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Analysis of volatile flavour compounds by Proton Transfer Reaction-Mass Spectrometry: fragmentation patterns and discrimination between isobaric and isomeric compounds

Katja Buhr[*], Saskia van Ruth, Conor Delahunty

Department of Food Science, Food Technology and Nutrition, University College Cork, Western Road, Cork, Ireland

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Abstract

The behaviour of 53 flavour compounds in Proton Transfer Reaction-Mass Spectrometry (PTR-MS) was investigated. Obtained spectra showed general rules on fragmentation patterns of alcohols, aldehydes, ketones and esters. Alcohols and aldehydes split off water while ketones hardly show any fragmentation. The mass fragments at $m/z = 55$ and 69 are potential markers for the presence of aldehydes and mono-unsaturated alcohols. Esters hydrolyse dependent on the ratio of the carbon chain length of their alcoholic part vs. their acidic part. Although fragmentation of individual compounds generally complicates the headspace spectra of complex mixtures, it can provide relevant information on discrimination of isobaric and isomeric compounds. (Int J Mass Spectrom 221 (2002) 1–7)

Keywords: Flavour; Fragmentation; Isobaric compounds; Isomeric compounds; PTR-MS

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1. Introduction

Proton Transfer Reaction-Mass Spectrometry (PTR-MS) is a relatively new MS technique which basically implements H_3O^+ as the ionising agent in a chemical ionisation. The advantage of using H_3O^+ as the primary ion lies in its non-dissociative proton transfer reaction with most volatile organic compounds, whereas it does not react with any natural components of air. Compared to conventional MS, the non-dissociative character of the proton transfer reactions leads to less complex spectra and opens the opportunity to skip a previous separation of the compounds. Detection limits of a few ppbv allow an analysis of the headspace without any previous concentration step. Therefore, PTR-MS is a very fast and powerful tool for obtaining real-time data, for example, in process control and time intensity studies [1–3].

It has been successfully implemented not only for environmental research [4,5] and non-invasive medical applications [6,7] but also for food analysis, especially for the determination of flavour volatiles [2]. On-line monitoring of coffee roasting [8], emission of volatile organic compounds from berryfruit [9], degradation of meat [1,2], as well the discrimination of different mozzarella cheeses [10] are some of the applications which have been recently published.

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[*] Corresponding author. E-mail: k.buhr@ucc.ie

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Relatively few data have been published on fragmentation of individual volatile flavour compounds [2,11,12]. On the one hand, fragmentation is preferably avoided in order not to complicate the analysis. On the other hand, it may help to separate compounds. However, for analysing complex mixtures of volatile compounds like food flavours, basic data on the behaviour of individual compounds is essential.

In the present study, the fragmentation patterns of 53 individual volatile flavour compounds were evaluated. Furthermore, the possibilities for discrimination of isobaric and isomeric compounds by PTR-MS were explored.

2. Materials and methods

2.1. Materials

Fifty-three volatile flavour compounds (Tables 1–3) were individually diluted with distilled water for PTR-MS analysis. Concentrations used were ≤0.01% (v/v), dependent on solubility and partition coefficients of each compound, respectively. Preliminary experiments ascertained that resulting headspace concentrations were not close to the lower or upper detection limits of the instrument.

2.2. Method

An aqueous solution of the individual flavour compounds (10 mL) was placed in a glass vial (100 mL). The headspace was drawn at 50 mL/min, 15 mL/min of which was led into the PTR-MS (Ionicon Analytik, Austria). Samples were analysed according to the method described by Lindinger and co-workers [2,3], while employing a constant drift voltage of 600 V. Transmission of the ions through the quadrupole was considered according to the specification of the instrument. Background and transmission corrected spectra were averaged over five cycles. Presented PTR-MS spectra (Tables 1–3) were obtained by normalising the most abundant mass fragment to an intensity of 100.

Table 1
Alcohols, their molecular weight (MW) and intensities of their major ions determined by Proton Transfer Reaction-Mass Spectrometry

Compound	MW	Intensities[a] of major[b] ions						
		m/z	*m/z*	*m/z*	*m/z*	*m/z*	*m/z*	*m/z*
Methanol	32	33 (100)						
Ethanol	46	47 (100)	45 (37)	65 (6)				
1-Propanol	60	43 (100)	41 (37)					
2-Propanol	60	43 (100)	41 (37)					
1-Butanol	74	57 (100)	41 (6)	58 (5)				
2-Butanol	74	57 (100)	41 (7)	58 (5)				
t-Butanol	74	57 (100)	41 (6)	58 (5)				
1-Pentanol	88	57 (100)	41 (7)	58 (5)				
2-Pentanol	88	43 (100)	71 (84)	41 (25)	72 (5)			
3-Methyl-1-butanol	88	43 (100)	71 (82)	41 (27)	70 (7)	72 (5)		
1-Hexanol	102	43 (100)	85 (53)	57 (36)	41 (35)			
2-Hexanol	102	43 (100)	85 (58)	57 (36)	41 (33)	45 (6)		
cis-3-Hexen-1-ol	100	83 (100)	55 (59)	84 (7)				
1-Octanol	130	57 (100)	43 (58)	71 (48)	41 (20)			
2-Octanol	130	57 (100)	43 (58)	71 (47)	129 (32)	41 (21)	113 (5)	
3-Octanol	130	57 (100)	43 (58)	71 (49)	129 (26)	41 (19)	113 (5)	
1-Octen-3-ol	128	69 (100)	111 (92)	129 (14)	112 (9)	41 (9)	57 (6)	70 (6)
2-Nonanol	144	43 (100)	57 (70)	41 (50)	71 (38)	85 (14)	127 (5)	

[a] Data is presented by normalising the background and transmission corrected counts per second of the most abundant mass fragment to a value of 100. All other intensities are calculated relative to the most abundant mass fragment.

[b] Data on mass fragments with intensities below 5 not shown.

Table 2
Aldehydes and ketones, their molecular weight (MW) and intensities of their major ions determined by Proton Transfer Reaction-Mass Spectrometry

Compound	MW	Intensities of major ions[a]								
		m/z	*m/z*	*m/z*	*m/z*	*m/z*	*m/z*	*m/z*	*m/z*	*m/z*
Aldehydes										
Propanal	58	59 (100)	41 (5)							
Butanal	72	55 (100)	73 (7)	56 (5)						
Pentanal	86	69 (100)	41 (21)	87 (7)	70 (7)	57 (5)				
Hexanal	100	83 (100)	55 (47)	84 (7)	101 (6)					
Heptanal	114	97 (100)	55 (40)	98 (9)	115 (8)	69 (6)				
Octanal	128	69 (100)	111 (95)	129 (27)	112 (9)	41 (8)	70 (6)	55 (6)		
Nonanal	142	69 (100)	143 (52)	83 (42)	125 (30)	57 (24)	55 (10)	41 (9)	70 (6)	144 (6)
Ketones										
Diacetyl	86	87 (100)	59 (7)	88 (5)						
2-Butanone	72	73 (100)	74 (5)							
2-Pentanone	86	87 (100)	45 (9)	88 (8)						
2-Hexanone	100	101 (100)	102 (8)							
2-Heptanone	114	115 (100)	116 (9)							
3-Heptanone	114	115 (100)	116 (9)							
4-Heptanone	114	115 (100)	116 (9)							
2-Octanone	128	129 (100)								
3-Octanone	128	129 (100)								
2-Nonanone	142	143 (100)	144 (10)							
2-Decanone	156	157 (100)	158 (11)							

[a] For definition of intensities and major ions see footnote in Table 1.

Table 3
Esters, their carbon chain length ratio, their molecular weight (MW) and intensities of their major ions determined by Proton Transfer Reaction-Mass Spectrometry

Compound	Carbon chain length ratio[a]	MW	Intensities of major ions[b]				
			m/z	*m/z*	*m/z*	*m/z*	*m/z*
Methyl acetate	0.50	74	75 (100)	43 (9)			
Ethyl acetate	1.00	88	61 (100)	43 (70)	89 (27)	41 (5)	
Propyl acetate	1.50	102	61 (100)	43 (66)	103 (5)		
Butyl acetate	2.00	116	61 (100)	43 (44)	117 (16)		
Hexyl acetate	3.00	144	61 (100)	43 (79)	85 (12)	57 (8)	
Methyl butyrate	0.25	102	103 (100)				
Ethyl butyrate	0.50	116	117 (100)	89 (53)	43 (14)	118 (8)	
Propyl butyrate	0.75	130	89 (100)	43 (35)	131 (9)	71 (9)	
Butyl butyrate	1.00	144	89 (100)	43 (31)	71 (9)	145 (7)	
Isobutyl butyrate	1.00	144	57 (100)	89 (64)	43 (31)	41 (12)	
Butyl isobutyrate	1.00	144	89 (100)	43 (30)	41 (11)		
Isobutyl isobutyrate	1.00	144	89 (100)	57 (92)	43 (37)	41 (19)	
Ethyl acetate	1.00	88	61 (100)	43 (70)	89 (27)	41 (5)	
Ethyl propionate	0.67	102	75 (100)	103 (66)	57 (14)		
Ethyl butyrate	0.50	116	117 (100)	89 (53)	43 (14)	118 (8)	41 (6)
Ethyl pentanoate	0.40	130	131 (100)	57 (13)	103 (11)	132 (5)	
Ethyl hexanoate	0.33	144	145 (100)	146 (9)	117 (7)	43 (8)	71 (5)

[a] Carbon chain length ratio is the number of carbon atoms of the alcoholic part divided by the number of carbon atoms of the acidic part of the molecule.

[b] For definition of intensities and major ions see footnote in Table 1.

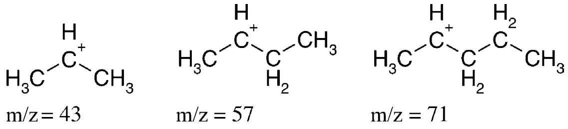

Fig. 1. Alkyl fragments of saturated alcohols.

3. Results and discussion

3.1. Fragmentation patterns

3.1.1. Alcohols

PTR-MS spectra of 18 individual alcohols are presented in Table 1. Generally, a high degree of fragmentation is observed. The protonated molecular ion shows the most abundant intensity for methanol and ethanol only. The other alcohols split off water and break up to non-specific alkane fragments at $m/z = 43$ and 57 as shown in Fig. 1. Data on the lower alcohols is consistent with Lindinger et al. [2] who found 100% of the mass spectral abundance for the molecular ion in case of methanol and ethanol. Results are slightly different in the case of propanol. A mass spectral abundance of 20% for the mass 61 for 1-propanol and still 10% in the case of 2-propanol was reported by the same author, whereas the mass spectral abundance for the molecular ion fell below an intensity of 5 in the present study. This result was confirmed for higher saturated alcohols, which all showed intensities below 5 for the MH^+ ion. Unsaturated alcohols like *cis*-3-hexen-1-ol and 1-octen-3-ol (Fig. 2) showed less fragmentation and more specific fragments, which can be explained by resonance stabilisation due to their double bond.

3.1.2. Aldehydes

PTR-MS spectra of eight individual aldehydes show less fragmentation compared to the alcohols (Table 2). For propanal the most abundant mass fragment is the molecular ion itself, whereas a loss of water leads to the main fragment in the case of butanal ($m/z = 55$), pentanal ($m/z = 69$), hexanal ($m/z = 83$) and heptanal ($m/z = 97$). Further fragmentation of octanal and nonanal leads to $m/z = 69$ being the dominant signal in the PTR-MS spectra of these compounds.

Data is consistent with Lindinger et al. [2] who reported 100% of the mass spectral abundance for the molecular ion in the case of propanal as well. Data was slightly different in the case of butanal. The same authors report a mass spectral abundance of 35% for $m/z = 55$ and 65% for the molecular ion represented by $m/z = 73$. In the present study, the mass fragment ion at $m/z = 55$ was found to be the most abundant fragment. The presence of $m/z = 55$ can be complicated by the presence of the isobaric water cluster $(H_2O)_2H_3O^+$. According to Hansel et al. [3],

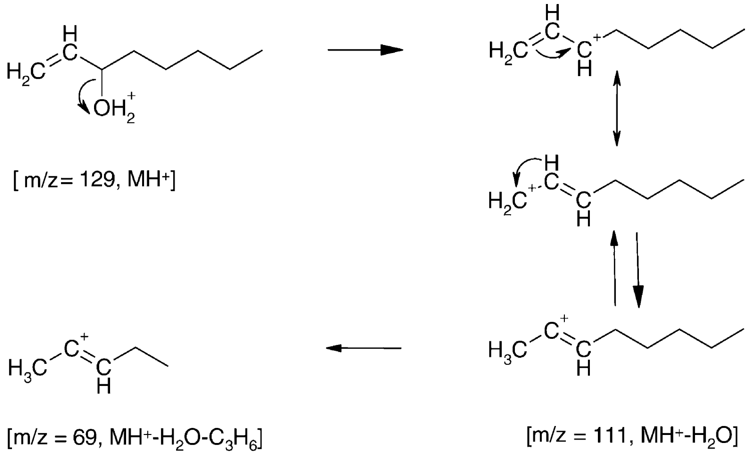

Fig. 2. Fragments of octanal and 1-octen-3-ol.

discrimination between a water cluster and a volatile organic compound is possible by variation of the drift voltage as well as the presence of the isotopic ion resulting from the presence of 1.1% ^{13}C for each of the four carbon atoms. In the present study, the identity of the ion at $m/z = 55$ is confirmed by the presence of the isotopic ion $m/z = 56$ with an intensity of 5% which is close to the expected isotopic abundance of 4.4%.

Generally, fragment ions at $m/z = 55$ and 69 appear quite abundant for all the aldehydes. The occurrence of the fragment ion $m/z = 69$ in the headspace spectra of aldehydes and mono-unsaturated alcohols was also reported by Fall et al. [11] who discussed isoprene as well as various isomers of methylbutanal, methylbutenol and pentenol as possible sources for the occurrence of the fragment ion at $m/z = 69$ in the headspace of leaves after freeze–thaw wounding. As long as the presence of the isotopic ion confirms that the ion at $m/z = 55$ does not result from the water cluster $(H_2O)_2H_3O^+$, both fragments can be regarded as suitable markers for the presence of aldehydes and mono-unsaturated alcohols in general.

3.1.3. Ketones

Ketones showed hardly any fragmentation (Table 2). The protonated molecular ion was the most abundant mass in the PTR-MS spectrum, often followed by the isotopic ion, which was detected for all the ketones. Therefore, a discrimination between isomeric ketones is impossible in the case of 2-, 3-, and 4-heptanone as well as 2- and 3-octanone.

3.1.4. Esters

PTR-MS spectra of 17 esters are presented in Table 3. Presented normalised intensities for hexyl acetate are in agreement with data published by Fall et al. [12].

Generally, the molecular ion itself and the corresponding protonated acids resulting from hydrolysis are the two dominant fragments in the PTR-MS spectra of esters. The extent of hydrolysis was found to depend on the carbon chain length of the acidic vs. the alcoholic part. Carbon chain length ratios have been calculated by dividing the number of carbon atoms of the alcoholic part of the molecule by the number of carbon atoms in the acidic part of the molecule (Table 3). Esters with a carbon chain length ratio smaller than 0.75 showed the molecular ion itself as the most abundant ion in the PTR-MS spectrum. If the carbon chain length of the acidic part is longer, leading to a ratio of 0.75 or higher, the products from hydrolysis lead to the most abundant mass fragments. As acids have a higher proton affinity than alcohols, the protonated acid generally is the main fragment. Only for isobutyl butyrate in which case the positive charge is stabilised due to the presence of a tertiary carbon atom, the alcoholic part represented by the ion at $m/z = 57$ is the most abundant mass fragment.

The effect of double bonds was not part of the present study. Fall et al. [12] reported that fragmentation of the unsaturated esters *cis*-3-hexenyl acetate and *trans*-2-hexenyl acetate leads to the main fragment at $m/z = 83$, which represents a protonated hexenyl rest. Acetic acid, which is represented by a signal at $m/z = 61$, was not detected at all because double bonds have an even stronger stabilising effect compared to tertiary carbon atoms.

The characteristic break-up patterns of hexyl acetate, ethyl hexanoate and the four isomeric butyl butyrates allow clear discrimination of these isobaric esters by PTR-MS.

3.2. Discrimination of isobaric and isomeric compounds

3.2.1. Discrimination of aldehydes from their corresponding ketones and mono-unsaturated alcohols

PTR-MS spectra of the isobaric compounds 1-octen-3-ol (Table 1) as well as octanal and 2-octanone (Table 2) were compared in order to discriminate an aldehyde from its corresponding ketone and mono-unsaturated alcohol. They share the molecular weight at $m/z = 128$, represented by a protonated molecular ion at $m/z = 129$ in their spectra. As 2-octanone does not show fragmentation at all, it can be clearly distinguished from octanal and 1-octen-3-ol, which showed quite similar break-up patterns. The ion at $m/z = 129$ represents the protonated molecular ion, the fragment ion at $m/z = 111$ results from a loss of water and further fragmentation of the side chain leads to the main fragment at $m/z = 69$. Formula sketches of these fragments are presented in Fig. 2. The molecular ion is generally of higher intensity for the aldehyde compared to the unsaturated alcohol; for octanal (Table 2) the relative intensity of the molecular ion with $m/z = 129$ is 27 compared to 14 for 1-octen-3-ol (Table 1). This is confirmed by the results for hexanal (Table 2) and *cis*-3-hexen-1-ol (Table 1). The relative intensity of the molecular ion represented by the mass 101 is 6 for the aldehyde compared to 1 for the unsaturated alcohol. This leads to the conclusion that the intensity of the molecular ion provides helpful information for the discrimination of aldehydes and their isobaric mono-unsaturated alcohols.

3.2.2. Discrimination of alcohols from isobaric esters

The PTR-MS spectra of the three isobaric compounds 1-octanol, ethyl pentanoate and propyl butyrate show fairly different break-up patterns. 1-Octanol fragments to alkane fragments with the masses 43, 57 and 71 and can be clearly discriminated from its isobaric esters. For the esters the spectra are governed by the protonated molecular ion itself for ethyl pentanoate, and by the hydrolisation product for propyl butyrate.

3.2.3. Discrimination of isomeric compounds

Discrimination of isomeric compounds in PTR-MS provides a further challenge. As ketones are not likely to fragment, discrimination is virtually impossible for 2-, 3-, and 4-heptanone as well as 2- and 3-octanone. In the case of 1-, 2-, and 3-octanol (Table 1), the main fragments 43, 57 and 71 show the same pattern and, therefore, do not open a possibility for discrimination. However, primary and secondary alcohols can be separated in terms of intensity of the $[MH^+–H_2]$ species, which is represented by an ion at $m/z = 129$ for the octanols. This fragment is of lower intensity for primary alcohols compared to the secondary ones.

Characteristic break-up patterns for isomeric compounds were also reported by Fall et al. [11] for 2- and 3-methylbutanal with regard to aldehydes.

Isomeric esters can be clearly distinguished due to their different break-up patterns as discussed in Section 3.1.4.

4. Conclusions

The present study provides some basic data on the behaviour of individual compounds in PTR-MS. As PTR-MS is a one-dimensional technique with limited separation capacities, the importance of a careful analysis of the single compounds before turning to complex systems cannot be overemphasised. Still, it could be shown that characteristic fragmentation patterns, although preferably avoided in order not to complicate the analysis, present a possibility to distinguish between isobaric and even isomeric compounds.

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