SIFT studies of the reactions of H_3O^+, NO^+ and O_2^+ with a series of aldehydes and ketones

Patrik Španěl[a],*, Yufeng Ji[b], David Smith[a]

[a]*Department of Biomedical Engineering and Medical Physics, Keele University, Thornburrow Drive, Hartshill, Stoke-on-Trent, ST4 7QB, UK*
[b]*Anhui Institute of Optics and Fine Mechanics, Academia Sinica, PO Box 1125, Hefei, Anhui, People's Republic of China*

Abstract

The results are reported of a selected ion flow tube (SIFT) study of the rate coefficients and the ionic products of the reactions of H_3O^+, NO^+ and O_2^+ with some 11 aldehydes and nine ketones including the structural isomers of some. We assume that the 20 exothermic H_3O^+ proton transfer reactions proceed at the collisional rate and on this basis the large majority of the remaining 40 reactions included in this study also proceed close to the collisional rate. A variety of reaction processes are seen to occur. The H_3O^+ reactions proceed via proton transfer which for the ketones produces the protonated molecules only but which in the aldehyde reactions H_2O elimination from the protonated molecule also occurs. The NO^+ reactions with the aldehydes proceed largely via the process of hydride ion transfer whereas ion–molecule association is the dominant process in the NO^+/ketone reactions with charge transfer also evident in some cases. The O_2^+ reactions with both the aldehydes and ketones proceed largely via charge transfer which in all reactions is partially dissociative producing several ionic products for the more polyatomic reactant molecules. Different products are observed in the reactions of O_2^+ with some of the structural isomers. © 1997 Elsevier Science B.V.

Keywords: SIFT; Ion–molecule reactions; Proton transfer; Hydride ion transfer; Charge transfer; Chemical ionisation

1. Introduction

We have developed our selected ion flow tube (SIFT) method for the detection and quantifica-

tion of trace gases in ambient air and human breath with the primary objectives to utilise this new technique in such important areas as medical and environmental research [1–3] and for monitoring indoor environments for health and safety practice [4,5]. This new technique is based on the chemical ionisation of the trace gases in air (and breath) to the exclusion of the major air gases

---

* Corresponding author.
Dedicated to Professor Keith R. Jennings.

(N_2, O_2, H_2O, CO_2 and Ar) using specific, selected precursor positive ions to ionise the trace gas molecules which are introduced into the inert carrier gas of a SIFT apparatus in an air sample. Thus the new ions created in the carrier gas, which are characteristic of the trace gases in the air sample, are detected and counted using mass spectrometry and the partial pressures of the trace gases in the sample are then determined. We have shown that the most useful precursor ions are H_3O^+, NO^+ and O_2^+ because they do not react at a rapid rate with the major air gases and they do not result in excessive fragmentation ('cracking') of the trace gas molecules following the ion–molecule reactions. This facilitates the correct identification of the trace gases in multi-component mixtures such as polluted air and human breath. Of course, it is necessary to know which ions are produced in the reactions of the chosen precursor ion(s) with the trace gases in the air sample if they are to be properly identified, and to know the rate coefficients for the ion–molecule reactions if the trace gases are to be accurately quantified. In human breath alone there are a large number of trace gases, mostly organic compounds including hydrocarbons, alcohols, aldehydes, ketones and amines [6] but also some inorganic compounds including ammonia and nitric oxide [7]. No one precursor ion species can be used to detect all the organic and inorganic compounds that are likely to be present in such a complex mixture as breath, simply because they do not react with all molecular species at a significant rate. So, for example, whilst H_3O^+ ions react with a very large number of organic species [8–10] (by the process of proton transfer [11]), they do not react with some hydrocarbons and with some inorganic molecules including NO and NO_2 for which species O_2^+ is an appropriate precursor ion (with which they react by the process of charge transfer [12]). We have also found that NO^+ is also a very appropriate precursor ion, not least for distinguishing between the structural isomers of some organic compounds [13]. It is clear that to analyse complex mixtures a large database of the rate coefficients and product ions of the reactions of these chosen precursor ions

with a large number of organic and inorganic compounds is required and we have thus begun to establish this database. In our first exploratory studies [9,10,12] we looked at the reactions of only two or three molecules of a given type (i.e. alcohols, aldehydes, ketones, etc.) in order to obtain a sense of the reaction processes involved and their rates. In these initial studies certain reaction processes were seen to occur some what to our surprise; for example, the protonation of n-hexanal and 3-hexenal by H_3O^+ resulted not in the protonated parent molecule only but rather the major product ions are the hydrocarbon ions which result from the ejection of H_2O from the protonated molecule [9]. Also we observed in these preliminary studies that NO^+ reacts with ethanol by the little studied process of hydride ion transfer (producing the appropriate carboxy ion and an HNO molecule) [12]. Thus we have begun to carry out detailed surveys of the reactions of H_3O^+, NO^+ and O_2^+ with several classes of organic compounds using our conventional SIFT method [14]. Our first paper in this survey has involved the reactions of these ions with some 17 alcohols [13]. This study has revealed that H_2O elimination from alcohols protonated by H_3O^+ ions is a commonly occurring process and that hydride ion (H^-) transfer often occurs in the reactions of NO^+ with alcohols as does the process of hydroxide ion (OH^-) transfer which had barely been characterised prior to these studies. These findings could not have been predicted with confidence, yet an understanding of them is essential for our analysis procedure and they are of real interest to fundamental ion chemistry. It is clear that similar studies of other classes of organic compounds are also required. Who knows what new processes will be revealed? The present paper describes the results of our SIFT survey of the reactions of some aldehydes and ketones. Subsequent surveys will include the reactions of carboxylic acids and esters, amines and amides, aliphatic and aromatic hydrocarbons, organosulphur compounds and specific inorganic species of environmental and medical/biological occurrence.

2. Experimental

The measurement of the rate coefficients, k, and ion products of ion–molecule reactions at thermal energies using the SIFT technique is a well established procedure which has been discussed in numerous review and research papers (see [14]) and does not need to be discussed in detail here. It is sufficient to note that the reactant gas or vapour is introduced at a controlled, measured rate into the helium carrier gas of the SIFT into which, upstream, a mass selected swarm of reactant ions has been introduced and the loss rate of the reactant ions and the production rates of the product ions of the reaction are determined by the downstream mass spectrometer. From these observations together with other critical parameters, including the carrier gas flow velocity and the effective reaction time (length of the reaction zone), it is simple to determine the k for the reaction and the ion product branching ratios. For permanent reactant gases it is easy to measure and vary their flow rates using some form of flow metre/controller, but for 'sticky' organic vapours with which we are largely concerned in these surveys this can be a very difficult problem, pressure reduction methods of calibration being inaccurate because such vapours readily adsorb and stick to surfaces and the thermodynamic data required for flow meter calibrations (i.e. heat capacities) are mostly unavailable. So we have adopted the procedure in which we assume with justification [11] that the k for all exothermic proton transfer reactions proceed at the collisional rate, k_c, which can be calculated if the polarisability and the dipole moment of the reactant molecule are known [15]. Thus for all the exothermic H_3O^+ proton transfer reactions with which we are concerned in these surveys the measured k is taken to be equal to the respective k_c. Numerous experimental studies over decades have shown that only for exothermic proton transfer reactions is k always equal to k_c but that this is not necessarily so for exothermic reactions that proceed via different processes such as charge transfer and hydride ion transfer as is the case for many of the O_2^+ and NO^+ reactions with which we are concerned in these studies. Since we cannot measure the flow rates of most of the neat organic reactant vapours, we simple make a very dilute mixture of the vapour at an unknown partial pressure in 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
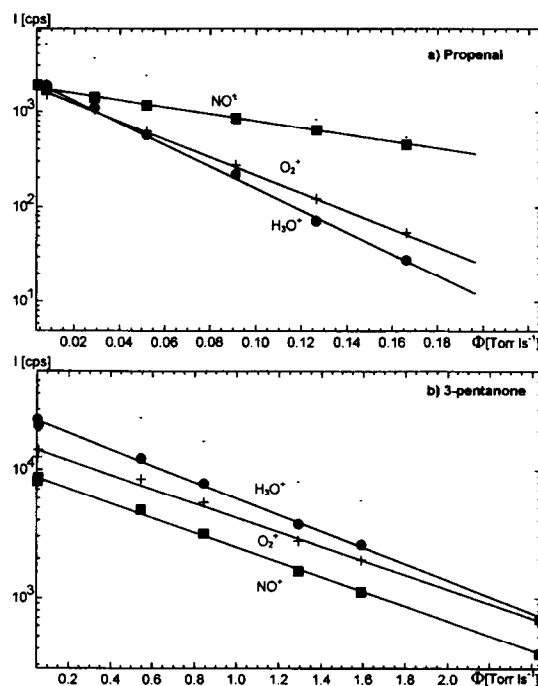

Fig. 1. Semi-logarithmic decay plots of the count rates, I (in counts per second, cps), of the simultaneously injected H_3O^+, NO^+ and O_2^+ primary ions as functions of the flow rate, Φ (in torr.litres per second), of air containing the vapour of (a) propenal and (b) 3-pentanone. Because these three primary ions do not react at a significant rate with the major components of air at the flow rates used, their decay rates are due only to their reactions with the organic molecules. Therefore, the slopes of these plots provide the relative rate coefficients of the reactions of the three ions with the propenal and 3-pentanone. Assuming that the H_3O^+ reactions proceed at the collisional rate (i.e. $k = k_c$) then the k for the NO^+ and O_2^+ reactions can be derived and these values are given in Table 1. Note that the reaction of NO^+ with propenal is clearly slower then the corresponding H_3O^+ and O_2^+ reactions. See Tables 2 and 3 for the products of these aldehyde and ketone reactions.

determine the absolute k for the reactions, but by injecting H_3O^+, NO^+ and O_2^+ ions simultaneously upstream, we can measure the relative decay rates of these three ion species as a function of the flow rate of the vapour/air mixture. Sample decay plots are shown in Fig. 1, which show the excellent quality of the data obtained using this procedure. Since for the H_3O^+ reactions $k = k_c$, then the k for the NO^+ and O_2^+ reactions can be obtained. Further discussion of this procedure is given in our first paper in this series of papers which is concerned with alcohol reactions [13] together with more sample data. The product ion distributions for the reactions are also determined from these measurements by injecting the H_3O^+, NO^+ and O_2^+ separately in the usual manner [14]. For the present study we selected 11 aldehydes and nine ketones as representative of these classes of organic compounds, choosing to include a few food flavour compounds which are of a specific interest in flavour research [16]. In all, this study involves some 60 reactions, many of which result in several different product ions. All the measurements were carried out in helium carrier gas at a pressure of approximately 0.5 torr at a temperature of 300 K.

3. Discussion of results

We will discuss the detailed results of this study in two major subsections, the first dealing with the aldehydes and in the second with the ketones and within each of these subsections we will discuss separately the H_3O^+, NO^+ and O_2^+ reactions. But first we make some general observation about the complete data set.

3.1. General comments

On the basis that all the H_3O^+ reactions proceed at the collisional rate, i.e. $k = k_c$, it is seen from the measurements of the comparative rate coefficients as outlined in the preceding section that all of the bimolecular reactions of NO^+ and O_2^+ with both the aldehydes and ketones, M, also proceed at or near the collisional rates (see Table 1). Most of the reactions of the NO^+ ions with the ketones proceed via termolecular associ-

ation producing ions of the kind $NO^+.M$, all are very efficient association reactions for which the effective bimolecular rate coefficient is close or equal to the collisional rate coefficient k_c, the one exception being the reactions of NO^+ with acetone.

Distinctly different processes occur in the reactions of the three ion species as can be seen by inspection of Tables 2 and 3. The H_3O^+ reactions proceed via proton transfer which for the smaller aldehydes and all the ketones included in this study produce only the protonated molecules $MH^+(+H_2O)$. However, for the larger aldehydes another reaction process occurs in which varying fractions of the protonated parent molecules dissociate with the ejection of an H_2O molecule leaving hydrocarbon ions of the type $(M-H_2O)^+$, a process which commonly occurs in the reactions of alcohols with H_3O^+ [13]. Clearly, in this process two water molecules are released which may be weakly bound together as the dimer $(H_2O)_2$, although we have no way of knowing whether or not this occurs. The reactions of NO^+ with the saturated aldehydes proceed mostly via hydride ion (H^-) transfer producing $(M-H)^+$ ions $(+HNO)$ and in the unsaturated aldehyde reactions either partial incorporation of the NO into the product ion occurs (the propenal reaction) or smaller fragment ions are formed (the trans-2-hexenal and cis-3-hexenal reactions). For the reactions of NO^+ with the ketones, ion/molecule association is the most common process as is mentioned above, with charge transfer occurring in the reactions of some of the larger ketones. The O_2^+ reactions with both the aldehydes and ketones appear mostly to proceed by charge transfer which is sufficiently exothermic to produce fragmentation of the excited $(M^+)^*$ ions thus resulting in two or more product ions. The detailed ion product distributions are given in Tables 2 and 3. In the subsequent sections of this paper we comment on the observed products of these many reactions and on what they say about the reaction processes occurring, noting that although the available thermochemical data on the product ions are limited, it is sometimes possible to identify the structure of the product ions from energetic considerations. In Sec. 4 of this paper

Table 1

Rate coefficients for the reactions of H_3O^+, NO^+ and O_2^+ with the aldehydes and ketones indicated

Molecule	m (u)	α (10^{-24} cm^3)	μ (D)	k_c (H_3O^+) [10^{-9} cm^3 s^{-1}]	k_c, k (NO^+) [0^{-9} cm^3 s^{-1}]	k_c, k (O_2^+) [10^{-9} cm^3 s^{-1}]
Formaldehyde	30	28	2.33	[3.4]	[3.0] < 0.1	[2.9] 2.2
Acetaldehyde	44	4.6	2.69	[3.7]	[3.2] 0.6	[3.1] 2.3
1-Propanal	58	6.5	2.52	[3.6]	[3.0] 2.5	[3.0] 3.1
1-Butanal	72	8.2	2.72	[3.8]	[3.2] 3.5	[3.1] 3.5
1-Pentanal	86	*10 ± 1*	*2.5 ± 0.3*	[3.6]	[3.0] 3.2	[2.9] 3.0
1-Hexanal	100	*12 ± 2*	*2.5 ± 0.3*	[3.7]	[3.1] 2.5	[3.0] 2.0
Propenal	56	6.4	3.1	[4.2]	[3.5] 1.4	[3.5] 3.4
trans-2-Hexenal	98	*12 ± 2*	*3.5 ± 0.5*	[4.6]	[3.8] 3.8	[3.7] 3.7
cis-3-Hexenal	98	*12 ± 2*	*3 ± 1*	[4.2]	[3.5] 3.1	[3.4] 2.8
Benzaldehyde	106	*13 ± 2*	*2.5 ± 1*	[3.7]	[3.1] 2.8	[3.0] 2.4
1,5-Pentanedial	136	*15 ± 2*	*1 ± 1*	[2.6]	[2.1] 2.1	[2.1] 2.1
Acetone	58	6.4	2.88	[3.9]	[3.3] 1.2	[3.3] 2.7
2-Butanone	72	8.1	*2.8 ± 1*	[3.9]	[3.2] 2.8	[3.2] 3.3
2-Pentanone	86	9.9	*2.8 ± 1*	[3.9]	[3.2] 3.1	[3.2] 3.0
3-Pentanone	86	9.9	*2.8 ± 1*	[3.9]	[3.3] 3.4	[3.2] 3.4
2-Hexanone	100	*12 ± 2*	*2.8 ± 1*	[4.0]	[3.3] 3.6	[3.2] 3.4
3-Hexanone	100	*12 ± 2*	*2.8 ± 1*	[4.0]	[3.3] 3.5	[3.2] 3.5
1-Phenylethanone	120	15.0	*2.8 ± 1*	[4.3]	[3.5] 3.6	[3.4] 3.4
Menthone	154	*17 ± 2*	*2 ± 1*	[3.4]	[2.8] 2.8	[2.7] 2.7
2,3-butanedione	86	8.2	0	[1.7]	[1.4] 1.3	[1.4] 1.4

Also given are their molecular weights, m, in atomic units u, their polarisabilities, α, in units of 10^{-24} cm^3 and their permanent dipole moments, μ, in Debye, D. The values of α and μ are known for some of the compounds included in this study and they are shown in regular type (taken from [18]). For the remaining compounds we have estimated their μ assuming that it does not change significantly with the number of carbon atoms in aldehyde and ketone molecules (note that in the absence of any published information, we have assumed that μ for 2,3-butanedione is zero), and their α by adopting the average values of the known polarisabilities of other organic molecules possessing the same number of carbon atoms. These are given in italics. Then the collisional rate coefficients, k_c, for all reactions have been calculated using the parameterised trajectory formulation of Su and Chesnavich [15] and these are given in the square brackets. Estimated errors in thus calculated rate coefficients are less than ± 20%. On the assumption that all the H_3O^+ reactions 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} cm^3 s^{-1}.

we make some comments on the value of these data to chemical ionisation mass spectrometry and to our trace gas analytical work, see also [1,2,3].

3.2. Aldehyde reactions

We have included in this study some saturated and some unsaturated monoaldehydes, including the isomers 2-hexenal and 3-hexenal, an aromatic monoaldehyde and one dialdehyde, chosen not only to explore the reactive behaviour of the various types of aldehyde, but because of the specific interest there is in some of them as food flavours [16].

3.2.1. H_3O^+ reactions

The saturated aldehydes formaldehyde (derived from paraldehyde), acetaldehyde and propanal each react with H_3O^+ producing only the protonated parent molecule, MH$^+$, e.g.:

$$H_3O^+ + CH_3CHO \rightarrow CH_3CHOH^+ + H_2O \quad (1)$$
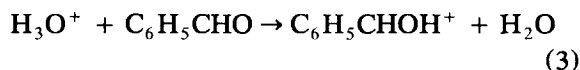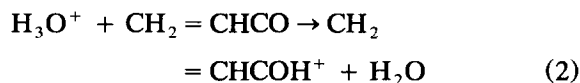
as dictated by the energetics of these reactions, which in these cases do not allow for fragmentation of the nascent MH$^+$ ions to release a second water molecule. Similarly, only the protonated parent molecules is produced in the propenal (acrolein) and benzaldehyde reactions thus:

Table 2
Products of the reactions of the aldehydes indicated with H_3O^+, NO^+ and O_2^+

Aldehydes	H_3O^+	NO^+	O_2^+
HCHO formaldehyde	CH_3O^+ (100) + H_2O	— No reaction	CH_2O^+ (60) HCO^+ (40)
CH_3CHO acetaldehyde	$C_2H_5O^+$ (100) + H_2O	$C_3H_5O^+$ (100) + HNO	$C_2H_4O^+$ (55) $C_2H_3O^+$ (45)
C_2H_5CHO 1-propanal	$C_3H_7O^+$ (100) + H_2O	$C_3H_5O^+$ (100) + HNO	$C_3H_6O^+$ (50) $C_3H_5O^+$ (50)
C_3H_7CHO 1-butanal	$C_4H_9O^+$ (95) + H_2O $C_4H_7^+$ (5) + $2H_2O$	$C_4H_7O^+$ (100) + HNO	$C_2H_4O^+$ (65) $C_4H_8O^+$ (35)
C_4H_9CHO 1-pentanal	$C_5H_{11}O^+$ (75) + H_2O $C_5H_9^+$ (25) + $2H_2O$	$C_5H_9O^+$ (100) + HNO	$C_2H_4O^+$ (60) $C_3H_6O^+$ (30) $C_4H_5O^+$ (10)
$C_5H_{11}CHO$ 1-hexanal	$C_6H_{13}O^+$ (50) + H_2O $C_6H_{11}^+$ (50) + $2H_2O$	$C_6H_{11}O^+$ (100) + HNO	C_4H_8 + (50) $C_2H_4O^+$ (30) $C_3H_5O^+$ (5) $C_4H_8O^+$ (5) $C_6H_9O^+$ (5)
CH_2 =CHCHO propenal	$C_3H_5O^+$ (100) + H_2O	$C_3H_3O^+$ (80) + HNO $NO^+.C_3H_4O$ (20)	$C_3H_3O^+$ (45) $C_2H_4^+$ (40) $C_3H_4O^+$ (15)
C_3H_7CH=CHCHO *trans* 2-hexenal	$C_6H_{11}O^+$ (100) + H_2O	$C_6H_9O^+$ (85) + HNO $C_4H_7O^+$ (15) + CH_3NCO	$C_2H_3O^+$ or $C_3H_7^+$ (30) $C_5H_9^+$ or $C_4H_5O^+$ (30) $C_4H_6O^+$ (20) $C_6H_{10}O^+$ (20)
C_2H_5CH=CHCH$_2$CHO *cis* 3-hexenal	$C_6H_9^+$ (65) + $2H_2O$ $C_6H_{11}O^+$ (35) + H_2O	$C_6H_9O^+$ (50) + HNO $C_5H_9^+$ (30) + $HCNO_2$ $C_4H_6O^+$ (20) + C_2H_4NO	$C_2H_3O^+$ (40) $C_5H_9^+$ (30) $C_4H_6O^+$ (15) $C_6H_{10}O^+$ (15)
C_6H_5CHO benzaldehyde	$C_7H_7O^+$ (100) + H_2O	$C_7H_5O^+$ (100) + HNO	$C_7H_6O^+$ (65) $C_7H_5O^+$ (35)
$OHC(CH_2)_3CHO$ 1,5-pentanedial (glutyraldehyde)	$C_5H_9O_2^+$ (50) + H_2O $C_5H_7O^+$ (30) + $2H_2O$ $C_2H_3O^+$ (20) + C_2H_5CHO	$C_5H_7O_2^+$ (100) + HNO	$C_2H_4O^+$ (65) $C_5H_6O^+$ (20) $C_4H_8O^+$ (15)$^+$

The molecular formulae of the ion products listed do not necessarily represent their structures; the percentage of each ion products is given in brackets. 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 a few cases the ionic products) are not well defined. Note the production of an additional H_2O molecule in some of the H_3O^+ reactions and the several fragment ions in some of the O_2^+ reactions. Note also that NO^+ ions associate with propenal molecules. It is interesting to note that the oxygen-containing (carboxy) product ions invariably associate with impurity H_2O molecules when H_2O is introduced into the helium carrier gas (see also [10]).

$$H_3O^+ + CH_2 = CHCO \rightarrow CH_2$$
$$= CHCOH^+ + H_2O \qquad (2)$$
$$H_3O^+ + C_6H_5CHO \rightarrow C_6H_5CHOH^+ + H_2O \qquad (3)$$

However, for the longer chain saturated aldehydes butanal, pentanal and hexanal we see the appearance of the H_2O elimination channel (which is common in the analogous alcohol reactions [13,17]). In the butanal reaction this process

represents just a very minor channel (see Table 2), but with increasing chain length it becomes an increasingly important process, which for the 1-hexanal reaction is comparable with the production of the parallel protonated parent molecule:
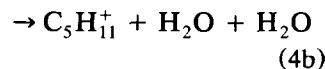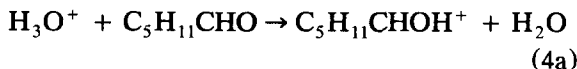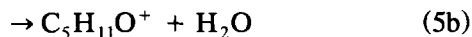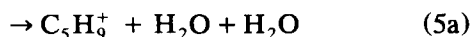
$$H_3O^+ + C_5H_{11}CHO \rightarrow C_5H_{11}CHOH^+ + H_2O \qquad (4a)$$
$$\rightarrow C_5H_{11}^+ + H_2O + H_2O \qquad (4b)$$

Table 3
Products of the reactions of the ketones indicated with H_3O^+, NO^+ and O_2^+

Ketones	H_3O^+	NO^+	O_2^+
CH_3COCH_3 acetone	$C_3H_7O^+$ (100) + H_2O	$NO^+.C_3H_6O$ (100)	$C_3H_6O^+$ (60) $C_2H_3O^+$ (40)
$CH_3COC_2H_5$ 2-butanone	$C_4H_9O^+$ (100) + H_2O	$NO^+.C_4H_8O$ (100)	$C_2H_3O^+$ (40) $C_4H_8O^+$ (35) $C_3H_5O^+$ (25)
$CH_3COC_3H_7$ 2-pentanone	$C_5H_{11}O^+$ (100) + H_2O	$NO^+.C_5H_{10}O$ (100)	$C_2H_3O^+$ (50) $C_3H_6O^+$ (20) $C_4H_7O^+$ (15) $C_5H_{10}O^+$ (15)
$C_2H_5COC_2H_5$ 3-pentanone	$C_5H_{11}O^+$ (100) + H_2O	$NO^+.C_5H_{10}O$ (100)	$C_3H_5O^+$ (70) $C_3H_4O^+$ (15) $C_5H_{10}O^+$ (15)
$CH_3COC_4H_9$ 2-hexanone	$C_6H_{13}O^+$ (100) + H_2O	$NO^+.C_6H_{12}O$ (100)	$C_2H_3O^+$ (40) $C_3H_6O^+$ (50) $C_5H_9O^+$ (5) $C_6H_{12}O^+$ (5)
$C_2H_5COC_3H_7$ 3-hexanone	$C_6H_{13}O^+$ (100) + H_2O	$NO^+.C_6H_{12}O$ (85) $C_6H_{12}O^+$ (15) + NO	$C_4H_7O^+$ (65) $C_6H_{12}O^+$ (25) C_3H_5 (5) $C_2H_3O^+$ (5)
$C_6H_5COCH_3$ 1-phenylethanone	$C_8H_9O^+$ (100) + H_2O	$NO^+C_8H_8O$ (95) $C_8H_8O^+$ (5) + NO	$C_8H_8O^+$ (25) $C_7H_5O^+$ (75)
$C_{10}H_{18}O$ menthone	$C_{10}H_{19}O^+$ (100) + H_2O	$C_{10}H_{18}O^+$ (100) + NO	$C_2H_3O^+$ (25) $C_3H_6O^+$ (35) $C_8H_{16}^+$ or $C_7H_{12}O^+$ (20) $C_{10}H_{10}^+$ or $C_9H_6O^+$ (15) $C_{10}H_{18}O^+$ (5)
$CH_3COCOCH_3$ 2,3-butanedione	$C_4H_7O_2^+$ (100) + H_2O	$C_4H_6O_2^+$ (65) + NO $C_2H_3O^+$ (35) + C_2H_3ONO	$C_4H_6O_2^+$ (20) $C_2H_3O^+$ (80)

The molecular formulae of the ion products listed do not necessarily represent their structures; the percentage of each ion products is given in brackets. 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 the ionic products for the complex molecule menthone) are not well defined.
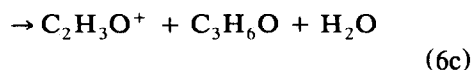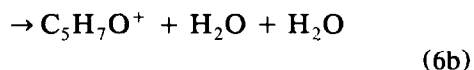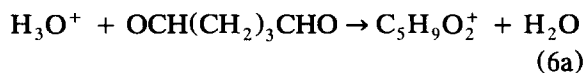
However, H_2O elimination occurs in only one of the two hexenal reactions (unsaturated *cis*-3-hexenal) and then it is the major channel (see Table 2 and [9]):

$$H_3O^+ + CH_3CH_2CH_2CH{=}CHCHO$$

$$\rightarrow C_5H_9^+ + H_2O + H_2O \qquad (5a)$$

$$\rightarrow C_5H_{11}O^+ + H_2O \qquad (5b)$$

whereas in the 2-*trans*-hexenal reaction only the parent protonated molecule is produced. We have attempted to explain this interesting result in a previous paper [9]. Thus there is a potential here for distinguishing between these two structural isomers, which are both known food flavours.

In the 1,5-pentanedial (glutaraldehyde, a commonly used sterilising agent) reaction we see examples of three processes occurring in parallel:

$$H_3O^+ + OCH(CH_2)_3CHO \rightarrow C_5H_9O_2^+ + H_2O \qquad (6a)$$

$$\rightarrow C_5H_7O^+ + H_2O + H_2O \qquad (6b)$$

$$\rightarrow C_2H_3O^+ + C_3H_6O + H_2O \qquad (6c)$$

In channel (6a) the protonated parent molecule is produced as the major product, in (6b) H_2O elimination occurs and (6c) is a classic case of the dissociation of the excited nascent protonated molecule at a C–C bond, in this case a dialdehyde reactant resulting in a carboxy ion and a neutral carboxy molecule (a propanal molecule, C_2H_5CHO). This dissociation process of the aldehyde (and ketone) chains commonly occurs in the more energetic reactions of these species with O_2^+ as can be seen by a glance at Tables 2 and 3.

3.2.2. NO⁺ reactions

The interaction of NO^+ with formaldehyde is unusual amongst reactions of this ion with organic molecules in that no reaction occurs. The reason for this is because there are no exothermic channels; charge transfer cannot occur because of the relatively large ionisation energy of formaldehyde (10.88 eV [18]) and hydride ion transfer which occurs in all of other 10 aldehyde reactions is also endothermic (using the thermochemical data given in [19]). The process of hydride ion (H^-) transfer has not been previously recognised to occur widely in ion–molecule reactions, but we have seen that it does so in the reactions of NO^+ with some alcohols [13] and now in the reactions of several aldehydes as can be seen in Table 2. That this process is so facile in these reactions is due to the special circumstance of the low recombination energy of NO^+ (so charge transfer is often endotherinic) and the stability of the HNO radical [19]. Note in Table 3 that this process does not occur at all in the ketone reactions.
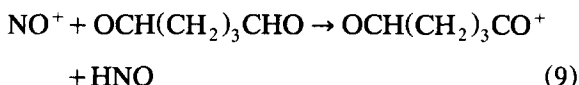
In all the reactions of the saturated monoaldehydes included in this study, ranging in complexity from acetaldehyde to hexanal and benzaldehyde, hydride ion transfer is the single process that occurs resulting in the production of the appropriate hydrocarbon ion and HNO, e.g.:

$$NO^+ + CH_3CHO \rightarrow CH_3CO^+ + HNO \qquad (7)$$

$$NO^+ + C_6H_5CHO \rightarrow C_6H_5CO^+ + HNO \qquad (8)$$
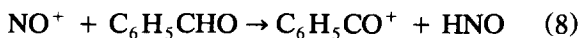
The energetics of reaction (7) require that the H^- ion is extracted from the CHO grouping (exothermic by 0.7 eV) rather than from the hy-drocarbon chain (endothermic by 0.8 eV). Similarly the energetics for the other saturated aldehydes indicate that H^- is extracted from CHO and not from the hydrocarbon chain.

The 1,5-pentanedial reaction also proceeds only via H^- abstraction with an obvious opportunity for abstraction from either end of the reactant molecule:

$$NO^+ + OCH(CH_2)_3CHO \rightarrow OCH(CH_2)_3CO^+$$

$$+ HNO \qquad (9)$$

In the reactions of the unsaturated aldehydes, H^- transfer is still the dominant process, but in these reactions other products are also seen, e.g. in the 2-hexenal reaction:

$$NO^+ + C_3H_7CH{=}CHCHO$$

$$\rightarrow C_6H_9O^+ + HNO \qquad (10a)$$

$$\rightarrow C_4H_7O^+ + C_2H_3NO \qquad (10b)$$
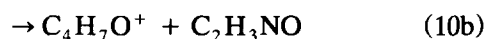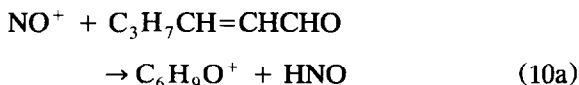
Although thermochemical data are not available to allow the energetics of these reactions to be traced with certainty, it seems very likely on simple energetic grounds that the neutral species C_2H_3NO is formed in reaction (10b) in which the NO is incorporated into the fragment of the hexenal molecule, because formation of C_2H_2 and HNO is endothermic.

Similar complex chemistry occurs in the 3-hexenal reaction as can be seen in the products of this reaction (Table 2), but again this chemistry cannot be traced with any certainty because of the lack of thermochemical data.

The reaction of NO^+ with propenal is unique amongst this series in that parallel hydride ion transfer and ion–molecule association occurs thus:

$$NO^+ + CH_2{=}CHCHO \rightarrow C_3H_4O^+ + HNO$$

$$(11a)$$

$$\rightarrow NO^+.C_3H_4O \qquad (11b)$$
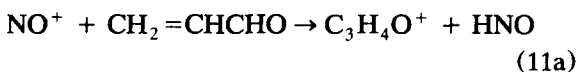
The association reaction (11b) is promoted by collisions of the excited association ion

$(NO^+.C_3H_4O^+)^*$ with carrier gas atoms which would otherwise dissociate back to the reactants [20]. Parallel reaction channels in which one involves ion–molecule association are not uncommon in ion chemistry (see, for example, the reactions of some hydrocarbon ions with some organic molecules [8,21]). This process appears to be more efficient when the reactant molecule is unsaturated and especially when no other exothermic reaction channels are available as is the case for the reactions of NO^+ with many of the ketones (see Sec. 3.3).

3.2.3. O_2^+ reactions

In contrast with the NO^+ reactions and as a consequence of the higher recombination energy of O_2^+, we characterised all these O_2^+ reactions as charge transfer which result in the parent reactant ions and at least one other ion fragment in each case as can be seen in Table 2. However, we cannot exclude the possibility that hydride ion transfer sometimes occurs producing the $(M–H)^+$ ions and an HO_2 radical (see reactions (12b), (13b) and (14b) below). The more complex the reactant molecule (greater atomicity) the more ion products, a feature often mirrored in electron ionisation. There are other reactions where the product neutrals cannot be positively identified (see the comments associated with reaction (15) below). Because of these uncertainties we do not include the neutral products of the O_2^+ reactions in Table 2 (and also Table 3).

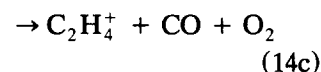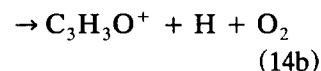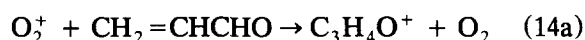The reactions of the smaller molecules in the series are exemplified by the formaldehyde reaction:

$$O_2^+ + HCHO \rightarrow CH_2O^+ + O_2 \qquad (12a)$$
$$\rightarrow HCO^+ + H + O_2 \qquad (12b)$$
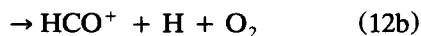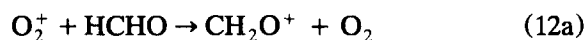
The parent ion (M^+) is formed in channel (12a) and the fragment ion $(M–H^+)$ formed in (12b) is the lower energy HCO^+ isomer (see Table 2) and not the higher energy isomer COH^+ as required by the available energy in the reaction [19]. The acetaldehyde and propanal reactions proceed by the same processes resulting in two approximately equally-important product ions in each case (see
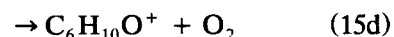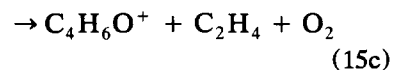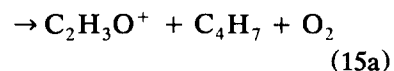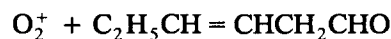
Table 2). The parent ion and the ion resulting from H atom loss are also the products of the benzaldehyde reaction:

$$O_2^+ + C_6H_5CHO \rightarrow C_7H_6O^+ + O_2 \qquad (13a)$$
$$\rightarrow C_7H_5O^+ + H + O_2 \qquad (13b)$$
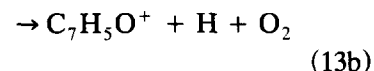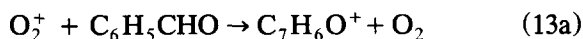
In the propenal reaction there are three product ions, the M^+ and $(M–H)^+$ ions together with the hydrocarbon ion $C_2H_4^+$ formed following the loss of a CO molecule:

$$O_2^+ + CH_2=CHCHO \rightarrow C_3H_4O^+ + O_2 \qquad (14a)$$
$$\rightarrow C_3H_3O^+ + H + O_2 \qquad (14b)$$
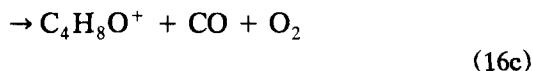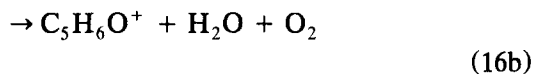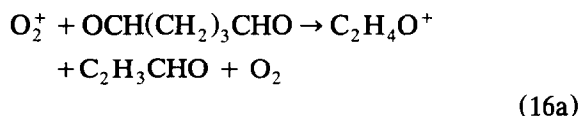$$\rightarrow C_2H_4^+ + CO + O_2 \qquad (14c)$$

As referred to above, the neutral products of reaction (14b) could also be the HO_2 radical. All the other reactions in this series result in the production of polyatomic fragment ions, variously carboxy and hydrocarbon ions and appropriate neutral molecules, the dissociation occurring at more than one position along the carbon chains of the excited $(M^+)^*$ ions formed in the charge transfer process. Typical of this is the 3-hexenal reaction:

$$O_2^+ + C_2H_5CH=CHCH_2CHO$$
$$\rightarrow C_2H_3O^+ + C_4H_7 + O_2 \qquad (15a)$$
$$\rightarrow C_5H_9^+ + HCO + O_2 \qquad (15b)$$
$$\rightarrow C_4H_6O^+ + C_2H_4 + O_2 \qquad (15c)$$
$$\rightarrow C_6H_{10}O^+ + O_2 \qquad (15d)$$

The neutral products of reaction (15b) could be $OH + CO_2$ or $CO + HO_2$. Similarly, there are

three product ions in the 1,5-petanedial. reaction:

$$O_2^+ + OCH(CH_2)_3CHO \rightarrow C_2H_4O^+$$
$$+ C_2H_3CHO + O_2$$

$$(16a)$$

$$\rightarrow C_5H_6O^+ + H_2O + O_2$$

$$(16b)$$

$$\rightarrow C_4H_8O^+ + CO + O_2$$

$$(16c)$$

Clearly, considerable rearrangement is required in the excited parent ion formed following charge transfer (or in the transient ion-molecule complex $O_2^+.M$) to produce the observed ions.

3.3. Ketone reactions

We have included in this study several saturated monoketones ranging from acetone to 2-hexanone and 3-hexanone, one with an aromatic core, 1-phenylethanone (acetophenone) and one with a non-aromatic cyclic core, menthone and a dione, 2,3-butanedione (diacetyl). The H_3O^+ and NO^+ reactions are notable for their simplicity as we will show, which greatly enhances their value for chemical ionisation.

3.3.1. H_3O^+ reactions

Minimal commentary is required on these reactions because all nine ketones included in this study react with H_3O^+ ions by exothermic non-dissociative proton transfer (as before, assumed to proceed at the collisional rate) to produce only a single product ion, i.e. the protonated parent molecule, e.g.:

$$H_3O^+ + CH_3COCH_3$$
$$\rightarrow CH_3COH^+CH_3 + H_2O$$

$$(17)$$
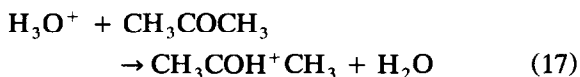
As is indicated, the protonation is surely at the oxygen in this and all these ketone reactions including the acetophenone reaction:

$$H_3O^+ + C_6H_5COCH_3 \rightarrow C_6H_5COH^+CH_3$$

$$(18)$$
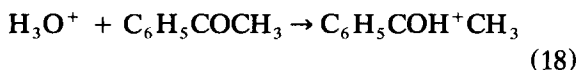
The proton affinities, PA, of all these ketones must, of course, exceed that of water (PA = 166.5 kcal/mol), but they do so by typically 30–40 kcal/mol. This represents the amount of energy available to rupture bonds in these molecules which simply is inadequate; hence the simplicity of these reactions, which as far as we can see from available thermochemical data will apply to all ketones including the diones like the 2,3-butanedione included in this study. This feature of H_3O^+ reactions with ketones greatly facilitates their detection using our SIFT analytical method.

3.3.2. NO^+ reactions

A process involved in most of these ketone reactions which is hardly observed in any of the other reactions involved in our surveys of the reactions of H_3O^+, NO^+ and O_2^+ with alcohols, aldehydes and ketones is ion–molecule collisional association resulting in ions of the type $NO^+.M$. e.g.:

$$NO^+ + CH_3COCH_3 \rightarrow NO^+.CH_3COCH_3 \quad (19)$$
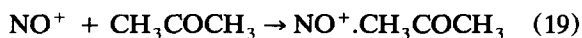
These reactions proceed via the formation of a long-lived complex ion which lives long enough to collide with a carrier gas atom (helium in these experiments) which removes a fraction of the excitation energy thus preventing dissociation back to the reactants [20]. As can be seen by inspection of Table 2a, the effective bimolecular rate coefficients for these association reactions are close to their respective k_c, except that for the acetone reaction (19) which is approximately 0.5 k_c. Thus even at the helium pressure at which these experiments were conducted (0.5 torr), these association reactions are proceeding under the so-called high pressure limiting conditions [20]. This is the only process occurring also in the 2-butanone, 2- and 3-pentanone and 2-hexanone reactions, but in the 3-hexanone and acetophenone reactions we see that a small fraction of the collisions with NO^+ result in charge transfer, e.g.:

$$NO^+ + C_2H_5COC_3H_7 \rightarrow NO^+.C_6H_{12}O \quad (20a)$$
$$\rightarrow C_6H_{12}O^+ + NO$$

$$(20b)$$
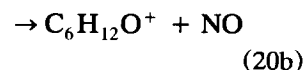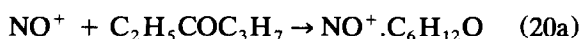
This indicates that the ionisation energies of these ketones are somewhat smaller than that of NO molecules (9.26 eV [19]) and this is consistent with the available data [19] which shows that the ionisation energies of the smaller ketones are greater than that of NO (hence charge transfer is endothermic and is not observed) but that they gradually reduce with increasing size of the ketone molecules. Charge transfer is the only process that occurs in the menthone reaction:

$$NO^+ + C_{10}H_{18}O \rightarrow C_{10}H_{18}O^+ + NO \qquad (21)$$
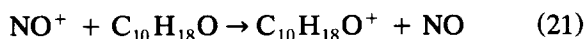
which must indicate that the ionisation energy of menthone is appreciably less than that of NO.

A somewhat surprising result is the observation of two products in the 2,3-butanedione reaction:

$$NO^+ + CH_3COCOCH_3 \rightarrow C_4H_6O_2^+ + NO \qquad (22a)$$

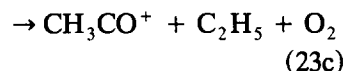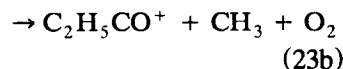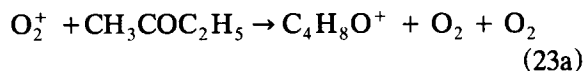$$\rightarrow C_2H_3O^+ + C_2H_3ONO \qquad (22b)$$
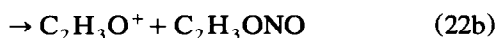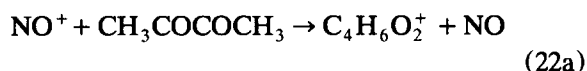
The major channel (22a) is non-dissociative charge transfer, whereas reaction (22b) involves the cleaving of the weak central C–C bond in the molecule and the formation of the molecule C_2H_3ONO as demanded by the energetics of the reaction (the formation of separated C_2H_3O and NO is endothermic by 0.6 eV).
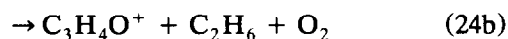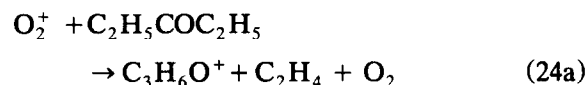
3.3.3. O_2^+ reactions

The low ionisation energies of these ketones ensure that in these O_2^+ reactions charge transfer with dissociation is inevitable. Thus all these reactions are characterised as charge transfer reactions in which the parent ionised molecules are evident in each case but only as a minor fraction of the product distribution for the larger ketones. Most of these ketones can be represented as R_1COR_2, where R_1 and R_2 are variously the alkyl groups CH_3, C_2H_5, C_3H_7 and C_4H_9, and the phenyl group C_6H_5 in the single case of acetophenone. Thus we commonly see the splitting off of one of the alkyl radicals in these energetic charge transfer reactions with the formation of the RCO^+ carboxyl ion, and also the elimination of a hydrocarbon molecule in some

cases which clearly involves rearrangement within the excited nascent parent ketone ion prior to the dissociation.

In both the acetone and 2-butanone reactions we see both parent ion production and the elimination of the alkyl radicals, e.g.:

$$O_2^+ + CH_3COC_2H_5 \rightarrow C_4H_8O^+ + O_2 + O_2 \qquad (23a)$$

$$\rightarrow C_2H_5CO^+ + CH_3 + O_2 \qquad (23b)$$

$$\rightarrow CH_3CO^+ + C_2H_5 + O_2 \qquad (23c)$$

With increasing complexity of the ketone these O_2^+ reactions become more complex with additional processes occurring including hydrocarbon elimination Indeed, C_2H_4 elimination is the major process which occurs in the 3-pentanone reaction:

$$O_2^+ + C_2H_5COC_2H_5$$
$$\rightarrow C_3H_6O^+ + C_2H_4 + O_2 \qquad (24a)$$
$$\rightarrow C_3H_4O^+ + C_2H_6 + O_2 \qquad (24b)$$
$$\rightarrow C_5H_{10}O^+ + O_2 \qquad (24c)$$

Note (in Table 3) the very different products for the reactions of the 2-pentanone and 3-pentanone isomers which might be used as a diagnostic under favourable conditions.

The hexanone reactions are even more complicated with four product channels being observed as indicated in Table 3 and five products are evident in the menthone reaction, but again the aromatic ring remains intact in the acetophenone reaction in which charge transfer is the dominant process, apparently together with CH_3 elimination:

$$O_2^+ + C_6H_5COCH_3 \rightarrow C_8H_8O^+ + O_2 \qquad (25)$$

$$\rightarrow C_7H_5O^+ + (CH_3 + O_2) \qquad (26)$$
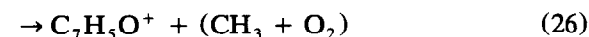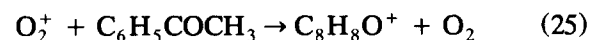
However, we cannot exclude the possibility that the CH_3O_2 radical is formed in the reaction.

In the 2,3-butanedione reaction the major product channel is the result of the dissociation of the parent ion at the central carbon–carbon bond, although the parent ion is still observed as a minor product:

$$O_2^+ + CH_3COCOCH_3$$

$$\rightarrow CH_3CO^+ + CH_3CO + O_2 \qquad (27a)$$

$$\rightarrow C_4H_6O_2^+ + O_2 \qquad (27b)$$
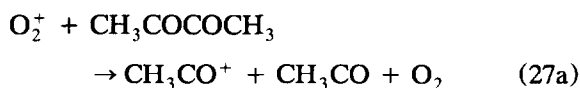
Compare this result with that for the corresponding NO^+ reaction (22) (see also Table 3) which is less exothermic and as a consequence the parent ion is the major product and fragmentation is less likely.

4. Concluding remarks

In accordance with expectations, the reactions of O_2^+ with both the aldehydes and ketones proceed via charge transfer with considerable fragmentation for the more polyatomic reactant molecules and little more need be said about these reactions. Of greater interest in this limited study is the focus that the results bring to the interesting processes of H_2O elimination following the protonation of some aldehydes by H_3O^+, a process which is also common in the reactions of H_3O^+ with some alcohols [13], but which does not occur in the ketone reactions, this being of some interest in chemical ionisation mass spectrometry [22,23]. Also of interest is the focus the results bring to the processes of hydride ion transfer which occurs in the NO^+ reactions with the aldehydes but not with the ketones which react almost exclusively via association as was also observed many years ago [24,25]. Again the analytical value of these observations is clear.

The value of chemical ionisation in mass spectroscopic analysis and diagnosis has long been appreciated [23]. One objective of our studies is to expand the data base required for the analysis of complex mixtures such as human breath [6] using our SIFT method [2]. To this end we are studying the reactions of these chosen precursor ions H_3O^+, NO^+ and O_2^+ with carboxylic acids, esters, ethers, amines, hydrocarbons, organosul-

phur compounds and selected inorganic species such as NO, NO_2, NH_3 and H_2S, all of which are variously important in medical and environmental analysis.

Acknowledgements

References

[1] D. Smith, P. Spanel. Int. Rev. Phys. Chem. 15 (1996) 231.
[2] P. Spanel, D. Smith. Med. Biol. Eng. Comput. 34 (1996) 409.
[3] D. Smith, P. Spanel. Rapid Commun. Mass Spectrom. 10 (1996) 1183.
[4] P. Spanel, P. Rolfe, B. Rajan, D. Smith. Ann. Occup. Hyg. 40 (1996) 615.
[5] P. Spanel, J. Cocker, B. Rajan, D. Smith. Ann. Occup. Hyg. (1996) 41 (1997) 373.
[6] A. Manolis. Clin. Chem. 29 (1983) 5.
[7] S.A. Kharitonov, D. Yates, P.J. Barnes. Eur. Respir. J 8 (1995) 295.
[8] Y. Ikezoe, S. Matsuoka, M. Takebe, A. Viggiano. Gas Phase Ion-Molecule Reaction Rate-Constants Through 1986, Maruzen, Tokyo, 1987.
[9] P. Spanel, M. Pavlik, D. Smith. Int. J. Mass Spectrom. Ion Processes 145 (1995) 177.
[10] P. Spanel, D. Smith. J. Phys. Chem. 99 (1995) 15551.
[11] D.K. Bohme. In: P. Ausloos (Ed.), Interactions Between Ions and Molecules, Plenum, New York, 1975, 489 p.
[12] P. Spanel, D. Smith. J. Chem. Phys. 104 (1996) 1893.
[13] P. Spanel, D. Smith. Int. J. Mass Spectrom. Ion Processes, (1997) In print. (Invited paper for the Chava Lifshitz Special Issue).
[14] D. Smith, N.G. Adams. Ads. At. Mol. Phys. 24 (1987) 1.
[15] T. Su, W.J. Chesnavich. J. Chem. Phys. 76 (1982) 5183.
[16] H. Maarse, D.G. Van Der Heij (Eds.), 'Developments in Food Science, Volume 35, Trends in Flavour Research', Elsevier, Amsterdam, 1994.
[17] C. Warneke, J. Kuczynski, A. Hansel, A. Jordan, W. Vogel, W. Lindinger. Int. J. Mass Spectrom. Ion. Processes 154 (1996) 61.
[18] D.R. Lide (Ed.). CRC Handbook of Chemistry and Physics, CRC, Boca Raton, 1991.
[19] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard. J. Phys. Chem. Ref Data 17 (suppl. 1) (1988) and subsequent software updates.

[20] A. Fontyn, M.A.A. Clyne (Eds.). Reactions of Small Transient Species: Kinetics and Energetics, Academic Press, New York, 1983.

[21] N.G. Adams, D. Smith. Chem. Phys. Lett. 54 (1978) 530.

[22] G.A. Eiceman. Crit. Rev. Anal. Chem. 22 (1991) 471.

[23] A.G. Harrison. Chemical Ionisation Mass Spectrometry (2nd Edn.), CRC Press, Boca Raton, Florida, 1992.

[24] D.F. Hunt. Adv. Mass Spectrom. 6 (1974) 517.

[25] D.F. Hunt, J.F. Ryan. J. Chem. Soc. Chem. Commun. 620 (1972).