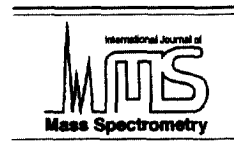




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Selected ion flow tube studies of the reactions of H_3O^+ , NO^+ , and O_2^+ with some organosulphur molecules

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Abstract

We report the results of a selected ion flow tube (SIFT) study of the reactions of H_3O^+ , NO^+ , and O_2^+ with eight organosulphur molecules, *M*. If we assume that all the exothermic proton transfer reactions of H_3O^+ occur at the collision rate (i.e. the rate coefficients, *k*, are equal to the collisional rate coefficient, *k_c*), it is seen that the *k* for most of the NO^+ and O_2^+ reactions also are equal to or close to *k_c*. However, the reaction of H_3O^+ with one of the chosen reactants, CS_2 , is known from our previous SIFT study to be slightly endothermic, and therefore it proceeds more slowly than the collisional rate. The ionic product of seven of the H_3O^+ reactions is only the protonated parent molecule MH^+ , but in one reaction, that of thiolacetic acid CH_3COSH , elimination of an H_2S molecule occurs in a fraction of the collisions. The NO^+ reactions mostly proceed via charge transfer, producing the parent molecular ion M^+ , but the reaction with ethanthiol is unusually complicated, with four processes occurring in parallel (charge transfer, H^- and SH^- transfer, and ion-molecule association), and the reaction with thiolacetic acid occurs exclusively and rapidly via SH^- transfer. The O_2^+ reactions proceed by dissociative charge transfer, often with the production of three or more ionic fragments of the parent molecular ion. Sample mass spectra obtained using our SIFT method of analysis of the vapours emitted by cut onion and crushed garlic are presented and discussed, noting the presence of some organosulphur molecules and other organic species. (Int J Mass Spectrom 176 (1998) 167–176) © 1998 Elsevier Science B.V.

Keywords: Selected ion flow tube; Ion-molecule reactions; Organosulphur molecules; Proton transfer; Charge transfer; Trace gas analysis; Chemical ionization

1. Introduction

We are carrying out extensive surveys of the reactions of H_3O^+ , NO^+ , and O_2^+ ions with a wide

variety of organic and inorganic molecular species, including many that are known to be present in trace amounts in atmospheric air and in human breath [1,2] and are emitted by fruit and food products [3]. Thus, we are constructing a database for our selected ion flow tube (SIFT) method of trace gas analysis [4–6]. The above ionic species are being exploited for the

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Table 1

Rate coefficients for the reactions of H_3O^+ , NO^+ , and O_2^+ with the organosulphur molecules indicated

Molecule	m (u)	α (10^{-24} cm ³)	μ (D)	k , k_c (H_3O^+) (10^{-9} cm ³ s ⁻¹)	k , k_c (NO^+) (10^{-9} cm ³ s ⁻¹)	k , k_c (O_2^+) (10^{-9} cm ³ s ⁻¹)
Carbon disulphide	76	8.8	0	0.25 (1.8)	0.1 (1.5)	0.7 (1.5)
Dimethyl sulphide	62	7 ± 2	1.50	(2.5)	2.2 (2.1)	2.2 (2.1)
Dimethyl disulphide	94	10 ± 2	1.5	(2.6)	2.4 (2.2)	2.3 (2.1)
Ethanthiol	62	7.4	1.58	(2.6)	1.9 (2.2)	2.4 (2.2)
Thiolacetic acid	76	8.5	1.7	(2.8)	2.4 (2.3)	2.3 (2.3)
1-3 Dithiane	120	15 ± 3	1.5	(2.9)	2.3 (2.4)	2.3 (2.3)
Diallyl sulphide	114	14 ± 3	1.5	(2.9)	2.5 (2.4)	2.4 (2.3)
Diallyl disulphide	146	17 ± 3	1.5	(3.0)	2.4 (2.5)	2.3 (2.4)

Also given are their molecular weights of the reactant molecules, m , in atomic units, u, their polarisabilities, α , in units of 10^{-24} cm³ and their permanent dipole moments, μ , in Debye, D. The values of α and μ are known for only three of the compounds included in this study, and they are shown in regular type (taken from [17]). For the remaining compounds (shown in italic) we have estimated their dipole moments assuming they do not change significantly with the number of carbon atoms in the organosulphur molecule and their polarisabilities by adopting the average values of the known polarisabilities of similar organic molecules possessing the same number of carbon atoms. The collisional rate coefficients, k_c , for all reactions have been calculated using the parameterised trajectory formulation of Su and Chesnavich [16] and these are given in the square brackets. The estimated uncertainty in these calculated rate coefficients is $\pm 25\%$. On the assumption that all the H_3O^+ reactions (except the CS_2 reaction) proceed at the collisional rates, the rate coefficients, k , for the NO^+ and O_2^+ reactions have been experimentally derived by the procedure described in the text. The k and k_c are given in units of 10^{-9} cm³s⁻¹.

selective ionisation (chemical ionisation [7]) of the trace gases in the air and breath; they are the most suitable ions because they do not react at a significant rate with the major air components (N_2 , O_2 , CO_2 , H_2O , and Ar), yet they do react rapidly with most organic and many inorganic gases and vapours.

To date, we have determined the rate coefficients and the ionic products for the reactions of H_3O^+ , NO^+ , and O_2^+ ions with 17 alcohols [8], 11 aldehydes, and 9 ketones [9], 9 carboxylic acids and 8 esters [10], and 10 ethers [11]. These data have revealed the trends in reactivity of these precursor ions with particular molecular types and are providing a better understanding of the fundamental aspects of this ion-molecule chemistry. They are also essential when interpreting the mass spectra that are obtained when complex mixtures such as breath and fruit and vegetable emissions are analysed.

The data are revealing many examples of reaction processes hitherto not greatly explored, such as the elimination of H_2O molecules after the protonation of some alcohols, aldehydes, and carboxylic acids by H_3O^+ [8–10], hydride ion transfer (H^-), hydroxide ion (OH^-) transfer in the reactions of NO^+ with some alcohols, aldehydes, acids, and ethers [8–11], facile ion-molecule association between NO^+ and most

ketones [9], and even alkoxide ion (CH_3O^- and $\text{C}_2\text{H}_5\text{O}^-$) transfer in the reactions of NO^+ with some esters and ethers [10,11]. These data are in substantial agreement with the data obtained previously for the reactions of NO^+ ions [12,13]. Our data reveal that the reactions of O_2^+ with almost all these organic compounds proceed via charge transfer, often with the productions of several fragment ions [8–11].

In this article we report the results of a study of the rate coefficients and ion product distributions for the reactions of the three ions with eight organosulphur compounds, variously chosen because they are apparently present in the breath of persons with liver dysfunction (dimethyl sulphide, carbon disulphide [1]), and are emitted by crushed garlic (1-3 dithiane, diallyl sulphide, diallyl disulphide [3]). We also include one thioalcohol (ethanthiol) and one thioacid (thiolacetic acid) to compliment and extend our analogous surveys of the reactions of alcohols [8] and carboxylic acids [10]. The organosulphur compounds included in this limited study are listed in Tables 1 and 2. In addition, we have used our chosen precursor ions to study the vapours emitted by cut onion and crushed garlic, and some resulting analyses of these vapours are presented that illustrate the value of our SIFT analytical method [4–6].

Table 2

Products of the reactions of the organosulphur molecules with H_3O^+ , NO^+ , and O_2^+

	H_3O^+	NO^+	O_2^+
Carbon disulphide CS_2	$\text{CS}_2\cdot\text{H}^+(100) + \text{H}_2\text{O}$	Products not identified	$\text{CS}_2^+(100)$
Dimethyl sulphide $(\text{CH}_3)_2\text{S}$	$(\text{CH}_3)_2\text{S}\cdot\text{H}^+(100) + \text{H}_2\text{O}$	$(\text{CH}_3)_2\text{S}^+(100) + \text{NO}$	$(\text{CH}_3)_2\text{S}^+(60)$ $\text{CH}_3\text{S}^+(25)$ $\text{CH}_2\text{S}^+(15)$
Dimethyl disulphide $(\text{CH}_3)_2\text{S}_2$	$(\text{CH}_3)_2\text{S}_2\cdot\text{H}^+(100) + \text{H}_2\text{O}$	$(\text{CH}_3)_2\text{S}_2^+(100) + \text{NO}$	$(\text{CH}_3)_2\text{S}_2^+(80)$ $\text{CH}_3\text{CH}_2\text{S}^+(10)$ $\text{CH}_3\text{S}_2^+(5)$ $\text{CH}_2\text{S}^+(5)$
Ethanthiol $\text{C}_2\text{H}_5\text{SH}$	$\text{C}_2\text{H}_5\text{SH}\cdot\text{H}^+(100) + \text{H}_2\text{O}$	$\text{C}_2\text{H}_5\text{SH}^+(50) + \text{NO}$ $\text{C}_2\text{H}_5\text{S}^+(20) + \text{HNO}$ $\text{C}_3\text{H}_5^+(15) + \text{HNOS}$ $\text{NO}^+\cdot\text{C}_2\text{H}_5\text{SH}(15)$	$\text{C}_2\text{H}_5\text{SH}^+(50)$ $\text{CH}_3\text{S}^+(25)$ $\text{CH}_2\text{S}^+(10)$ $\text{C}_2\text{H}_4^+(10)$ $\text{C}_2\text{H}_5^+(5)$ $\text{CH}_3\text{CO}^+(100)$
Thiolacetic acid CH_3COSH	$\text{CH}_3\text{COSH}\cdot\text{H}^+(80) + \text{H}_2\text{O}$ $\text{CH}_3\text{CO}^+(20) + \text{H}_2\text{S} + \text{H}_2\text{O}$	$\text{CH}_3\text{CO}^+(100) + \text{HSNO}$	
1-3 Dithiane c- $\text{C}_4\text{H}_8\text{S}_2$	$\text{c-C}_4\text{H}_8\text{S}_2\cdot\text{H}^+(100) + \text{H}_2\text{O}$	$\text{c-C}_4\text{H}_8\text{S}_2^+(100) + \text{NO}$	$\text{C}_4\text{H}_8\text{S}_2^+(45)$ $\text{C}_4\text{H}_7\text{S}^+(30)$ $\text{C}_3\text{H}_6\text{S}^+(25)$ $\text{C}_3\text{H}_5\text{S}^+(20)$ $\text{C}_3\text{H}_4\text{S}^+(20)$ $(\text{C}_3\text{H}_5)_2\text{S}^+(10)$ $\text{C}_5\text{H}_7\text{S}^+(10)$ Hydrocarbon ions(40)
Diallyl sulphide $(\text{C}_3\text{H}_5)_2\text{S}$	$(\text{C}_3\text{H}_5)_2\text{S}\cdot\text{H}^+(100) + \text{H}_2\text{O}$	$(\text{C}_3\text{H}_5)_2\text{S}^+(100) + \text{NO}$	$(\text{C}_3\text{H}_5)_2\text{S}_2^+, \text{C}_3\text{H}_5\text{S}^+$ $\text{C}_3\text{H}_5\text{S}_2^+, \text{C}_3\text{H}_4\text{S}^+$ major products
Diallyl disulphide ^a $(\text{C}_3\text{H}_5)_2\text{S}_2$	$(\text{C}_3\text{H}_5)_2\text{S}_2\cdot\text{H}^+(100) + \text{H}_2\text{O}$	$(\text{C}_3\text{H}_5)_2\text{S}_2^+(100) + \text{NO}$	

The molecular formulas of the ion products listed do not necessarily represent their structures; the percentage of each ion product is given in parentheses. The neutral products are given only for the H_3O^+ and NO^+ and not for the O_2^+ reactions for which the neutral products (and in some cases the ionic products) are not readily defined.

^aThe ion products of the diallyl disulphide reactions have been inferred from the vapour emissions from crushed garlic (see text).

2. Experimental

Measurements of the rate coefficients, k , and ion products of ion-molecule reactions at thermal energies using the SIFT technique have been discussed in numerous review and research papers (see [12–14]). So here, it is sufficient to say that a reactant gas or vapour is introduced at a controlled, measured flow rate into the helium carrier gas of the SIFT into which a current of mass selected reactant ions (in the present experiments H_3O^+ , NO^+ , and O_2^+) has been introduced upstream, and the loss rate of the reactant ions and the production rates of the product ions of the ion-molecule reaction that occurs are determined by the downstream mass spectrometer/detection system. From these data, together with other critical param-

eters including the carrier gas flow velocity and the length of the reaction zone (i.e. the effective reaction time), the k for the reactions and the ion product branching ratios are determined [12].

It is straightforward to measure the flow rates of most permanent reactant gases, but this is more difficult for many organic vapours because the thermodynamic data required for capillary and flow meter calibrations (i.e. heat capacities) are mostly unavailable, and volume/pressure reduction methods of flow measurements are inaccurate because such vapours often stick to vessel surfaces. The organosulphur compounds used in the present studies are particularly sticky so we have again adopted the following procedure.

We justifiably assume [15] that the values of k for

all appreciably exothermic proton transfer reactions of H_3O^+ proceed at the collision rate, k_c , which can be calculated if the polarisability and the dipole moment of the reactant molecule, M , are known [16,17]. Unfortunately these molecular parameters are not known for all eight organosulphur molecules and so we have to make estimates for some of them to obtain approximate values for the k_c . It is well known from numerous experimental studies [15,18] that proton transfer reactions proceed at their respective collision rates if the proton affinity (PA) of the acceptor molecule, M , exceeds that of the donor molecule, in this case H_2O . Thus, for such exothermic proton transfer reactions, $k = k_c$. Again, unfortunately, the PA of some of these organosulphur molecules are not known, but all but one, CS_2 , apparently have a PA greater than that of water because our results show that they react rapidly with H_3O^+ (see the beginning of the Results section). Fortunately, we have an accurate value for the k for the slightly endothermic reaction of H_3O^+ with CS_2 from a previous SIFT study [19]. However, other exothermic reactions that proceed via processes such as charge transfer and hydride ion transfer (by which many of the O_2^+ and NO^+ reactions with organic molecules occur [20]) do not necessarily proceed at the collision rate (i.e. k cannot be assumed to be equal to k_c). So the values of k for the NO^+ and O_2^+ reactions must be determined experimentally. To do this we make a very dilute mixture of the reactant (organosulphur molecule) vapour at an unknown (but low) partial pressure in dry cylinder air in a plastic bag and use this as the reactant gas in these SIFT experiments. The flow rate of this mixture (essentially air) is readily measured using standard flow meters. Of course, using this procedure we cannot determine the absolute k for the reactions, but by introducing H_3O^+ , NO^+ , and O_2^+ ions simultaneously into the carrier gas, we can measure the relative decay rates of these three ion species as a function of the flow rate of the vapour/air mixture. Because $k = k_c$ for the H_3O^+ reactions (except for the CS_2 reaction), then the value of k for the NO^+ and O_2^+ reactions can be obtained. More discussion of this procedure and the possible influence of metastable states of the primary ions together with sample

primary ion decay plots are given in the previous papers in this series [8–11]. The product ion distributions for the reactions are also determined from these measurements in the usual manner [12,13].

To obtain the analyses of the onion and garlic vapours we simply introduced a piece of freshly cut onion into a 3-L plastic bag and inflated it with dry cylinder air; similarly we placed a garlic clove into a bag, crushed it, and then inflated the bag with the dry air. Then by injecting each of the H_3O^+ , NO^+ , and O_2^+ ions separately into the SIFT, we flowed the vapour/air mixtures separately into the helium carrier gas and multiscanned the downstream (analytical) mass spectrometer over appropriate ranges for a period of typically 1 minute for each precursor ion while storing the total spectra (primary and product ions). Sample spectra and our interpretation of them are presented in Sec. 4.

All the measurements of the rate coefficients and the ion product distributions, and the analyses of the onion and garlic emissions, were carried out in helium carrier gas at a pressure of ~ 0.5 Torr at a temperature of 300 K.

3. Results and discussion

The decay rates of the three reactant ions with six of the eight reactants were comparable and in close relation to their respective calculated collisional rate coefficients k_c (as calculated using the procedure outlined in the footnote to Table 1). This strongly indicates that all seven reactions proceed at their respective collision rates (i.e. that $k = k_c$). The calculated k_c and the derived k are given in Table 1. The exceptions are the proton transfer reactions between H_3O^+ and CS_2 and $(\text{C}_3\text{H}_5)_2\text{S}_2$ (see the discussions in Sec. 3.1). The former reaction is known from our previous SIFT study to be slightly endothermic [19] and therefore proceeds at a rate appreciably slower than collisional. The measured value for the k value for this reaction is also given in Table 1; it can also be seen that the k value for the O_2^+/CS_2 charge transfer reaction is equal to $0.5 k_c$ and that the NO^+/CS_2 reaction is very slow (see later comments).

To our knowledge, there has been very little previous work on the ion chemistry of organosulphur reactions. The proton transfer reactions of H_3O^+ with CH_3SH , $\text{C}_2\text{H}_5\text{SH}$ and $(\text{CH}_3)_2\text{S}$ have been investigated and, as expected, were found to be fast [21].

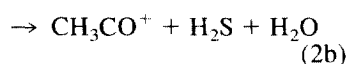
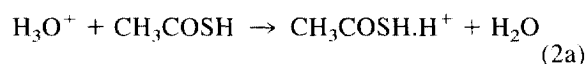
The ion product distributions for all the reactions are shown in Table 2. Only those ion products that represent >2% of the product distribution have been included. We now discuss the H_3O^+ , NO^+ , and O_2^+ reactions separately.

3.1. H_3O^+ reactions

A glance at Table 2 reveals that the only product ion of seven of these reactions is the protonated parent molecule as exemplified by the dimethyl sulphide reaction:



These include the CS_2 reaction, which proceeds more slowly than the collision rate (Table 1) because the PA of CS_2 (679 kJ/mol [19]) is less than that of H_2O (696 kJ/mol [19,22]). In only one of these reactions are two products observed:



In reaction (2b), an H_2S molecule is ejected from the protonated molecule, leaving the very stable carboxy ion, the reaction being only 25 kJ/mol exothermic using the thermochemical data given in [22]. This process is analogous to H_2O elimination, which occurs as a minor channel after the protonation of most carboxylic acids by H_3O^+ [10].

It must be noted that the data obtained for the diallyl disulphide reactions were not obtained directly from the pure material because we could only acquire this substance with a purity of 80%, the other 20% being "other sulphides." Our analysis showed that the vapour above the liquid consisted mostly of diallyl monosulphide with barely 2% of the vapour being the disulphide, presumably because of its lower vapour

pressure. However, the disulphide and not the monosulphide was clearly present in the vapour emitted by crushed garlic (see Fig. 2) and from the relative signal heights of the ions at m/z 147 (the protonated disulphide) produced when H_3O^+ is the precursor ion for the analysis and that at m/z 146 (the disulphide cation) formed when NO^+ is the precursor ion, we conclude that both these reactions (and indeed the O_2^+ reaction) are fast, as we have indicated in Table 1. Clearly, H_3O^+ is an excellent ion for the detection of these organosulphur molecules.

3.2. NO^+ reactions

Five of these eight reactions proceed via charge transfer as exemplified by the dimethyl sulphide (dimethyl thioether) reaction:



These results obviously indicate that the ionisation energies of these organosulphur molecules are less than that of nitric oxide (9.26 eV). The reaction of NO^+ with most ethers, R-O-R , in which charge transfer is endothermic (because their ionisation energies exceed that of NO [22]), proceed mostly via hydride ion transfer [11,23,24]. The ionisation energy of CS_2 is 10.1 eV, so charge transfer with NO^+ cannot occur and there are no other exothermic bimolecular channels. The slow reaction observed is probably because of termolecular association producing $\text{NO}^+.\text{CS}_2$, but we could not identify the ion product.

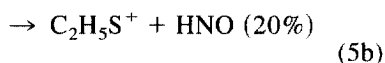
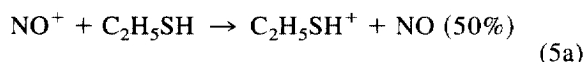
The thiolacetic acid reaction is again exceptional in this series of eight reactions in that the only reaction process that occurs is SH^- transfer, thus:



Again, the stable carboxy cation is the ionic product together with an HSNO molecule. According to the thermochemical data given in [22], reaction (4) is endothermic by 21 kJ/mol for the product neutral structure HNOS . Clearly reaction (4) is exothermic because it proceeds rapidly at 300 K (Table 1), which requires that the heat of formation of the HSNO molecule is less than 150 kJ/mol. Reaction (4) is

analogous to hydroxide ion, OH^- , transfer often seen in the reactions of NO^+ with carboxylic acids [10], which also result in a stable carboxy cation and a nitrous acid (HNO_2) molecule.

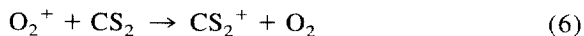
The most complicated of these NO^+ reactions is that of ethanthiol, in which four ionic products result:



In this reaction we see (a) charge transfer, (b) hydride ion, H^- , transfer, (c) SH^- transfer as in reaction (4), and (d) ion-molecule association. According to the available data, the ionisation energy of ethanthiol is 9.28 eV [17], which is somewhat greater than that of NO (9.26 eV) and thus reaction (5a) should not be so fast. However, the difference between these ionisation energies is only 20 meV, which is less than the mean interaction energies of the ions/reactant molecules in the SIFT experiment. Nevertheless, this slight endothermicity for charge transfer allows the other more exothermic processes to occur. Of special interest is the association channel (5d). Association often occurs in parallel with charge transfer when the latter process is slightly endothermic, a phenomenon well illustrated by the reactions of NO^+ with some ketones [9] and carboxylic acids [10].

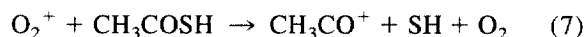
3.3. O_2^+ reactions

Multiple products are observed for most of these reactions, the two exceptions being the CS_2 reaction, which is an example of nondissociative charge transfer, resulting in only the parent cation:



and the thiolacetic acid reaction for which the only product ion is CH_3CO^+ as it is for the SH^- transfer

reaction (4). However, we consider this O_2^+ reaction to be a dissociative charge transfer reaction:



because the neutral products are unlikely to be bound as HSO_2 and reaction (7) is exothermic by 196 kJ/mol [22] to give separated SH and O_2 neutral products as indicated.

The relatively high recombination energy of O_2^+ of 12.2 eV (compared with NO^+) allows the parent cations, formed by charge transfer, to fragment along several channels, and thus “cracking patterns” are observed (Table 2), with the parent cations being variously a major or a minor product. Multiple products are observed for the diallyl sulphide and diallyl disulphide reactions, which effectively disqualifies O_2^+ as a precursor ion for these compounds in SIFT analytical work. Also, the reaction of O_2^+ with the cyclic 1-3 dithiane is sufficiently energetic to break the ring in a fraction of the collisions, resulting in the production of $\text{C}_3\text{H}_6\text{S}^+ + \text{CH}_2\text{S}$.

4. Vapour emissions from cut onion and crushed garlic

4.1. Cut onion

The mass spectra obtained over the mass range from 10 to 150 u when the air/onion vapour was introduced into the SIFT using both H_3O^+ and O_2^+ as precursor ions are shown in Fig. 1. It is possible to interpret these spectra with the aid of the large amount of data we have obtained for the reactions of these precursor ions with many organic compounds [8–11]. Obvious features in the spectrum in Fig. 1(a) are the ions at m/z 19 (H_3O^+) and at m/z 37, 55, and 73, the hydrated hydronium ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{1,2,3}$, which inevitably form from H_3O^+ in ternary collisions when wet air is introduced into the SIFT [25]. There are many other product ions that emphasise the richness of the onion vapour, but outstanding are those at m/z 59, 77, 91, and 109. Which molecules in the onion vapour are indicated by these ions? Their identification is greatly facilitated by the corresponding spectra obtained with O_2^+ as the precursor ion [Fig. 1(b)];

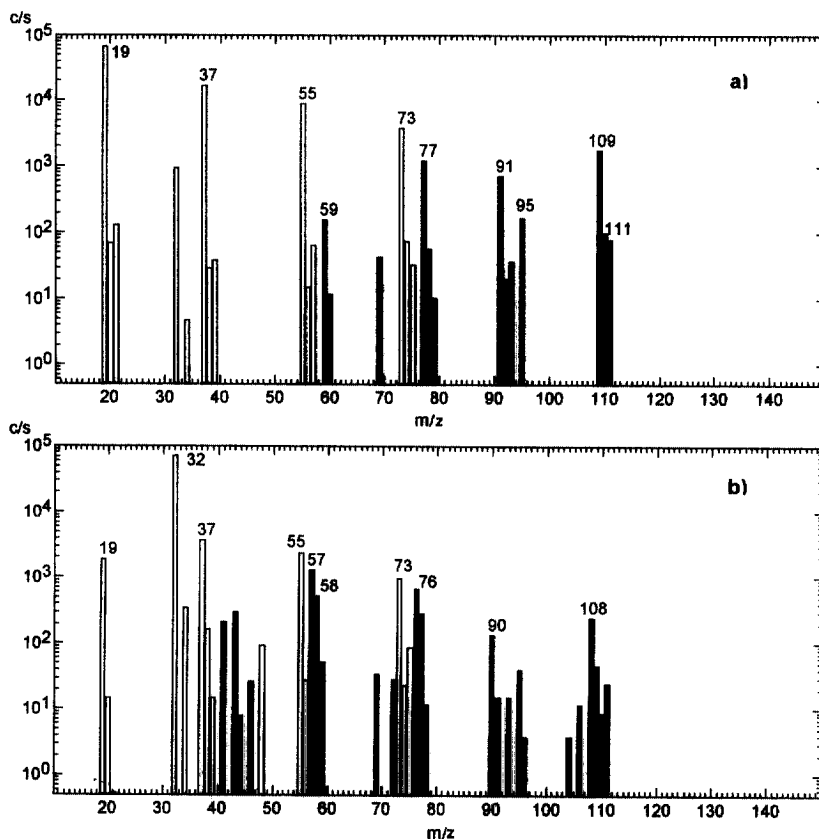


Fig. 1. The SIFT mass spectra (in semilogarithmic form) obtained when an air/onion vapour mixture is introduced into the helium carrier gas using (a) H_3O^+ precursor ions and (b) O_2^+ precursor ions. The ions at masses m/z 19, 37, 55, and 73 are the hydrated hydronium ions in both spectra. The product ions m/z 59 in (a) and m/z 57 and 58 in (b) derive from 1-propanal, m/z 77 in (a) and m/z 76 in (b) derive from 1-propanthiol, and m/z 91 and its hydrate 109 in (a) and m/z 90 and its hydrate 108 in (b) derive from propanal-S-oxide.

note the ions at m/z 57 and 58, 76, and 90 and 108. The 59^+ ion (from H_3O^+) and 57^+ , 58^+ ions (from O_2^+) are respectively the protonated molecule, MH^+ , $(\text{M}-\text{H})^+$, and M^+ . According to our database, the molecule M that fits this profile is 1-propanal, $\text{C}_2\text{H}_5\text{CHO}$, which protonates in reaction with H_3O^+ and partially dissociates after charge transfer with O_2^+ [9]. The ions at m/z 77 (from H_3O^+) and 76 (from O_2^+) derive from 1-propanthiol, $\text{C}_3\text{H}_7\text{SH}$, and are the protonated molecule and its cation respectively. 1-Propanthiol is known to be emitted by cut onion [3]. The 77^+ peak is also partly the hydrate of the protonated propanal, $\text{C}_2\text{H}_5\text{CHO} \cdot \text{H}^+ \cdot \text{H}_2\text{O}$, and the ion at m/z 95 is the corresponding hydrate of the propanthiol (18 u greater mass in each case).

The ions at m/z 91 and 109 in the H_3O^+ spectrum and m/z 90 and 108 in the O_2^+ spectrum derive from one particular molecule M and are, respectively, MH^+ and its hydrate and M^+ and its hydrate. To determine the molecular formula of M we carefully scanned the spectrum around m/z 91 and 109 to obtain the abundance ratios of their ($^{13}\text{C} + ^{33}\text{S}$) and ^{34}S isotopic variants at m/z 92, 93, 110, and 111. These spectra are reproduced in Fig. 2. Simple analyses of these indicate that the molecular formula of M is $\text{C}_3\text{H}_6\text{OS}$. There are several possible structures for this, but it is surely propanal-S-oxide, which is the known lachrymatory factor in onion vapour, and it is known to cleave to give mainly an S atom and propanal [3]. This explains the presence of propanal in the onion vapour. There are

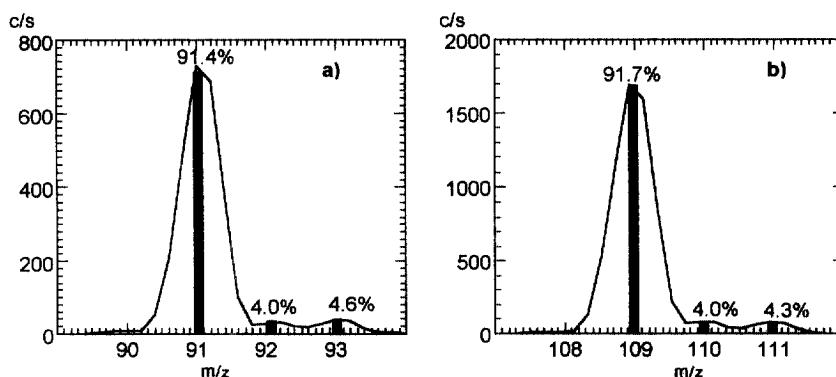


Fig. 2. Limited mass spectral scans around the ion peaks (a) m/z 91 and (b) its monohydrate m/z 109, in the air/onion spectrum obtained using H_3O^+ precursor ions as shown in Fig. 1(a). These spectra were obtained to determine the abundance ratios of ($^{13}\text{C} + ^{33}\text{S}$) and ^{34}S in these ions to establish the molecular formulas of the ions.

many other ions in the spectra at lower levels that at this stage we do not attempt to identify.

4.2. Crushed garlic

The distinctive odour of crushed garlic is known to be due to organosulphur compounds, notably diallyl disulphide and its S-oxide, triallyl disulphide and 1-3 dithiane [3]. These compounds were identified using calibrated gas chromatography mass spectrometry (GCMS) equipment. They are observed in our quick-look spectra, but they are not the major organic species that we detect as being immediately emitted after crushing the garlic clove. Fig. 3 shows respectively the spectra observed for H_3O^+ and NO^+ as the precursor ions. Again, the H_3O^+ hydrates are obvious in Fig. 3(a), but several other ions are present. This spectrum is relatively simple to interpret in the low mass range below m/z 80. The ions at m/z 33, 51, and 69 are due to the presence of methanol (i.e. $\text{CH}_3\text{OH}_2^+(\text{H}_2\text{O})_{0,1,2}$, [8]) and those ions at m/z 45, 63, and 81 are due to acetaldehyde (i.e. $\text{CH}_3\text{CHOH}^+(\text{H}_2\text{O})_{0,1,2}$, [9]), and these two compounds constitute the major compounds emitted immediately after crushing the garlic clove.

In the H_3O^+ spectrum [Fig. 3(a)], the ion at m/z 49 is the smallest organosulphur molecule that is present and is protonated methanthiol, CH_3SH_2^+ . The heavier ions at m/z 121, 147, and 163 are also sulphur-bearing molecular ions, and isotopic analyses performed as

described above shows that they each have two sulphur atoms. The analogous spectrum with NO^+ as the precursor ion [Fig. 3(b)] shows ions at m/z 120, 146, and 162. These two spectra indicate that molecules with two sulphur atoms at masses of 120, 146, and 162 u are present in the protonated form (from H_3O^+) and as the parent cations (from NO^+). These molecules are the 1-3 dithiane, a six-membered ring with molecular formula $\text{C}_4\text{H}_8\text{S}_2$, diallyl disulphide, $(\text{C}_3\text{H}_5)_2\text{S}_2$, and diallyl disulphide-S-oxide, $(\text{C}_3\text{H}_5)_2\text{SS}(\text{O})$ mentioned above. The diallyl trisulphide is not represented in either of these spectra.

Although we cannot positively identify compounds for which there are many isomeric forms by using our SIFT analytical method, the mass spectra can be acquired quickly, and real time variations in the emission rates of particular species can be monitored, which is an advantage over GCMS. Also, by knowing the rate coefficients for the reactions of the component molecules of the air/vapour mixture, we can determine accurately and simultaneously the partial pressures of the various molecules in the mixture.

5. Conclusions

These studies of the reactions of H_3O^+ , NO^+ and O_2^+ with several organosulphur compounds (and our previous studies of their reactions with many other

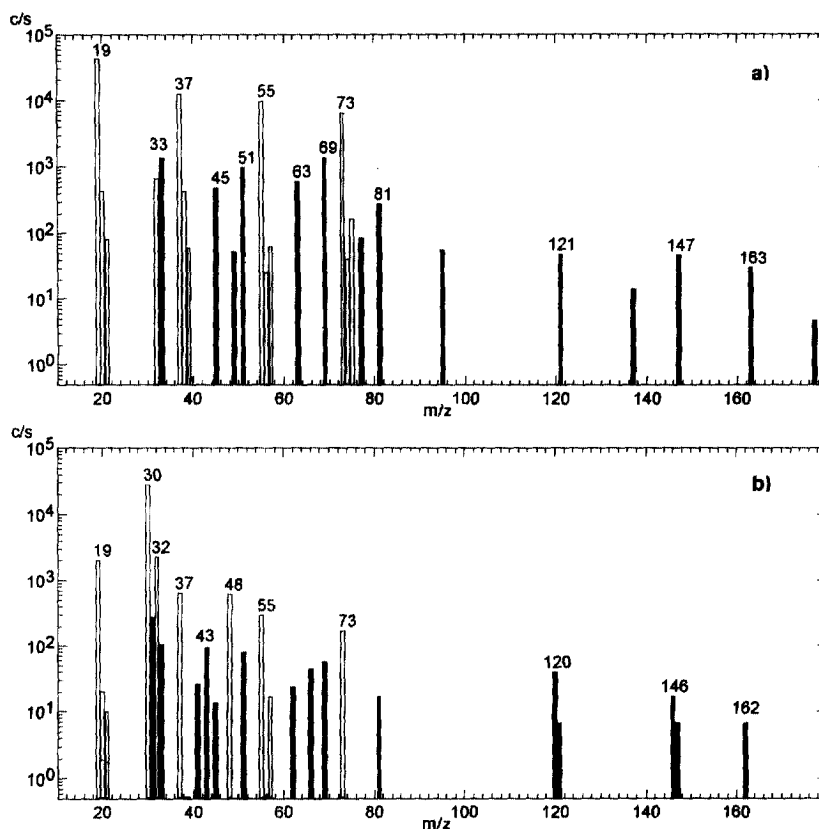


Fig. 3. The SIFT spectra (in semilogarithmic form) obtained when an air/garlic vapor mixture is introduced into the helium carrier gas using (a) H_3O^+ precursor ions m/z 19 and (b) NO^+ precursor ions (30). Again, the hydrated hydronium ions are obvious and inevitably appear in the spectrum when wet air is introduced into the carrier gas. The ion at m/z 48 in (b) is $\text{NO}^+\cdot\text{H}_2\text{O}$. The ions in (a) at m/z 33, 51, and 69 are due to the presence of methanol and those at m/z 45, 63, and 81 are due to acetaldehyde. The heavier ions at m/z 121, 147, and 163 in (a) are sulphur-bearing molecular ions as are those at m/z 120, 146, and 162 in (b); they derive respectively from 1-3 dithiane, diallyl disulphide, and diallyl disulphide-S-oxide.

organic compounds) show that these ions are very useful as chemical ionisation agents in our SIFT analytical method for the rapid detection (and quantification) of these sulphur-bearing species and other organic species in the vapours emitted by food products. It is the use of two or even all three of these precursor ions on the same air/vapour mixture that gives greater certainty to the proper identification of the various trace gases. In the examples presented here for the analysis of onion and garlic emissions, H_3O^+ with O_2^+ were found to be the most suitable for onion and H_3O^+ and NO^+ were most suitable for garlic. The kinetic data are not only important in

extending the required database for our SIFT analytical method, but also represent a useful contribution to the fundamental studies of ion–molecule reactions.

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