene is illustrated in Fig. 3. Assuming a Kekule structure for benzene, then cleavage (via ozonolysis) of one double bond [8] will result in a neutral species with a MW of (M + 32), which in an IMS system can pick up a proton to produce the ion with an m/z value of (M + 33). If two double bonds are broken then two ion species are possible (corresponding to (M + 7) and m/z 59). The third major peak is the (M + 17)$^+$ peak. This does not arise directly from an ozonolysis reaction. However, for benzene, for example, the zwitterionic intermediate in the ozonolysis reaction.
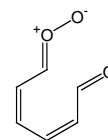
may undergo ring reformation ultimately producing
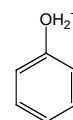
with an m/z value corresponding to (M + 17).

Table 2
Ion assignments for the ^{63}Ni and continuous corona ion mobility spectra obtained from 0.8 ppm 1,4-dimethylbenzene

Source	Ions in peak A		Ions in peak B		Ions in peak C	
	m/z and assignment	Relative intensity	m/z and assignment	Relative intensity	m/z and assignment	Relative intensity
^{63}Ni	RIP	100	Not present	–	m/z 136: M·NO$^+$	6[a]
	m/z 79 (in tail)	3				
Corona	RIP	100	m/z 113 (M + 7)$^+$	50	m/z 121: (M − CH$_3$)NO$^+$	10
	m/z 79 (in tail)	13			m/z 123: (M + 17)$^+$	10
					m/z 129	8
					m/z 136: M·NO$^+$	35[a]
					m/z 139: (M + 33)$^+$	8
					m/z 130,155 (in tail)	8,8

The ions produced by the ^{63}Ni source are also produced by the combination of the ^{63}Ni and corona sources. Intensities are relative to the most intense peak. The RIP intensity in both cases includes the typical ions H$_3$O$^+$(H$_2$O)$_x$, where x = 1–4. The additional ions observed with the combined ^{63}Ni/corona source are shown in bold.

[a] These intensities contain a contribution from M$^+$ ions at the same mobility, thought to be produced from dissociation of the M·NO$^+$ ion at the interface to the mass spectrometer.
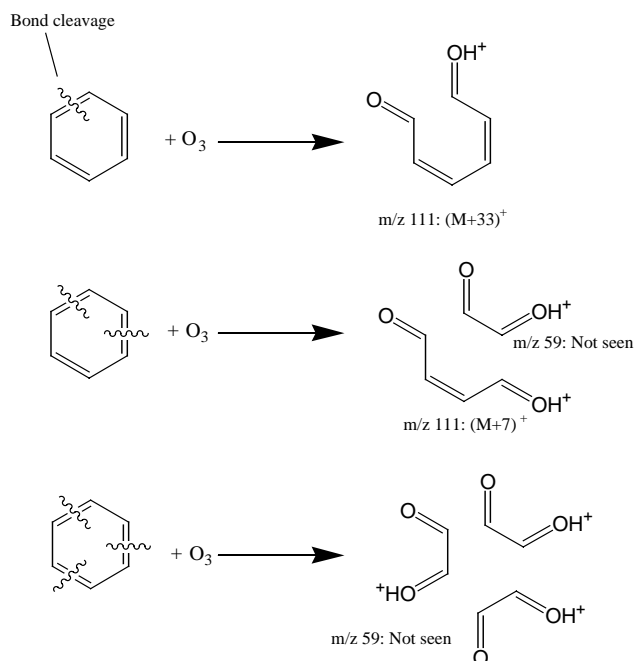
Fig. 3. The use of benzene as an example of the product ions that may be seen following ozonolysis and protonation. It is not known why the ion with *m/z* value 59 is not observed experimentally. Note: This approach can be used in order to interpret the IMS spectra of any unsaturated compound. In the case of larger, more substituted unsaturated hydrocarbons the number of possible product ions grows rapidly.

Similar product ion distributions can be written for the 1,4-dimethyl benzene, however with increasing substituents present on the ring the number of potential product ions grows significantly. Note: the prediction of ions for any un-saturated compound is no guarantee of the presence of that ion in the mobility spectrum. The reason for this product ion selection has not been pursued in this current work.

However, despite the above mechanistic explanation, observed reaction rates for the reaction of aromatic compounds with ozone [9] indicate that the rate constants are such that at the concentrations of reagents in this system the experimentally observed product ions will not be produced.

The only reactions capable of proceeding sufficiently rapidly to generate the ions observed, from the concentrations of reagents available, are ion–molecule reactions. It is thus proposed that ozonolysis-type reactions are occurring in which one partner is an ion.

4. Conclusions

The detection of aromatic hydrocarbons using standard continuous corona discharge sources in the positive ion mode of an IMS system can result in increased complexity in the IMS spectra due to ozonolysis-type ion–molecule reactions.

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