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A selected ion flow tube study of the reactions of H_3O^+, NO^+, and O_2^+ with saturated and unsaturated aldehydes and subsequent hydration of the product ions

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Abstract

We have carried out a selected ion flow tube (SIFT) study of the reactions of H_3O^+, NO^+, and O_2^+ ions with several saturated and unsaturated aldehydes. This study is mainly directed toward providing the essential data for a projected SIFT mass spectrometry (SIFTMS) study of the volatile emissions from cooked meats, which always include aldehydes. Thus, it is necessary to know the rate coefficients and the product ions of the reactions of the above-mentioned ions, used as the precursor ions for SIFTMS analyses, with the aldehydes, if proper identification and quantification of the emitted species are to be achieved. The results of this study show that the reactions of H_3O^+ with the aldehydes, M, result in the protonated molecules MH^+ and for the saturated aldehydes also in $(M - OH)^+$ ions resulting from the loss of a H_2O molecule from the nascent MH^+ ion. The NO^+ reactions invariably proceed via the process of hydride ion, H^-, transfer producing $(M - H)^+$ ions, but parallel minor association product ions $NO^+ \cdot M$ are observed for some of the unsaturated aldehyde reactions. The O_2^+ reactions proceed by way of charge transfer producing nascent M^+ ions that partially dissociate producing fragment ions. Because water vapour is invariably present in real samples analysed by SIFTMS, the current experiments were also carried out following the introduction of humid laboratory air into the helium carrier gas of the SIFT. Thus, the reactions of the product ions that form hydrates were also studied as a prelude to future SIFTMS studies of the (humid) emissions from cooked meats. (Int J Mass Spectrom 213 (2002) 163–176) © 2002 Elsevier Science B.V.

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1. Introduction

Considerable effort has been given to the study of the emission of volatile organic compounds (VOCs) from fresh and cooked foods, including cooked meats [1–10]. Most studies have exploited gas chromatography mass spectrometry (GCMS), because with this it is possible to separate and identify the many different components of the emissions. GCMS analyses have revealed the great complexity of food emissions, especially from cooked meats [3–10]. A

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disadvantage of GCMS is that it cannot be readily exploited to observe the emissions in real time. Also chemical changes of the emitted VOCs can occur during storage of the air/VOC samples. Our recently developed analytical technique [11–13] called selected ion flow tube mass spectrometry (SIFTMS) [14], is currently capable of analysing the emissions from foods in real time, when the abundance of the VOCs in the air/VOCs sample exceeds about ten parts per billion (ppb) [12]. The principles involved in SIFTMS are given in some recent papers [13–17]. We have demonstrated the value of SIFTMS for food research in a paper devoted to this topic [14], in which we present the results of pilot studies of VOC emissions for cut onion, crushed garlic, and ripe bananas. This limited study indicates how the time variations in the observed concentrations monitored using SIFTMS can be used to understand the chemistry taking place in the food sample when onion is cut and garlic is crushed.

We are now turning our attention to the SIFTMS analyses of VOC emissions for cooked meat. It is seen that many saturated and unsaturated aldehydes are always emitted [1–10]. So to prepare for the detection and quantification of aldehydes from cooked meats, we have carried out a SIFT study of the reactions of H_3O^+, NO^+, and O_2^+ ions with six saturated aldehydes and seven unsaturated aldehydes, all of which have been observed as components of the emissions from cooked meats [1–10]. The above-mentioned positive ions are those used in SIFTMS as precursor ions for the chemical ionisation [18] of the trace organic species present in an air sample [11–13,17]. A similar approach (the PTRMS drift tube method [19]) has been used exploiting H_3O^+ ions to analyse a wide range of organic compounds in air [20,21]. Therefore, it is desirable, as we will see later, to know the rate coefficients and the product ions of the reactions of these three precursor ions with any trace gas species that we want to detect and quantify. Such critical kinetic data are then included in the extensive database on which SIFTMS analyses depend. By many SIFT studies [22–31], we have produced a database that currently comprises several hundred reactions of the above precursor ions with a variety of organic and inorganic species, including some aldehydes [14,23], a database that is constantly being extended. The aldehydes included in the present study range from the saturated *n*-butanal to *n*-decanal and the unsaturated 2-butenal to *trans*-2 nonenal and *trans,trans*,2,4-decadienal. We will see that there are some interesting and consistent trends in the reactivity of the different precursor ions with the saturated and unsaturated aldehydes, knowledge of which is a great help in the identification of aldehydes in food emissions.

An inevitable problem in the analyses of most food emissions is the copious amount of water vapour that is also emitted. This is especially severe for on-line sampling of cooking meat, the headspace sample consisting of close to 100% water vapour that displaces the air. When using most analytical methods, attempts are made to eliminate the bulk of the water vapour from the sample. This is very important in GCMS analyses [3–10]. However, we make no attempt to remove water vapour when analysing humid samples using SIFTMS. Indeed, we make positive use of its presence to assist in the analyses. This has been particularly valuable in the analysis of the trace gases in human breath as we emphasise in a recent article [32]. But this approach does demand an understanding of the involvement of water vapour in the ion chemistry on which SIFTMS is based [33]. Specifically, we must understand how the relatively large amounts of water vapour in the sample convert the precursor ions to their hydrates. This is especially important when H_3O^+ is the precursor ion [33]. It is also essential to know if the product ions of the H_3O^+, NO^+, and O_2^+ reactions with the species to be analysed associate with water molecules to form their hydrates. If they do form hydrates, these must be included in the SIFTMS analyses to ensure accurate quantification [17]. Thus, in this study, we have observed the reactions of all three precursor ion species with the aldehydes also when humid laboratory air is introduced into the helium carrier gas of the SIFT instrument. In this way, we have noted which of the product ions of the many reactions associate with water molecules.

2. Experimental

The laboratory SIFT instrument at the Heyrovsky Institute in Prague was used for the present experiments. The SIFT is a standard technique for the study of ion–molecule reactions at thermal energies which has been described in numerous review articles (see, e.g. [34]. In the present studies, H_3O^+, NO^+, and O_2^+ ions are created in a microwave discharge through a mixture of water vapour and air (at a total pressure of about 0.1 Torr). These precursor ions are then injected into helium carrier gas (at a pressure of about 0.7 Torr) either separately or together (see below) by way of a quadrupole mass filter operated at a suitably high or low resolution. The ions are convected along the flow tube by the carrier gas and as usual are sampled downstream by way of a pinhole/quadrupole mass spectrometer and detected and counted by a channeltron/amplifier/pulse counting system connected to a computer.

In a conventional SIFT study of the rate coefficients and products of ion–molecule reactions, the permanent reactant gases can be flowed into the carrier gas/precursor ion swarm at a measured and controlled rate. Then the count rates of the reactant ion (e.g. H_3O^+, NO^+, O_2^+) and the product ions of the reaction are determined as a function of the reactant gas flow rate. From these data the rate coefficient and the product ion distribution (ratio) are obtained by a standard procedure [34]. However, because of the "sticky" nature of the aldehydes, this procedure is not useful. So the approach we take to the determination of the rate coefficients, k, and ion product distributions for the reactions of the liquid aldehydes included in this study is essentially identical to that taken for all our previous studies of the reactions of several other classes of liquid organic compounds [22–31]. This procedure is described in detail in our alcohols article [22] and outlined in several subsequent papers [23–31], so only a brief outline of the method is required here and is as follows.

It is known that proton-transfer reactions proceed at collision when the proton affinity of the acceptor molecule exceeds that of the donor molecule [35]. Thus we are able to assume that the k for the H_3O^+ reactions proceed gas kinetically with rate coefficient, k_c, because the proton affinities, PA, of the aldehydes included in this study exceed the PA of the H_2O molecule; then the $k = k_c$. So the k for the H_3O^+/aldehyde reactions need not be measured; rather a value of k_c can be adopted The k_c can be calculated if the polarisabilities and dipole moments of the reactant molecules are known or can be estimated [36]. However, it cannot be assumed that the NO^+ and O_2^+ reactions proceed at the kinetic rate, because it is known that the reaction processes involved (e.g. charge transfer and hydride ion transfer) sometimes proceed more slowly than the gas kinetic rate [22–31]. So the corresponding k values for the NO^+ and O_2^+ reactions with each particular aldehyde are obtained from the relative decay rates of all three reactant ions (H_3O^+, NO^+, and O_2^+) as these ions are simultaneously injected into the helium carrier gas of the SIFT whilst a weak mixture of the aldehyde in relatively dry helium is introduced at a measured flow rate into the helium. Note that the absolute flow rates of the aldehyde/helium mixture are not required. These experimentally derived k values are listed in Table 1 and are subject to an uncertainty of ± 20 %. As can be seen from Table 1, it turns out that the actual derived k values for the NO^+ and O_2^+ reactions are within error equal to their respective k_c values.

The identity of product ions and their percentages for these reactions are obtained in the following way. A small amount of the aldehyde/helium mixture, sufficient to reduce the reactant ion count rate by no more than ten percent, was introduced into the carrier gas. The downstream analytical mass spectrometer was then multiply-scanned to record all the reactant and product ion count rates to form a clear mass spectrum as is exemplified in Fig. 1(a). The percentage product ion distribution was simply obtained from the ratio of the individual product ion count rates and their sum. It is worthy of note that any residual electronic (and vibrational) excitation in the NO^+ and O_2^+ reactant ions is quenched by the additions of a small amount of air to the helium carrier gas [22–31]. All these measurements were carried out in helium carrier gas at a pressure of about 0.7 Torr at room temperature.

Table 1
Rate coefficients given in units of 10^{-9} cm^3 s^{-1} for the reactions of H_3O^+, NO^+, and $O_2{}^+$ with the saturated and unsaturated aldehydes indicated; Also given are the molecular weights m, polarisabilities α, and the permanent dipole moments μ of the aldehyde molecules (the estimated uncertainties in the rate coefficients listed are ±20%)

Compound	Molecule	m (Da)	α[a] (10^{-24} cm^5)	μ_r[a] (D)	k_c (H_3O^+)[b]	k_c (NO^+)[b]	k (NO^+)[c]	k_c (O_2^+)[b]	k (O_2^+)[c]
n-Butanal	C_4H_8O	72	8.2	2.72	[3.8]	[3.2]	3.3	[3.1]	3.2
2-Methyl-propanal	C_4H_8O	72	*8 ± 1*	2.5 ± 0.3	[3.8]	[3.2]	3.1	[3.1]	3.0
3-Methyl-butanal	$C_5H_{10}O$	86	*10 ± 1*	*2.5 ± 0.3*	[3.6]	[3.0]	3.0	[2.9]	2.4
n-Heptanal	$C_7H_{14}O$	114	*14 ± 2*	*2.5 ± 0.3*	[3.7]	[3.1]	3.3	[3.0]	3.2
n-Octanal	$C_8H_{16}O$	128	*16 ± 2*	*2.5 ± 0.3*	[3.8]	[3.1]	3.0	[3.0]	2.8
n-Decanal	$C_{10}H_{20}O$	166	*20 ± 2*	*2.5 ± 0.3*	[3.9]	[3.2]	3.3	[3.1]	3.2
2-Butenal	C_4H_6O	70	8.5	3.67	[4.8]	[4.0]	4.1	[3.9]	4.3
Trans-2-pentenal	C_5H_8O	84	*10 ± 1*	3.5 ± 0.5[d]	[4.6]	[3.9]	4.0	[3.8]	4.2
Trans-2-methyl-2-butenal	C_5H_8O	84	*10 ± 1*	3.5 ± 0.5	[4.6]	[3.9]	4.0	[3.8]	3.8
Trans-2-heptenal	$C_7H_{12}O$	112	*14 ± 2*	3.5 ± 0.5	[4.7]	[3.9]	3.9	[3.8]	3.6
Trans-2-octenal	$C_8H_{14}O$	126	*16 ± 2*	3.5 ± 0.5	[4.8]	[3.9]	4.1	[3.8]	4.2
Trans-2-nonenal	$C_9H_{16}O$	140	*18 ± 2*	3.5 ± 0.5	[4.8]	[4.0]	3.8	[3.9]	3.7
Trans, trans,-2,4-decadienal	$C_{10}H_{16}O$	152	*20 ± 2*	3.5 ± 0.5	[4.9]	[4.0]	4.2	[3.9]	4.2

[a] Values shown in regular type are taken from [40] and values of α shown in italics were estimated by adopting the values for similar molecules. Corresponding μ values were estimated to be the same for all saturated aldehydes (using an average value of 2.5 D) and for all unsaturated aldehydes (using an average value of 3.5 D).

[b] Collisional rate coefficients, k_c, given in the square brackets have been calculated using the parameterised trajectory formulation of Su and Chesnavich [36].

[c] Rate coefficients, k, for the NO^+ and O_2^+ reactions have been derived experimentally on the assumption that the corresponding H_3O^+ reactions proceed at their collisional rates.

To determine which product ions formed hydrates, each experiment was repeated with a sufficient amount of humid laboratory air entering the carrier gas to partially convert reactant H_3O^+ ions to the $H_3O^+(H_2O)_{0,1,2,3}$ hydrates (the concentration of H_2O molecules in the carrier gas can be calculated from the count rates of these ions, see [33]). Then it was immediately apparent which of the product ions of the individual aldehyde reactions formed hydrates. The rate coefficients of the association reactions of the product ions relative to that for the association reaction of H_3O^+ with H_2O was determined from the ion count rates in the spectrum following the procedure discussed in a recent article on the influence of humidity on SIFTMS analyses [33]. An example of such a spectrum is shown in Fig. 1(b). Similar experiments were also conducted for the NO^+ and O_2^+ reactant ions using similar flows of laboratory air into the carrier gas, which also indicated the efficiency of hydration of the product ions of these reactions.

The aldehyde samples were obtained from Sigma-Aldrich with the following purities (*n*-butanal 99%, 2-methyl-propanal 99+%, 3-methyl-butanal 97%, *n*-heptanal 95%, *n*-octanal 99%, *n*-decanal 95%, 2-butenal 99+% mostly *trans, trans*-2-pentenal 95%, *trans*-2-methyl-2-butenal 98%, *trans*-2-heptenal 97%, *trans*-2-octenal 94%, *trans*-2-nonenal 97%, and *trans, trans*,-2,4-decadienal 85%).

3. Preliminary remarks on the ion chemistry

H_3O^+ ions invariably undergo efficient proton transfer reactions with all the saturated aldehydes, M, included in this study and so the protonated aldehydes, MH^+, are always significant in the product ion spectrum. Further to this, a parallel, usually 8minor, reaction channel is often observed (see Table 2) which is the result of the spontaneous loss of a H_2O molecule from the nascent $(MH^+)^*$ product ion, as, for example, in the *n*-heptanal reaction:

$$H_3O^+ + CH_3(CH_2)_5CHO \rightarrow C_7H_{14}OH^+ + H_2O \tag{1a}$$

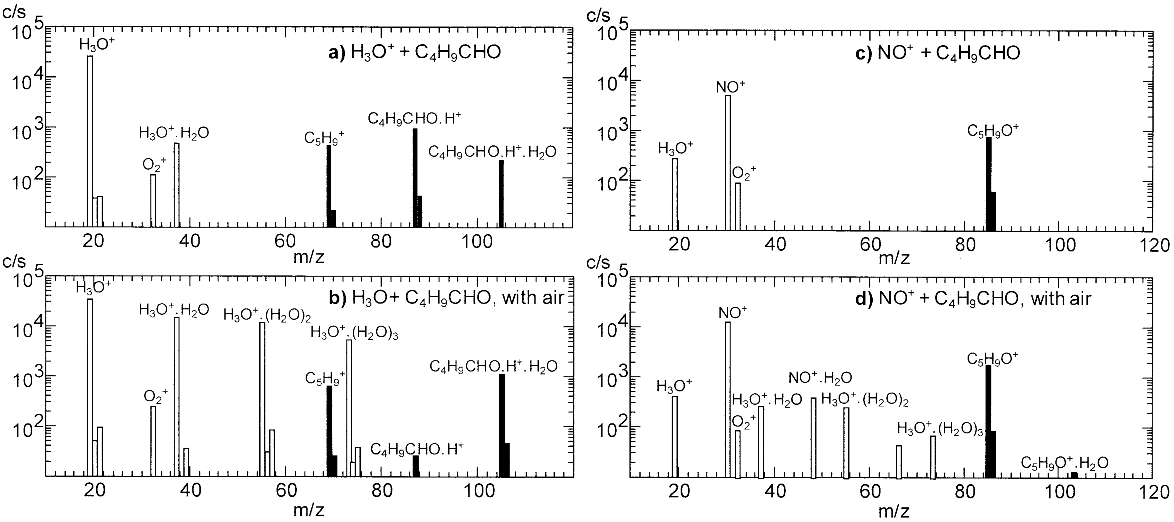

Fig. 1. SIFT/MS spectra of 3-methyl-butanal C_4H_9CHO obtained using H_3O^+ and NO^+ precursor ions. Note that all the mass spectra are represented on a semilogarithmic scale using counts per second as a measure of the detected ion signals. The count rates of the precursor ions H_3O^+ and NO^+ and their hydrates, $H_3O^+ \cdot (H_2O)_{1,2,3}$ and $NO^+ \cdot (H_2O)_{1,2}$, are shown as open bars. Count rates of the product ions that appear after a small flow of the aldehyde sample is introduced into the flow tube are shown as black bars. (a) The product ions for the H_3O^+ reaction are $C_5H_9^+$ and $C_4H_9CHO \cdot H^+$ and a small signal of the hydrate is present due to a trace of H_2O in helium carrier gas. (b) The hydrate ion $C_4H_9CHO \cdot H^+ \cdot H_2O$ becomes the major product ion when humid air is introduced. (c) The product ion $C_5H_9O^+$ of the NO^+ reaction is formed by hydride ion transfer. (d) With humid air added, the sequences of $H_3O^+ \cdot (H_2O)_{1,2,3}$ and $NO^+ \cdot (H_2O)_{1,2}$ ions are formed, but only a very small count rate of the $C_5H_9O^+ \cdot H_2O$ hydrate is observed.

$$\rightarrow C_7H_{13}^+ + 2H_2O \qquad (1b)$$

The elimination reaction (1b) results in the production of a hydrocarbon ion. For the unsaturated aldehydes, the water elimination channel is absent and only MH^+ product ions are apparent (see Table 3). When water vapour is present in the helium carrier gas, the MH^+ ions usually associate with water molecules producing monohydrate ions $MH^+ \cdot (H_2O)$:

$$MH^+ + H_2O + He \rightarrow MH^+ \cdot (H_2O) + He \qquad (2)$$

In some cases the dihydrate ions $MH^+ \cdot (H_2O)_2$ are formed [37]. Hence, in the presence of appreciable concentrations of water molecules, the product MH^+ hydrates may be the dominant species in the product ion spectrum. Also, successive three-body association reactions partially convert H_3O^+ precursor ions into the hydrated hydronium (water cluster) ions $H_3O^+ \cdot (H_2O)_{1,2,3}$. This is the process by which the hydrated hydronium ions shown in Fig. 1(b) are formed. These hydrated ions may then behave as additional precursor ions, because they are usually very reactive with polar molecules, undergoing ligand switching reaction [37,38] of the kind:

$$H_3O^+ \cdot H_2O + M \rightarrow MH^+ \cdot (H_2O) + H_2O \qquad (3)$$

This process contributes to the production of the hydrated ions, but is generally minor compared to the three-body association process. We have discussed these phenomena in a recent paper [33]. The presence of water molecules has less effect when NO^+ and O_2^+ are the precursor ions, since these ions do not so readily form adduct ions with H_2O molecules [see Fig. 1(d)]. Hence, O_2^+ and NO^+ hydrates do not complicate the ion chemistry to the same extent as the H_3O^+ hydrates. When O_2^+ and NO^+ hydrates are present they are partially converted to the hydrated hydronium ions $H_3O^+ \cdot (H_2O)_{1,2,3}$ in reaction sequences well understood following detailed research in atmospheric ion chemistry [39] [see Fig. 1(d)].

Table 2
Products of the reactions of H_3O^+, NO^+, and O_2^+ with the saturated aldehydes and the percentage product distributions; also given in brackets associated with the *m/z* values of the hydrated ions are the three-body rate coefficients in units of 10^{-27} cm^6 s^{-1} for the association reactions of the product ions with H_2O

Compound IE (eV)[a]	MW	Formula	$H_3O^{+\,b}$	*m/z*	Hydrates (k_3)	$NO^{+\,b}$	*m/z*	$O_2^{+\,b}$	*m/z*	Hydrates (k_3)
n-Butanal	72	C_4H_8O	95% $C_4H_8O\cdot H^+ + H_2O$	73	91 (10)	$C_4H_7O^+ + HNO$	71[c]	50% $C_4H_8O^+ + O_2$	72	90 (0.6)
9.8			5% $C_4H_7^+ + 2\ H_2O$	55				50% $C_2H_4O^+ + C_2H_4 + O_2$	44	62 (0.3)
2-Methyl-propanal	72	C_4H_8O	$C_4H_8O\cdot H^+ + H_2O$	73	91 (10)	$C_4H_7O^+ + HNO$	71[c]	70% $C_4H_8O^+ + O_2$	72	90 (0.1)
9.71								5% $C_4H_7O^+ + H + O_2$	71	. . .[d]
								25% $C_3H_7^+ + HCO + O_2$	43	. . .[d]
3-Methyl-butanal	86	$C_5H_{10}O$	70% $C_5H_{10}O\cdot H^+ + H_2O$	87	105 (12)	$C_5H_9O^+ + HNO$	85[c]	10% $C_5H_{10}O^+ + O_2$	86	104 (0.1)
			30% $C_5H_6^+ + 2\ H_2O$	69				10% $C_4H_7O^+ + CH_3 + O_2$	71	89 (0.5)
								45% $C_3H_6O^+ + C_2H_4 + O_2$	58	76 (0.5)
								35% $C_2H_4O^+ + C_3H_6 + O_2$	44	62 (0.5)
n-Heptanal	114	$C_7H_{14}O$	80% $C_7H_{14}O\cdot H^+ + H_2O$	115	133 (10)	$C_7H_{13}O^+ + HNO$	113[c]	20% $C_7H_{12}^+ + H_2O + O_2$	96	. . .[d]
			20% $C_7H_{13}^+ + 2\ H_2O$	97				10% $C_5H_{10}O^+ + C_2H_4 + O_2$	86	104 (10)
								10% $C_4H_7O^+ + C_3H_7 + O_2$	71	89 (0.1)
								35% $C_5H_{10}^+ + C_2H_4O + O_2$	70	. . .[d]
								15% $C_2H_4O^+ + C_5H_{10} + O_2$	44	62 (0.5)
								~10% other products	114	
n-Octanal	128	$C_8H_{16}O$	85% $C_8H_{16}O\cdot H^+ + H_2O$	129	147 (8)	$C_8H_{15}O^+ + HNO$	127[c]	20% $C_8H_{14}^+ + H_2O + O_2$	110	. . .[e]
			15% $C_8H_{15}^+ + 2\ H_2O$	111				10% $C_6H_{13}^+ + C_2H_3O + O_2$	85	. . .[d]
								45% $C_6H_{12}^+ + C_2H_4O + O_2$	84	. . .[d]
								15% $C_6H_{10}^+ + (H_2O + C_2H_4) + O_2$	82	. . .[d]
								10% $C_5H_8^+ + (H_2O + C_3H_6) + O_2$	68	. . .[d]
								~10% other products	128	
n-Decanal	156	$C_{10}H_{20}O$	97% $C_{10}H_{20}O\cdot H^+ + H_2O$	157	175 (11)	$C_{10}H_{19}O^+ + HNO$	155[c]	15% $C_{10}H_{18}^+ + H_2O + O_2$	138	. . .[e]
			3% $C_{10}H_{19}^+ + 2\ H_2O$	139				20% $C_8H_{16}^+ + C_2H_4O + O_2$	112	. . .[d]
								10% $C_8H_{14}^+ + (H_2O + C_2H_4) + O_2$	110	. . .[d]
								10% $C_7H_{12}^+ + (H_2O + C_3H_6) + O_2$	96	. . .[d]
								10% $C_6H_{10}^+ + (H_2O + C_4H_8) + O_2$	82	. . .[d]
								5% $C_6H_9^+ + (H_2O + C_4H_9) + O_2$	81	. . .[d]
								10% $C_5H_{11}^+ + C_5H_9O + O_2$	71	. . .[d]
								10% $C_5H_{10}^+ + C_5H_{10}O + O_2$	70	. . .[d]
								10% $C_5H_8^+ + (H_2O + C_5H_{10}) + O_2$	68	. . .[d]

[a] Ionisation energies are given in electron volts when known from [45].

[b] Percentages indicate the branching ratios at helium pressure of 0.7 Torr in the presence of a small amount of air. The molecular formulae of the ion products listed do not necessarily represent their structures.

[c] Association with water of the products of the NO^+ reactions is slow (three-body rate coefficient $<5 \times 10^{-29}$ cm^6 s^{-1}).

[d] No hydrated ions observed.

[e] Hydrated ion count rate could not be measured due to overlapping *m/z*.

Table 3

Products of the reactions of H_3O^+, NO^+, and $O_2{}^+$ with the unsaturated aldehydes and the percentage product distributions; Also given in brackets associated with the *m/z* values of the hydrated ions are the three-body rate coefficients in units of 10^{-27} cm^6 s^{-1} for the association reactions of the product ions with H_2O

Compound IE (eV)[a]	MW	Formula	H_3O^+ [b]	*m/z*	Hydrates (k_3)	NO^+ [b]	*m/z*	$O_2{}^+$ [b]	*m/z*	Hydrates (k_3)
2-Butenal 9.73	70	C_4H_6O	$C_4H_6O \cdot H^+ + H_2O$	71	89 (0.4)	$C_4H_5O^+ + HNO$	69[c]	30% $C_4H_6O^+ + O_2$	70	88 (1.4)
								65% $C_4H_5O^+ + H + O_2$	69	87 (0.04)
								5% $C_3H_6{}^+ + CO + O_2$	42	. . .[e]
Trans-2-pentenal	84	C_5H_8O	$C_5H_8O \cdot H^+ + H_2O$	85	103 (3)	95% $C_5H_7O^+ + HNO$	83[c]	60% $C_5H_8O^+ + O_2$	84	102 (0.9)
						5% $C_5H_8O \cdot NO^+$	114[d]	15% $C_5H_7O^+ + H + O_2$	83	101 (0.6)
								15% $C_4H_8{}^+ + CO + O_2$	56	. . .[d]
								10% $C_4H_7{}^+ + HCO + O_2$	55	. . .[e]
Trans-2-methyl-2-butenal 9.59	84	C_5H_8O	$C_5H_8O \cdot H^+ + H_2O$	85	103 (2)	98% $C_5H_7O^+ + HNO$	83[c]	95% $C_5H_8O^+ + O_2$	84	102 (2)
						<2% $C_5H_8O \cdot NO^+$	114[d]	5% $C_5H_7O^+ + H + O_2$	83	101 (1)
trans-2-heptenal	112	$C_7H_{12}O$	$C_7H_{12}O \cdot H^+ + H_2O$	113	131 (4)	85% $C_7H_{11}O^+ + HNO$	111[c]	30% $C_7H_{12}O^+ + O_2$	112	130 (0.3)
						15% $C_7H_{12}O \cdot NO^+$	142[d]	25% $C_5H_7O^+ + C_2H_5 + O_2$	83	101 (0.3)
								15% $C_5H_8{}^+ + C_2H_4O + O_2$	68	. . .[d]
								15% $C_3H_5O^+ + C_4H_7 + O_2$	57	75 (0.5)
								15% $C_4H_8{}^+ + C_3H_4O + O_2$	56	. . .[d]
Trans-2-octenal	126	$C_8H_{14}O$	$C_8H_{14}O \cdot H^+ + H_2O$	127	145 (5)	80% $C_8H_{13}O^+ + HNO$	125[c]	5% $C_7H_{12}O^+ + O_2$	126	144 (0.8)
						20% $C_8H_{14}O \cdot NO^+$	156[d]	5% $C_5H_8O^+ + C_3H_6 + O_2$	84	102 (0.7)
								5% $C_5H_7O^+ + C_3H_7 + O_2$	83	101 (0.7)
								25% $C_6H_{10}{}^+ + C_2H_4O + O_2$	82	. . .[d]
								25% $C_4H_6O^+ + C_4H_8 + O_2$	70	88 (0.5)
								10% $C_5H_9{}^+ + C_3H_5O + O_2$	69	. . .[d]
								10% $C_3H_6O^+ + C_5H_8 + O_2$	58	76 (1)
								15% $C_3H_5O^+ + C_5H_9 + O_2$	57	75 (1)
Trans-2-nonenal	140	$C_9H_{16}O$	100% $C_9H_{16}O \cdot H^+ + H_2O$	141	159 (7)	80% $C_9H_{15}O^+ + HNO$	139[c]	10% $C_9H_{15}O^+ + O_2$	140	158 (0.4)
						20% $C_9H_{15}O \cdot NO^+$	170[d]	10% $C_9H_{14}{}^+ + H_2O + O_2$	122	. . .[e]
								10% $C_6H_{10}O^+ + C_3H_6 + O_2$	98	116 (1)
								20% $C_7H_{12}{}^+ + C_2H_4O + O_2$	96	. . .[d]
								20% $C_5H_8O^+ + C_4H_8 + O_2$	84	102 (0.7)
								20% $C_5H_7O^+ + C_4H_9 + O_2$	83	101 (0.5)
								10% $C_4H_6O^+ + C_5H_{10} + O_2$	70	88 (2)
								10% other products	57	75 (1.5)
									58	76 (1.8)
Trans,trans,-2,4-decadienal	152	$C_{10}H_{16}O$	$C_{10}H_{16}O \cdot H^+ + H_2O$	153	171 (2)	80% $C_{10}H_{15}O^+ + HNO$	151[c]	20% $C_{10}H_{16}O^+ + O_2$	152	171 (0.1)
						15% $C_{10}H_{16}O^+ + NO$	152	80% $C_5H_5O^+ + C_5H_{11} + O_2$	81	99 (<0.01)
						5% $C_{10}H_{16}O \cdot NO^+$	182[d]			

[a] Ionisation energies are given in electron volts known from [45].

[b] Percentages indicate the branching ratios at helium pressure of 0.7 Torr in the presence of a small amount of air. The molecular formulae of the ion products listed do not necessarily represent their structures.

[c] Association with water of the products of the NO^+ reactions is slow (three-body rate coefficient $<5 \times 10^{-29}$ cm^6 s^{-1}).

[d] No hydrated ions observed.

[e] Hydrated ion count rate could not be measured due to overlapping *m/z*.

NO^+ ions can undergo charge transfer reactions with molecules that have low ionisation energies such as some hydrocarbons [29] and ketones [23], but this is not a significant process in the aldehyde reactions (although it does occur in the dienal reaction; see Table 3). Rather, the dominant process that occurs in both the saturated and unsaturated aldehyde reactions is hydride ion, H^- transfer (as, e.g. in reaction (4a) involving *trans*-2-heptenal):

$$NO^+ + CH_3(CH_2)_3CH{=}CHCHO$$

$$\rightarrow C_7H_{11}O^+ + HNO \tag{4a}$$

$$\xrightarrow{He} NO^+ \cdot C_7H_{12}O \tag{4b}$$

Indeed, H^- transfer is the only process that is observed in the NO^+/saturated aldehyde reactions. The $(M - H)^+$ ions formed in these NO^+ reactions associate only very slowly with water molecules forming $(M - H)^+ \cdot H_2O$ ions. In some of the unsaturated aldehyde reactions, partial association of the NO^+ with the unsaturated aldehyde is observed as is indicated by reaction (4b). We discuss this very interesting process later.

O_2^+ ions invariably undergo charge transfer reactions with the aldehyde molecules, M, producing parent M^+ ions and additional fragment ions as in the *n*-butanal reaction:

$$O_2^+ + CH_3CH_2CH_2CHO$$

$$\rightarrow (CH_3CH_2CH_2CHO)^+ + O_2 \tag{5a}$$

$$\rightarrow C_2H_4O^+ + C_2H_4 + O_2 \tag{5b}$$

As we will see, a common fragmentation pathway involves the loss of ethylene as exemplified by reaction (5b) and some of the larger aldehydes lose water or acetaldehyde. Some of the product parent cations, M^+, and some of the fragment ions of these O_2^+ reactions also efficiently associate with water molecules. These secondary hydration reactions must be accounted for when determining the ion product distributions of the primary reactions.

We now discuss some of the interesting details of the H_3O^+, NO^+, and O_2^+ reactions for the saturated and unsaturated aldehydes under separate subheadings.

4. Results

4.1. General comments: rate coefficients

We have discussed previously that we have relied on calculated values for the collisional rate coefficients, k_c, for the H_3O^+/aldehyde proton transfer reactions and then experimentally determined the values of k for the NO^+ and O_2^+ reactions relative to those for the respective H_3O^+ reactions. However, in this we meet a problem. To calculate the k_c values for the H_3O^+/aldehyde reactions using the generally accepted formulation of Su and Chesnavich [36], it is necessary to know—or to be able to estimate—the polarisabilities, α, and the permanent dipole moments, μ, of the aldehyde molecules. Unfortunately, α and μ are known only for the smallest of the saturated aldehydes included in this study, which are 2-butanal, and the smallest unsaturated aldehyde, 2-butenal [40]. α is estimated to increase by 2×10^{-24} cm^3 for each additional carbon in the aldehyde molecules, based on trends observed for similar compounds [40]. Accompanying this increase in α is an increase of the reduced mass, μ_r, of the H_3O^+/aldehyde reactive pair. The calculated k_c varies with $(\alpha/\mu_r)^{1/2}$ and this diminishes the sensitivity of k_c to α. Thus, the μ values are not expected to vary much with the chain length of the saturated and unsaturated aldehydes (see Table 1); they are essentially independent of the chain length for the smaller aldehydes [40]. So we can estimate the μ values for the saturated aldehydes based on the known value for 2-butanal and those for the unsaturated aldehydes based on the known value for 2-butenal (see Table 1). Fortunately, this estimation procedure does not result in unacceptable errors in the derived k_c. The k_c values along with the estimated uncertainties for both the saturated and unsaturated aldehydes for the H_3O^+ reactions are given in Table 1. Note that the larger μ for the unsaturated aldehydes result in larger k_c values compared to those for the saturated aldehydes. All the reactions included in this study proceed at or close to their collisional rates, which is usually the case for the reactions of H_3O^+, NO^+, and O_2^+ with a wide variety of organic molecules [22–31].

The association channels observed in some of the unsaturated aldehyde reactions are not sufficiently important to allow detailed studies of their dependence on the helium carrier gas pressure. The introduction of humid laboratory air to promote cluster ion production resulted in no measurable change in the derived values of k for the NO^+, including those in which partial association is observed (see Table 3).

As has been emphasised throughout this article, many of the product ions [MH^+, M^+, $(M - H)^+$, etc.] of these H_3O^+, NO^+, and O_2^+ reactions associate with water molecules. These estimated k_3 values in helium are also given in Tables 2 and 3. We now make some detailed comments on the products of individual reactions.

4.2 Saturated aldehydes

4.2.1 H_3O^+ reactions.

We have observed in a previous study of the reactions of some saturated aldehydes with H_3O^+ [23] that H_2O elimination from the nascent $(MH^+)^*$ ions does not occur for the low molecular weight species (i.e. formaldehyde, acetaldehyde and propanaldehyde) but does occur for the longer chain aldehydes, being a 5% channel for 1-butanal [23] [in agreement with the present data (see Table 2)]. A larger branching ratio into the H_2O elimination channel has been observed in the somewhat higher energy PTR-MS drift tube experiment that uses air as the carrier gas [21]. Thus, it is no surprise to see that H_2O elimination occurs in longer-chain saturated aldehydes included in this study (see Table 2) as is exemplified by the *n*-heptanal reaction (1).

The branching ratio for the H_2O elimination channel decreases as the size of the aldehyde molecule increases from *n*-heptanal (20%) to *n*-octanal (15%) to *n*-decanal (5%), all being lower percentages than the 50% observed for *n*-hexanal in our previous study [23] By analogy with electron ionisation (EI) fragmentation, a plausible mechanism for this H_2O elimination involves the formation of a cyclic intermediate containing at least 4 carbons (a six-membered ring including the O and H atoms) [41]. H_2O elimination is not observed at all in the reaction of the branched 2-methyl-propanal, in contrast to its isomer *n*-butanal where a small but obvious elimination channel (5%) is evident. The absence of the water elimination channel is understandable because the six membered ring cannot form. On the other hand, protonation by H_3O^+ of the branched isomer of *n*-pentanal, 3-methyl-butanal, where a six-membered ring is possible, does result in the elimination of H_2O (30%), which is comparable to for the corresponding reaction of *n*-pentanal (25%).

As mentioned previously, the MH^+ product ions of these reactions readily associate with water molecules to form the monohydrate ions $MH^+ \cdot (H_2O)$, but the addition of a second H_2O molecule to form $MH^+ \cdot (H_2O)_2$ is much slower. All the k_3 values for these association reactions given in Table 2 (and Table 3) refer only to monohydrate formation. Interestingly, these rate coefficients do not appear to change with the alkyl chain length and the corresponding effective two body rate coefficients are approximately 10% of k_c. Numerous SIFT studies have shown that hydrocarbon ions formed in thermal energy ion-molecule reactions rarely associate with water molecules under SIFT conditions [17,37,42]. This is also apparent in this study. The hydrocarbon ions formed in these H_2O elimination reactions do not rapidly associate with H_2O molecules [see Figs. 1 (a) and 1 (b) where the count rates of the $C_5H_9^+$ ions do not reduce after addition of air, whereas the count rate of the MH^+ ions do]. Unfortunately, the potential association products of these hydrocarbon ions with H_2O molecules, would have the same mass-to-charge (*m/z*) ratio as the MH^+ ions, so any small k_3 value cannot be determined quantitatively.

4.2.2. NO^+ reactions

Our previous study of the reactions of NO^+ with aldehydes [23] showed that for unsaturated aldehydes the only process that occurred was hydride ion (H^-) transfer and this is also the case for the longer chain saturated aldehydes included in this study, as can be seen in Table 2. Using the available thermochemical data [43,44], it can be shown that the H^- ion is extracted from the CHO group and not from the hydrocarbon chain [23]. The products of these reactions are RCO^+ ions and HNO molecules e.g.

$$NO^+ + C_3H_7CHO \rightarrow C_3H_7CO^+ + HNO \tag{6}$$

The RCO^+ ions so formed show little propensity to associate with H_2O molecules as is indicated in the footnote to Table 2, a fact which we have been well aware of for some time [14] and which assists in the analysis of aldehydes using NO^+ precursor ions in SIFTMS.

The simplicity of the NO^+ product spectra [Figs. 1(c) and 1(d)] and the fact that the product spectra are essentially unaffected by the presence of water, makes the NO^+ ion an ideal precursor for quantitative analysis of mixtures of aldedydes. Our data indicate, however, that aldehyde isomers cannot be independently quantified using NO^+ alone.

4.2.3. O_2^+ reactions

Because of the higher recombination energy of O_2^+ ions (12.06 eV compared to that of NO^+ ions of 9.25 eV [45]), exothermic charge transfer can occur in the reactions of O_2^+ with the aldehydes included in this study. This process occurs in all the reactions and is sufficiently exothermic to result in significant fragmentation of the nascent parent cations $(M^+)^*$ in all cases, as can be seen in Table 2. Not surprisingly, many of the fragment ions observed in these reactions are also observed in the EI mass spectra of these compounds [46]. Both reactions are initiated by ionisation of the parent neutral forming a radical cation. Indeed, similarities between O_2^+ reactions and EI reactions have been noted before [28]. Some of the fragment ions formed in the O_2^+ reactions associate efficiently with water. Based on our previous work [17,37], those ions that associate with water will contain an oxygen atom. Hydrocarbon ions do not associate efficiently with water under typical SIFT conditions [37].

We can use the product ion mass together with the clustering data and the well understood EI fragmentation [41,47] to provide clues as to the identity of the product ions and neutrals formed in the O_2^+ reactions. For example, reaction (5) of O_2^+ with *n*-butanal forms two product ions, the parent ion $C_4H_8O^+$ and a fragment ion with *m/z* 44, which is $C_2H_4O^+$ that associates relatively efficiently with water and thus contains an oxygen atom. Based on the EI mass spectral analyses of fragmentation patterns in aldehydes and the energetics, this product ion is the ethenol cation arising from β cleavage and hydrogen transfer [41,47], with ethylene as the neutral product mediated via a six-membered ring [41]. $C_2H_4O^+$ is not formed in the reaction of O_2^+ with 2-methylpropanal, because the required six-membered ring cannot be formed. Instead, α-cleavage leads to formation of the isopropyl cation and the formyl radical [47]. Hydrogen atom loss is also partially observed in this reaction.

Formation of the characteristic ethenol ion (see *m/z* 44 in Table 2) together with the alkene neutral is observed for longer chain aldehydes. However, when the chain becomes longer than five carbons, formation of the alkene ion and C_2H_4O neutral product (most likely rearranged to acetaldehyde [41,43,48]) becomes competitive and is preferentially formed in aldehydes with seven or more carbon atoms. Water elimination, another characteristic reaction, is observed for the saturated aldehydes containing more than five carbons (see Table 2). Products arising from simple chain cleavage (with and without hydrogen transfer) are also observed. When the alkyl chain becomes very long (eight to ten carbons) only hydrocarbon ions are formed in O_2^+ reactions.

4.3 Unsaturated aldehydes

4.3.1. H_3O^+ reactions

The loss of an H_2O molecule from the nascent $(MH^+)^*$ ions formed in the reactions of H_3O^+ with the unsaturated aldehydes included in this study is not observed, as can be seen by a glance at Table 3. Importantly, all of the unsaturated aldehydes investigated in this study have the double bond in the same position relative to the carbonyl carbon (and they are of the readily available *trans*-configuration). Our data show that the location of the double bond in the “2” position inhibits the hydride transfer involved in water elimination. Indeed, previously [14,23] we have found that reaction of *cis*-3-hexenal with H_3O^+ results in H_2O elimination whilst this does not occur in the corresponding *trans*-2-hexenal reaction [49].

Again, the MH^+ product ions of these reactions also readily associate with water molecules as is clearly indicated by the estimated three-body rate coefficients for their reactions listed in Table 3. Note that the rate coefficients increase with the chain length of the reactant ion. This phenomenon is loosely explained by the greater number of vibrational degrees of freedom in the larger ions and hence the increased number of sites in which the binding energy of the $(MH^+ \cdot (H_2O))^*$ nascent ion can be stored prior to its stabilisation in collisions with a helium carrier gas atoms [50]. Curiously, this phenomenon is not obvious for the protonated saturated aldehydes (see Table 2).

4.3.2. NO^+ reactions

Hydride ion transfer remains the dominant process in these reactions, but also observed are minor association channels producing $NO^+ \cdot M$ ions as is illustrated by the trans-2-heptanal reaction Eq (4). Previously, we have observed that association readily occurs for the reactions of NO^+ with ketones [23], a phenomenon that we attribute to the proximity of the ionisation energies (IE) of the ketones and NO and which we call “charge transfer complexing” [23,29]. Thus, it is envisaged that the charge is delocalised around the $(NO \cdot \text{aldehyde})^{+*}$ intermediate ion, which prolongs its lifetime against unimolecular dissociation and thus enhances the probability of collisional stabilisation by the helium carrier gas atoms. It seems likely that this situation exists for some of these NO^+/unsaturated aldehyde reactions, because the IE of these compounds are approaching that of NO. Unfortunately, the IEs of all these aldehydes are not known, but the limited data available (i.e. IE (2-butenal) = 9.73 eV; IE (2-methyl-2-butene) = 9.59 eV [45]) suggests that the IE decreases with increasing molecular size. Therefore, it seems very likely that the IE of the larger unsaturated aldehydes decreases toward that of NO and that the probability of charge transfer complexing occurring will increase as is observed (see Table 3). It is perhaps significant that the only unsaturated aldehyde in this limited series that does not obviously associate with the NO^+ ions is 2-butenal, that is the molecule with an IE that differs most from that of NO. On the other hand, it is interesting that in the NO^+ reaction with *trans-trans*-2,2-decadienal both charge transfer and association products are observed in parallel with the major hydride ion transfer product:

$$NO^+ + C_{10}H_{16}O \rightarrow C_{10}H_{15}O^+ + HNO \quad (7a)$$

$$\rightarrow C_{10}H_{16}O^+ + NO \quad (7b)$$

$$\xrightarrow{He} NO^+ \cdot C_{10}H_{16}O \quad (7c)$$

Clearly, for charge transfer to occur the IE of this aldehyde must be very close to that of NO (within about 50 meV at room temperature).

In common with the RCO^+ ions formed in the NO^+/saturated aldehyde reactions, the ions formed in the H^- transfer reactions of NO^+ with these unsaturated aldehydes associate very slowly with H_2O molecules, the k_3 values being some 1000 times smaller than for the association of the protonated aldehydes MH^+ (see the footnote to Table 3).

4.3.3. O_2^+ reactions

As observed for the saturated aldehydes, extensive fragmentation dominates the O_2^+ reactions with these unsaturated aldehydes (see Table 3). However, the characteristic reaction channels for the unsaturated aldehydes differ significantly from those of the saturated aldehydes. Perhaps most striking is the observation that most of the product ions formed in the large unsaturated aldehyde reactions contain oxygen while those in the saturated species do not. In addition, parent ion (M^+) formation is a minor but significant product channel for all the unsaturated aldehydes while it is absent or only a very minor product channel for saturated aldehydes larger than five carbons. H_2O elimination is not a major reaction channel for any of the unsaturated aldehydes. Here, both the *trans*-orientation and the position of the double bond probably play a role in inhibiting H_2O elimination [41,49].

The reactions with the relatively small *trans*-2-butenal and *trans*-2-pentenal (that cannot form the ring structure, see Sec. 4.2) appear to result in elimination of carbon monoxide rather than an alkene. It is also worthy of note that H-atom loss is the major channel in the reaction of O_2^+ with 2-butenal, but this process does not occur in the O_2^+/butanal reaction.

An example of a reaction of a larger unsaturated aldehayde is the reaction of *trans*-2-heptenal where five products are easily recognised:

$$O_2^+ + CH_3(CH_2)_3CH{=}CHCHO \rightarrow C_7H_{12}O^+ + O_2 \quad (8a)$$

$$\rightarrow C_5H_7O^+ + C_2H_5 + O_2 \quad (8b)$$

$$\rightarrow C_5H_8^+ + C_2H_4O + O_2 \quad (8c)$$

$$\rightarrow C_3H_5O^+ + C_4H_7 + O_2 \quad (8d)$$

$$\rightarrow C_4H_8^+ + C_3H_4O + O_2 \quad (8e)$$

We assign the product ions of this reaction according to their propensity to cluster with H_2O molecules, as is discussed previously. It is interesting to note that the $C_5H_7O^+$ ions formed in reaction (8b) associate with H_2O molecules, whereas the isomeric $C_5H_7O^+$ ions formed in the reaction of NO^+ with both *trans*-2-pentenal and *trans*-2-methyl-2 butenal (see Table 3) do not. Clearly, these observations indicate that these $C_5H_7O^+$ have different structures.

The reaction of the polyatomic *trans, trans,*-2,4-decadienal with O_2^+ defies the trend of an increasing number of products of the O_2^+/aldehyde reactions with increasing size in that only two products are observed

$$O_2^+ + C_{10}H_{16}O \rightarrow C_{10}H_{16}O^+ + O_2 \quad (9a)$$

$$\rightarrow C_5H_5O^+ + C_5H_{11} + O_2 \quad (9b)$$

The products of reaction (9b) can be formed by cleavage of a single bond (between carbons 5 and 6) and the identification of the ion products as an oxygen-containing ion is supported by a presence of a small hydrate signal.

5. Concluding remarks

Our primary motivation for carrying out this study was to extend our understanding of the reactions of H_3O^+, NO^+, and O_2^+ ions with aldehydes, which are major VOCs emitted by cooked meat [1–10]. Thus, it is our aim to use SIFTMS to study VOC emissions from various cooked meats in real time. The extension of our SIFTMS database that the present study represents will facilitate such studies.

Several general features of the ion chemistry of these ions with aldehydes are revealed by this study, which by their simplicity help to facilitate SIFTMS analyses. The H_3O^+ reactions are generally uncomplicated in that a single product ion species, MH^+, is formed (see also [21]), although for the saturated aldehydes minor H_2O elimination channels are evident resulting in $(M - OH)^+$ ions, which must be accounted for in accurate SIFTMS quantification. Similarly, the NO^+ reactions mostly result in a single product ion, $(M - H)^+$, but partial association occurs in most of the unsaturated aldehyde reactions resulting in $NO^+ \cdot M$ ions as minor products. Importantly, all the major products of the O_2^+ reactions with the longer chain saturated aldehydes are hydrocarbon ions which do not cluster with H_2O molecules Therefore, notwithstanding the large number of ion products, the reactions with O_2^+ may still be useful in identifying aldehydes emitted from foods. However, common product ions and the overlap of ion peaks in the product spectra will complicate data interpretation.

An additional aspect of this study (that has not been emphasised enough in our previous studies in support of SIFTMS) is the careful attention given to the clustering of the product ions of the primary H_3O^+, NO^+, and O_2^+ reactions. It is clearly essential to be able to recognise which of the product ions form hydrates, because it is generally the case that SIFTMS is used for the analysis of trace gases in humid samples. This is especially so for breath sampling [11,12] and for the proposed studies of cooking meats. For accurate quantification, the hydrates must be included in the product ion count rates [11,33]. Thus, in Tables 2 and 3 we have included estimates of the three-body rate coefficients for the association reactions with H_2O molecules of the product ions observed in the reactions.

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