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Selected ion flow tube, SIFT, studies of the reactions of H_3O^+, NO^+ and O_2^+ with compounds released by *Pseudomonas* and related bacteria

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Abstract

A selected ion flow tube, SIFT, study has been carried out of the reactions of H_3O^+, NO^+ and O_2^+ with some volatile organic compounds that are released by bacteria. The major intention is to prepare the way for an extensive study of the emissions from *Pseudomonas* bacteria in vitro using selected ion flow tube mass spectrometry, SIFT-MS, with a view to detecting the presence of these bacteria in vivo. This requires an extensive SIFT-MS database of the rate coefficients and product ion distributions for the reactions of the above precursor ions with those molecular species that are released by or implicated in the growth of bacteria. A partial list of these molecular species is given. The available SIFT-MS database already includes the kinetic data for the reactions of several of these compounds and the present study supplements this to include 2-methyl-1-butanol and 2-heptanol, 3-methyl-1-butyl acetate, 4-methyl-1,3-pentadiene, and dimethyl trisulphide and dimethyl tetrasulphide. The kinetic data obtained in the present study are compared with those obtained previously for classes of similar compounds.

Keywords: SIFT; *Pseudomonas*; Bacteria; Proton transfer; Charge transfer; SIFT-MS

1. Introduction

We dedicate this paper to Tilmann Märk, a long-time friend, erstwhile colleague and co-author, on the occasion of his 60th birthday, with special thanks from two of us (Patrik Španěl and David Smith) for the caring and support he gave to us during the scientifically productive and enjoyable period we spent in Innsbruck.

There is a growing interest in various fields, including meat spoilage, recently explored by Märk and his colleagues [1], and clinical research [2,3], in the detection of bacteria both in vitro and, ultimately, in vivo, by monitoring their release of volatile organic compounds, VOCs. If characteristic emissions can be recognised, then non-invasive detection of bacterial infection in the body may become a reality. It has long been known that serious bacterial infection is often recognised by odour [4] and now experiments have begun to identify the VOCs that combine to produce the odour [5]. Most studies have been carried out using gas chromatography mass spectrometry, GCMS, to identify the VOCs emitted by bioreactor cultures of specific bacteria or genus of bacteria, such as *Pseudomonas* [6–9]. A wide variety of compounds have been identified, including series of aliphatic alcohols, including pentanol and butanol isomers [7,8], high-order ketones, in particular 2-nonanone and 2-undecanone [8], dimethyl polysulphides, in particular dimethyl disulphide and dimethyl trisulphide [8,9] and alkenes [8,9]. A partial list of these compounds is given in Table 1.

The analysis of such complex mixtures, involving acceptably accurate quantification for clinical diagnosis, is challenging. Ideally, on-line real-time analyses are required obviating sample collection, which can introduce differential sampling and discrimination against low molecular weight volatiles. This is commonly the situation in GCMS analyses [8,9]. For this purpose, we have developed selected ion flow tube mass spectrometry, SIFT-MS [29–31], with which real-time analyses of ambient air, single exhalations of breath [32] and the headspace above liquids, such as urine [33–35], and cell cultures [36,37] can be achieved. SIFT-MS involves the combination of chemical ionisation using selected precursor ions H_3O^+, NO^+ and O_2^+ with

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Table 1
A partial list of the molecular species that are released by or implicated in the growth of various bacteria and the methods used for their detection with references

Molecule	Bacteria[a]	Detection methods[b]	SIFT reference
Ammonia, NH_3[c]	*Pseudomonas* strains	Chemical reaction [10]	[16,17]
Nitric oxide, NO[d]	*PA*	Chemiluminescence [11]	[18]
Trimethyl amine, C_3H_9N	*PMS*	GCMS [12]	[17]
Ethanol, C_2H_5OH[e]	*BS*, *ABM*	PTRMS [1], CIMS [13]	[16,19]
1-Butanol, C_4H_9OH	*BS*, *PA*, *PF*, *PPS*, *PMA*, *PPA*, *ABM*	PTRMS [1], GCMS [8], CIMS [13]	[19]
2-Methyl-1-butanol, $C_5H_{11}OH$	*EC*	GCMS [9]	Present study
3-Methyl-1-butanol, $C_5H_{11}OH$	*EC*, *KP*, *PA*, *PC*, *PF*, *PPA*, *PPS*, *PMA*, *PrM*	GCMS [7–9]	[19]
2-Heptanol, $C_7H_{15}OH$[f]	*PR*	SPME/GCMS [14]	Present study
3-Methyl-1-butyl acetate, $C_7H_{14}O_2$	*KP*, *PA*, *PrM*, *SA*, *BS*, *ABM*	PTRMS [1], GCMS [8], CIMS [13]	Present study
Acetone, CH_3COCH_3	*BS*	CIMS [13]	[16,20]
2-butanone, C_4H_8O	*BS*,*PA*,*PF*,*PPA*	GCMS [7,8], CIMS [13]	[20]
2-Pentanone, $C_5H_{10}O$	*SL*, *PR*	GCMS [7–9]	[20]
2-Heptanone, $C_7H_{14}O$[f]	*SL*, *PR*	GCMS [7–9] SPME/GCMS [14]	[21]
2-Nonanone, $C_9H_{18}O$	*PA*, *PMA*, *PPA*, *PR*, *SL*	GCMS [7–9]	[21]
2-Undecanone, $C_{11}H_{22}O$	*PA*, *PMA*, *PPA*, *PR*	GCMS [7–9]	[21]
2-Aminoacetophenone, C_8H_9NO[g]	*PA*	GC, GCMS [6,8]	[21]
Acetaldehyde, C_2H_4O	*BS*	CIMS [13]	[20]
Acetic acid, $C_2H_4O_2$[e, h]	*Pseudomonas*	CE/indirect UV [15]	[16,22]
Isoprene, C_5H_8	*BS*, *EC*, *SL*, *PA*, *PF*, *PPA*	GCMS [7–9], CIMS [13]	[16,23]
1-Undecene, $C_{11}H_{22}$	*PA*, *PF*, *PPA*	GCMS [7–9]	Not studied
Toluene, $C_6H_5CH_3$	*PA*, *ABM*	PTRMS [1], GCMS [8]	[23]
Dimethyl sulphide, C_2H_6S	*PPA*, *BS*	GCMS [9], CIMS [13]	[24]
Dimethyl disulphide, $C_2H_6S_2$	*EC*, *PA*, *PF*, *PPA*, *PPS*, *SL*, *ABM*	PTRMS [1], GCMS [7–9]	[24]
Dimethyl trisulphide, $CH_3S_3CH_3$	*EC*, *PA*, *PF*, *PMA*, *PPA*, *PPS*, *ABM*	PTRMS [1], GCMS [7–9]	Present study

Also listed are the source references to the kinetic data obtained from SIFT experiments that are used in SIFT-MS analyses of these molecular species.

[a] *BS*: *Bacillus subtilis*; *EC*: *Enterobacter cloacae*; *KP*: *Klebsiella pneumoniae*; *PA*: *Pseudomonas aeruginosa*; *PC*: *P. cepacia*; *PF*: *P. fluorescens*; *PMA*: *P. maltophilia*; *PMS*: *P. merguiensis*; *PPA*: *P. putida*; *PPS*: *P. putrefaciens*; *PR*: *Penicillium roqueforti*; *PrM*: *Proteus mirabilis*; *SL*: *Serratia liquefaciens*; *ABM*: bacteria mixture in meat (mesophilic total aerobic bacteria, *Pseudomonas* spp., *Enterobacteriaceae*, lactic acid bacteria, *Enterococcus* spp.).

[b] PTRMS: proton transfer reaction mass spectrometry, CIMS: chemical ionisation mass spectrometry, SPME: solid phase micro extraction, CE: capillary electrophoresis.

[c] Ammonia is involved in the denitrification process of bacteria [25].

[d] Bacteria can be forced into metabolic suicide by overproduction of NO [26].

[e] Ethanol (often) and acetic acid can be used as a carbon source for *Pseudomonas* [27].

[f] *PR* is able to catalyse the conversion of 2-heptanone to 2-heptanol [14].

[g] 2-Aminoacetophenone is said to be responsible for the grape-like odour in PA [6].

[h] Acetic acid has been used to treat *PA* in superficial wounds and burns [28].

fast flow tube technique. This allows the identification and accurate quantification of a wide range of VOCs and some inorganic compounds by employing more than one precursor ion to analyse the same mixture in order to verify compound identification [16]. Pertinent to the topic of this study is our recent SIFT-MS investigation of the VOC emissions from lung cancer cell lines in vitro in which acetaldehyde production was seen to be related to the number of cancer cells [37]. Using this same methodology we have now initiated a SIFT-MS study of the emissions from bacteria, beginning with *Pseudomonas*. Very recently, such a study has been carried out of the emissions of VOCs from *Bacillus subtilis* using chemical ionisation by H_3O^+ precursor ions in a SIFT instrument [13]. The detection of the low molecular weight species acetaldehyde, ethanol, acetone, butanol, acetoin, diacetyl and isoprene is reported. Of course, to perform these studies and SIFT-MS analyses, a database of the reactions of the chosen precursor ions with the species to be detected is required. A substantial database for SIFT-MS is already available that includes the rate coefficients and product ions of several of the compounds listed in Table 1 and some of those mentioned immediately above. The purpose of the present study is to extend the SIFT-MS database to include more of those compounds listed in Table 1 in preparation for a study of emissions from bacteria and in doing so to gain an understanding of the ion chemistry involved in the reactions. Hence, a SIFT study has been carried out of the reactions of H_3O^+, NO^+ and O_2^+ with 2-methyl-1-butanol and 2-heptanol, 3-methyl-1-butyl acetate, 4-methyl-1,3-pentadiene, dimethyl trisulphide and dimethyl tetrasulphide. This supplements our very recent study of the reactions of several ketones [21], some of which are also released by bacteria [8,9]. The results obtained are compared with those previously obtained for similar compounds.

2. Experimental

The standard SIFT technique has been described in numerous publications [29–31] so it is sufficient here to summarise it as follows. Precursor ions H_3O^+, NO^+ and $O_2{}^+$ are generated in a discharge ion source, mass selected by a quadrupole mass filter and then injected as selected ionic species into fast-flowing helium carrier gas in a flow tube. The vapours of the compounds included in this study, all liquids at room temperature, supported in dry air in sealable plastic bags, are then introduced at controlled flow rates into the ion swarm/carrier gas. This is achieved by simply puncturing the bag with a hypodermic needle that is connected directly to the inlet port of the SIFT instrument. The count rates of the precursor ions and the resulting product ions of the reactions of the particular compound with the chosen precursor ion species are determined by a downstream quadrupole mass spectrometer. This can be operated in two modes: (i) The full-scan mode, FSM, in which the analytical mass spectrometer is scanned over a predetermined *m*/*z* range to obtain a spectrum of the reactant and product ions. (ii) The multi-ion mode, MIM, in which the spectrometer is switched and dwells on selected reactant/product ions as their count rates are determined [30]. The FSM spectra are primarily used to identify the product ions and the MIM data are used to determine the rate coefficients and the product ion distributions [16,30]. Since the concentrations of the compound vapours in the dry air are unknown, the relative rate coefficients for the reactions of the three precursor ions are determined by measuring the decay rates of the H_3O^+, NO^+ and $O_2{}^+$ ions, simultaneously injected into the carrier gas, as the compound/dry air sample flow rate is varied. Then, it is assumed that the reactions of H_3O^+ with each compound, which are seen to occur by proton transfer (see Table 2), proceed at the collisional rate [40], which then provides absolute rate coefficients for the NO^+ and $O_2{}^+$ reactions (see the caption to Table 2 and Ref. [16]). Details of this technique have been given in several papers [16–24,29–31].

Additionally, in order to support SIFT-MS analyses that often involve humid samples [41,42], the rate coefficients and the ion product distributions were determined under three conditions: (i) Using dry helium carrier gas, i.e., with only the compound/dry air mixture entering the carrier gas. (ii) With laboratory air (relative humidity about 1.5%) also introduced into the carrier gas at a flow rate typical of that used for SIFT-MS analyses of ambient air and exhaled breath (2 Torr l/s [17]). (iii) With humid air (relative humidity about 6%) introduced at this same flow rate obtained above liquid water held near 37 °C. These extra experiments were carried out to observe any influence of air (N_2 and O_2) and water vapour on the production of hydrated ions [16,42].

To prevent condensation of water vapour and the compound vapour onto the sample inlet lines, they are heated to about 100 °C. All the present studies were carried out at a helium carrier gas pressure of 0.7 Torr at room temperature (296–300 K).

3. Results

The rate coefficients of five of the six reactions are measured to be at their respective collisional rate coefficients, as can be seen in Table 2. Unfortunately, the rate coefficients for the reactions of the dimethyl tetrasulphide could not be determined, because this compound could only be obtained in a mixture with dimethyl trisulphide. However, it seems very likely that the H_3O^+ reaction with dimethyl tetrasulphide will proceed at the collisional rate and likewise the NO^+ and $O_2{}^+$ reactions, since the reactions of H_3O^+, NO^+ and $O_2{}^+$ with of all the polyatomic organosulphur compounds we have studied previously do proceed at their respective collisional rate [24]. It is worthy of note that the reactions of the triatomic CS_2 molecule with these SIFT-MS precursor ions proceed relatively slowly [24], which must add a note of caution to the suggestion made above concerning the tetrasulphide reactions.

3.1. 2-Methyl-1-butanol, $C_2H_5CH(CH_3)CH_2OH$, and 2-heptanol, $C_5H_{11}CH(OH)CH_3$

In common with most primary and secondary aliphatic alcohols, the reactions of these compounds, MOH, with H_3O^+ proceed via the production of nascent $(MOH_2{}^+)^*$ protonated molecules, which release an H_2O molecule producing the appropriate hydrocarbon ion, M^+ [16,19]. This is the exclusive process for the reaction of the butanol isomer, the only product ion being $C_5H_{11}{}^+$, as can be seen in Table 2. However, we have observed previously that 1-octanol and 2-octanol partially fragment following protonation by H_3O^+ [19] and this is now seen to be the case for the 2-heptanol reaction that proceeds, thus:

$$H_3O^+ + C_5H_{11}CH(OH)CH_3 \rightarrow C_7H_{15}{}^+ + 2H_2O \qquad (1a)$$

$$H_3O^+ + C_5H_{11}CH(OH)CH_3 \rightarrow C_4H_9{}^+ + C_3H_7OH + H_2O \qquad (1b)$$

In both reactions a hydrocarbon ion is produced, which simplifies the detection and quantification of this compound because these ions do not associate with water molecules [23]. Reaction (1b) also results in the release of an alcohol molecule, as was observed for the reaction of H_3O^+ with the long-chain 1-octanol and 2-octanol isomers [19].

Both NO^+ reactions are simple and conform to those of most alcohols [19] in that they proceed via hydride ion (H^-) transfer, e.g.:

$$NO^+ + C_5H_{11}CH(OH)CH_3 \rightarrow C_7H_{15}O^+ + HNO \qquad (2)$$

Table 2
Experimentally derived rate coefficients, *k*, for the reactions of H_3O^+, NO^+ and O_2^+ with the compounds listed together with the product ions and the product distributions (in percent in brackets)

Molecule	α	μ	H_3O^+ product	[k_c]	NO^+ product	k [k_c]	O_2^+ product	k [k_c]
2-Methyl-1-butanol, $C_2H_5CH(CH_3)CH_2OH$, IE = 9.86 eV	10 ± 1	1.7 ± 0.2	$C_5H_{11}^+$ (100)	[2.8]	$C_5H_{11}O^+$ (100)	2.4 [2.4]	$C_5H_8^+$ (40), $C_5H_{10}^+$ (30), $C_4H_9^+$ (25), $C_2H_4^+$ (5)	2.3 [2.3]
2-Heptanol, $C_5H_{11}CH(OH)CH_3$, IE = 9.70 eV	14 ± 2	1.7 ± 0.2	$C_7H_{15}^+$ (90) $C_4H_9^+$ (10)	[3.0]	$C_7H_{15}O^+$ (100)	2.4 [2.5]	$C_2H_5O^+$ (50), $C_7H_{14}^+$ (25) $C_6H_{13}O^+$ (15), $C_6H_{11}^+$ (10)	2.4 [2.4]
3-Methyl-1-butyl acetate, $CH_3C(=O)OCH_2CH_2CH(CH_3)CH_3$, IE= n.a.	14 ± 2	1.8 ± 0.3	$C_7H_{14}O_2H^+$ (60) $C_5H_{11}^+$ (40)	[3.1]	$NO^+C_7H_{14}O_2$ (80) $C_2H_3O^+$ (15) $C_7H_{13}O_2^+$ (5)	2.4 [2.5]	$C_5H_{10}^+$ (80), $C_2H_3O^+$ (5) $C_5H_{11}O^+$ (10), $C_7H_{14}O_2^+$ (5)	2.4 [2.5]
4-Methyl-1,3-pentadiene, $CH_2{=}CHCH{=}C(CH_3)_2$, IE = 8.26 eV	10 ± 1.5	0.5 ± 0.2	$C_6H_{10}H^+$ (100)	[2.0]	$C_6H_{10}^+$ (100)	1.8 [1.6]	$C_5H_7^+$ (65), $C_6H_{10}^+$ (30) $C_6H_9^+$ (5)	1.8 [1.6]
Dimethyl trisulphide, CH_3SSSCH_3, IE = 8.73 eV	13 ± 2	1.5 ± 0.2	$C_2H_6S_3H^+$ (100)	[2.8]	$C_2H_6S_3^+$ (100)	1.9 [2.3]	$C_2H_6S_3^+$ (45), $CH_3S_3^+$ (15) $CH_3S_2^+$ (15), $CH_4S_2^+$ (10) $C_2H_5S^+$ (10), $CH_2S_2^+$ (5)	2.2 [2.2]
Dimethyl tetrasulphide, $CH_3SSSSCH_3$, IE= n.a.	16 ± 2	1.5 ± 0.2	$C_2H_6S_4H^+$ (100)	[2.9]	$C_2H_6S_4^+$ (100)	a [2.4]	$C_2H_6S_4^+$ (major ion)	a [2.3]

The known ionisation energy (IE, in unit of eV) of some compounds were obtained from NIST database [38]. The values of polarisabilities, α (in units of 10^{-24} cm^3), and permanent dipole moments, μ (in Debye), are estimated by adopting the values for similar compounds from [39]. Then, the collisional rate coefficients, k_c, for all reactions have been calculated using the parameterised trajectory formulation of Su and Chesnavich [40] and are given in square brackets. On the assumption that all the H_3O^+ reactions proceed at the respective collisional rates, the k values for the NO^+ and O_2^+ reactions have been experimentally derived by the procedure described in [16,30]. The k and k_c are given in units of 10^{-9} cm^3/s. Their estimated absolute and relative uncertainties respectively are ±25% and ±15%. n.a.: not available; a: these k values were not determined, but they are likely to be close to their respective k_c values (see the text).

The product ion of this 2-heptanol reaction is seen to form only a monohydrate, unlike protonated alcohols that form both mono- and dihydrates [16,19]. However, The carboxy ion formed in the 2-methyl-1-butanol reaction:

$$NO^+ + C_2H_5CH(CH_3)CH_2OH \rightarrow C_5H_{11}O^+ + HNO \quad (3)$$

is seen to form both mono- and dihydrates This is because this $C_5H_{11}O^+$ ion can rearrange to a cyclic structure of protonated 2-methyltetrahydrofuran [43] that is known to form a relatively strongly bound dihydrate (the first H_2O molecule is bound by 77.4 kJ/mol and the second by 54.8 kJ/mol [44]). The formation of these hydrates must be accounted for in SIFT-MS analyses of alcohols (see the discussion in Ref. [16]). It should be noted that for some alcohols hydroxide ion (OH^-) transfer is sometimes seen to compete with H^- transfer [19].

As is common in the reactions of O_2^+ with the longer chain aliphatic alcohols, charge transfer invariably occurs [19], the resultant cations undergoing dissociation producing several fragment ions, as can be seen in Table 2. This means that O_2^+ ions are not a useful precursor for SIFT-MS analyses of these compounds.

3.2. 3-Methyl-1-butyl acetate, $CH_3C(=O)OCH_2CH_2CH(CH_3)CH_3$

Our previous study of the reactions of several esters, $RCOOR_1$, where the radical R_1 is H, CH_3, C_2H_5 and C_3H_7 and the radical R is CH_3 and C_2H_5, has shown that they are largely stable when protonated by H_3O^+, the protonated ester $RCOOR_1H^+$ being the only product in most cases, although minor channels that lead to the production of a carboxyl ion, RCO^+, and an alcohol, HOR_1, are sometimes observed [22]. However, this secondary butyl acetate isomer exhibits different behaviour in that, following protonation, it partially dissociates (40%) apparently to acetic acid and a hydrocarbon ion, thus:

$$H_3O^+ + CH_3C(=O)OCH_2CH_2CH(CH_3)CH_3 \rightarrow C_7H_{14}O_2H^+ + H_2O \quad (4a)$$

$$H_3O^+ + CH_3C(=O)OCH_2CH_2CH(CH_3)CH_3 \rightarrow C_5H_{11}^+ + CH_3COOH + H_2O \quad (4b)$$

This clearly complicates the identification and quantification of these branched esters by SIFT-MS, although the production of a relatively unreactive hydrocarbon ion together with the protonated molecule eases the problem somewhat. Concerning hydration of the product ions, the experimental data showed, as expected [16], that the hydrocarbon ion did not hydrate and the protonated ester formed only a monohydrate.

The NO^+ reaction with this ester conforms with the other esters that we have studied previously (refereed to above) in that the major process that occurs is adduct formation together with additional minor channels:

$$NO^+ + CH_3C(=O)OCH_2CH_2CH(CH_3)CH_3 \xrightarrow{He} NO^+C_7H_{14}O_2 \quad (5a)$$

$$NO^+ + CH_3C(=O)OCH_2CH_2CH(CH_3)CH_3 \rightarrow CH_3CO^+ + C_5H_{11}NO_2 \quad (5b)$$

$$NO^+ + CH_3C(=O)OCH_2CH_2CH(CH_3)CH_3 \rightarrow C_7H_{13}O_2^+ + HNO \quad (5c)$$

The association channel (5a) is promoted by stabilising collisions of the nascent $(NO^+C_7H_{14}O_2)^*$ ion with the buffer gas and thus its branching fraction is increased with increasing helium pressure and by the presence of the molecular gases N_2 and O_2 in the helium carrier gas. The hydride ion transfer reaction (5c) is facilitated by the easier loss of the H atom from the tertiary carbon [45]. Note that the adduct ion formed in reaction (5a) and the carbonyl ion formed in reaction (5b) do not hydrate and that the product ion of reaction (5c) forms only a monohydrate.

Again, multiple products result following the energetic charge transfer reaction of this ester with O_2^+, as can be seen in Table 2. The most abundant product $C_5H_{10}^+$ is also a prominent peak ($m/z = 70$) on the EI mass spectrum [46], indicating that it is produced by favourable fragmentation of the parent radical cation.

3.3. 4-Methyl-1,3-pentadiene, $CH_2{=}CHCH{=}C(CH_3)_2$

This diene, like the similar compound isoprene (2-methyl-1,3-butadiene, $CH_2{=}CHC(CH_3){=}CH_2$) [23], is readily protonated by H_3O^+ producing the protonated parent molecule $C_6H_{10}H^+$ only. The latter ion does not form a hydrate under SIFT-MS conditions and this makes its identification and quantification more straightforward. Isoprene is found in exhaled breath of all individuals and is elevated in the breath of those suffering from various kinds of stress [47,48]. Some bacteria (see Table 1) release dienes and some alkenes. The reaction of this pentadiene with NO^+ proceeds via charge transfer producing the parent cation only:

$$NO^+ + CH_2{=}CHCH{=}C(CH_3)_2 \rightarrow C_6H_{10}^+ + NO \quad (6)$$

Charge transfer is allowed because of the low ionisation energy of the molecule, which is 8.26 eV [38] as compared to that of NO which is 9.26 eV [38]. The excess energy of 1 eV in the reaction is clearly insufficient to cause fragmentation of the parent cation. As stated previously, these hydrocarbon cations react only slowly with H_2O molecules [23], which simplifies their identification and quantification by SIFT-MS. The reaction of this diene with O_2^+ results in two major product hydrocarbon ions (see Table 2) and so it can be analysed using O_2^+ precursor ions in SIFT-MS, as is now routinely performed for isoprene [16,49].

3.4. *Dimethyl trisulphide, CH_3SSSCH_3, and dimethyl tetrasulphide, $CH_3SSSSCH_3$*

We have previously studied the reactions of dimethyl sulphide, CH_3SCH_3, and dimethyl disulphide, CH_3SSCH_3, with our three SIFT-MS precursor ions, since some aromatic foodstuffs emit these odious compounds, especially crushed garlic [50]. Dimethyl sulphide is also present in the exhaled breath of patients suffering from liver disease [16,51]. More appropriate to the present study is that these sulphides are released by some bacteria (see Table 1). The reactions of H_3O^+ with the monosulphide and the disulphide produce only the protonated parent molecules and the present study shows that this is the case also for the trisulphide and the tetrasulphide (see Table 2). It is somewhat surprising that the sulphur chain is not disrupted following protonation, but this might simply be because dissociation is not allowed energetically. The thermochemical data are not available for this to be checked. However, this very simple ion chemistry renders these organosulphur compounds readily accessible to SIFT-MS analyses. The analysis of these compounds is further simplified because the experimental data indicate that the protonated molecules do not efficiently form hydrates.

The NO^+ reactions with the dimethyl sulphide and dimethyl disulphide are also simple in that these reactions proceed via non-dissociative charge transfer producing only the parent cations [24]. The present study shows that this is also the case for the trisulphide and tetrasulphide, as can be seen in Table 2. Clearly, the energy excess in these charge transfer reactions is insufficient to allow dissociation of the nascent parent cations. This is not the case in the more energetic $O_2{}^+$ reactions in which multiple product ions result (see Ref. [24] and Table 2), again demonstrating that $O_2{}^+$ is not a useful precursor ion for the analysis of these compounds. Note that because a pure sample of the dimethyl tetrasulphide was not available, the product distribution for the reaction of this compound with $O_2{}^+$ could not be determined with any certainty.

4. Concluding remarks

By this SIFT study we have extended our SIFT-MS database to include the kinetic data for the reactions of H_3O^+, NO^+ and $O_2{}^+$ with several more compounds that are released by various kinds of bacteria. The processes involved in the ion chemical reactions of the various compound types, i.e., alcohols, esters, dienes and organosulphides, are seen to be consistent with those observed previously for the analogous compounds, especially for the diene and the two sulphides. However, a process hitherto not previously observed in our SIFT studies related to SIFT-MS analyses, has been observed in the reaction of H_3O^+ with the 3-methyl-1-butyl acetate, in which an acetic acid molecule is released from the nascent protonated ester. This is a reminder that although general trends in the reactions of the various compounds with the precursor ions H_3O^+, NO^+ and $O_2{}^+$ have emerged from the many SIFT studies that we have carried out in support of SIFT-MS, surprises still occur. The building of the database is a necessary and on-going procedure, especially when new media are to be investigated and analysed by SIFT-MS and those other techniques that rely on chemical ionisation.

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