SIFT studies of the reactions of H_3O^+, NO^+ and O_2^+ with a series of alcohols[1]

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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 some 17 alcohols ranging in complexity from methanol to octanol and menthol, and including some structural isomers. This study was carried out in order to extend the database (i.e. rate coefficients and product ions of appropriate ion/molecule reactions) required for the SIFT method of trace gas analysis which utilises the aforementioned ions for chemical ionisation. The H_3O^+ reactions proceed via exothermic proton transfer, which we assume to proceed at the collisional rate. Thus all of the 51 reactions (except two) occur at or close to the collisional rate. Only in a minority of these proton transfer reactions is the protonated parent molecule the single ion product; rather it is seen that the protonation of most of these alcohols by H_3O^+ is followed by the ejection of an H_2O molecule from the excited product ion thus leaving the appropriate hydrocarbon ion. The NO^+ reactions proceed largely via the processes of hydride ion transfer producing the appropriate carboxy ion (and HNO), and hydroxide ion transfer producing the appropriate hydrocarbon ion (and HNO_2). The O_2^+ reactions proceed via charge transfer, the large majority of the reactions resulting in more than one product ion, which are mostly hydrocarbon fragment ions but in a few cases carboxy ions are formed. The product ions for the reactions of the various structural isomers are sometimes different, and this offers a way of distinguishing between the isomeric forms of some alcohols. © 1997 Elsevier Science B.V.

Keywords: SIFT; ion–molecule reactions; proton transfer; hydride ion transfer; hydroxide ion transfer; charge transfer; trace gas analysis

1. Introduction

Chemical ionisation (i.e. "soft ionisation") using particular ionic species has been used for decades in association with mass spectrometry for the analysis of gases and vapours [1,2]. Thus, ionisation of specific molecules can be achieved using a variety of precursor (reagent) ions chosen to minimise the fragmentation of the molecules which greatly simplifies their identification (see [2] for a thorough discussion of chemical ionisation mass spectrometry). We are using chemical ionisation in conjunction with a selected ion flow tube (SIFT) to analyse complex gas mixtures such as environmental air and human breath. The proper choice of the precursor ions results in the ionisation of the trace gas molecules to the exclusion of the major component gases (N_2, O_2, CO_2, Ar). In this respect, the most valuable precursor ions are H_3O^+, NO^+

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[1] We are very pleased to dedicate this paper to Professor Chava Lifshitz in recognition of her many contributions to ion chemistry and on the occasion of her 60th birthday.

and O_2^+ [3–5]. H_3O^+ in reaction transfers a proton to a wide variety of other molecules at the gas kinetic (collisional) rate which can be readily calculated [6]. The only requirement for this proton transfer to occur efficiently is that the proton affinity (PA) of the acceptor molecule, M, exceeds the PA of H_2O, i.e. that the proton transfer reaction be exothermic [7]. For a simple proton transfer reaction the product ion is MH^+ and then accurate quantification of the trace gases can readily be achieved even in multicomponent mixtures such as human breath [8–11]. However, it is now recognised that simple, non-dissociative proton transfer is not the only process that occurs when H_3O^+ reacts with some organic molecules, but that the elimination of an H_2O molecule from the protonated ion MH^+ can occur, especially when M is a higher-order aldehyde [5,12] or an alcohol [13]. A good example of this process is the protonation of propanol by H_3O^+ for which the major product is $C_3H_7^+$, $C_3H_7OH_2^+$ being only a minor product, and it is interesting to note that the $C_3H_7^+/C_3H_7OH_2^+$ ratio differs for the two structural isomers of propanol (see [13] and Section 3). Obviously, it is essential to know the ion products of the reaction of each of the molecular species to be detected and quantified in a gas sample. Clearly it is therefore vital that the products of such "non-standard" proton transfer reactions should be known (from experiments) if these types of organic species are to be quantified in a gas sample using chemical ionisation by H_3O^+.

A further complication is that H_3O^+ does not transfer a proton to molecules which have proton affinities less than H_2O; these including some important atmospheric pollutants such as NO and NO_2, and some environmentally sensitive pollutants such as the chlorofluorocarbons. To detect and quantify these species in an air sample using chemical ionisation, it is necessary to resort to other precursor ions, stressing again that they must not react at a significant rate with the major atmospheric gases. Useful precursor ions are thus NO^+ [2,4,14,15] and O_2^+ [4,10,16] which react

variously with many molecules by the processes of charge transfer and hydride ion transfer [17]. Charge transfer sometimes produces not only the parent positive ion M^+ but also a fragment ion, the most common being $(M - 1)^+$, but greater fragmentation can occur [4,17]. NO^+ often reacts by hydride ion transfer with higher-order hydrocarbons producing $(M - 1)^+$ ions [17] and so it has been previously investigated as a chemical ionisation reagent in mass spectrometry [21]. In its reactions with alcohols both hydride ion transfer and the interesting process of hydroxide ion (OH^-) transfer have variously been observed [14,15,18]. So it is essential to determine the ion products of such reactions if they are to be used in analysis. Another complication in using NO^+ and O_2^+ precursor ions is that the rate coefficients, k, for the reactions, unlike those for the exothermic proton transfer reactions of H_3O^+ [7,17], cannot be assumed to be the upper-limit gas kinetic (collisional) rate coefficients, k_c, [4]. So the k must be determined experimentally for the reactions of NO^+ and O_2^+ with all those species which are to be quantified in a gas mixture.

We have previously measured the k and determined the ion products for the reactions of H_3O^+, NO^+ and O_2^+ with a number of organic and inorganic species [3–5], but the variety of molecules encountered in air and breath [19], emitted by plants [20,21] and by food and food products [22] is so great that these studies only modestly extend the required database. So we have now embarked on extensive studies of the reactions of organic compounds and selected inorganic species to better understand the reaction processes (via product identification) and the kinetics in order to extend the database. In this paper we report the results of a SIFT study of the reactions of H_3O^+, NO^+ and O_2^+ with a number of alcohols, some of which are known to be present in human breath [13,19,23], others which are emitted from plants [20,21], and some that are used as food flavours [22]. The number of alcohols that could be studied is endless, but we

limit this study mostly to saturated aliphatic alcohols together with one aromatic alcohol (phenol).

2. Experimental

The apparatus used for all these measurements was our standard selected ion flow tube (SIFT) which has been described in detail previously [24]. In the present studies, H_3O^+, NO^+ and O_2^+ ions are created in a microwave discharge through a mixture of argon and wet air (at a total pressure of about 0.1 Torr) and are then injected into helium carrier gas (at a pressure of about 0.5 Torr) either separately or together (see below) via a quadrupole mass filter operated at a suitably high or low resolution. The ions are convected along the flow tube by the carrier gas and as usual are sampled downstream via a pinhole/quadrupole mass spectrometer and detected and counted by a channeltron/amplifier/pulse counting system connected to a computer.

In a conventional SIFT study of the rate coefficients and products of ion–molecule reactions, the next stage of the experiment is to introduce the reactant gas into the carrier gas/ion swarm at a measured and controlled rate, and then to acquire the count rates of the reactant ion (e.g. H_3O^+, NO^+, O_2^+) and the product ions of the reaction as a function of the reactant gas flow rate. From these data the rate coefficient and the product ion distribution (ratio) are obtained by a standard procedure [24]. For permanent reactant gases this is usually a simple procedure using calibrated mass flow meters and flow controllers. This procedure can also be used for the vapours of some organic liquids if the calibration constant for the vapour for the particular flow meter is known; if not, a known weak mixture of the vapour in an inert gas (e.g. helium, argon or nitrogen) can be used. The latter method is the one we first chose for the present studies of the reactions of this series of alcohols,

but it was immediately apparent that the tendency of these vapours to stick onto the surface of the vessel (glass and stainless steel were tried) resulted in the adsorption of the vapours at quite unpredictable degrees, which meant that the mixture concentrations were totally unreliable and essentially useless for kinetic studies. So for these studies we adopted the following procedure.

We need to determine both the rate coefficients and the ion product distributions of the reactions to an acceptable accuracy if the data are to be used for trace gas analysis. The determination of the ion product distributions can be obtained accurately in the usual way by injecting the reactant ion species only, determining the fraction of each product ion as a function of the flow rate of the reactant gas, and extrapolating the count rate/flow rate curves to zero flow to eliminate any effects due to secondary reactions [24]. The point to appreciate is that the flow rate need not be known absolutely for the product ratio measurements but it must be known for the rate coefficient determinations, and since we cannot measure these flow rates accurately we make the following assumption which is justified by numerous experiments [7] to obtain the rate coefficients first for the H_3O^+ reactions, and then for the NO^+ and O_2^+ reactions.

Exothermic proton transfer reactions always proceed at or close to the collisional rate, i.e. the measured k is equal to the collisional rate coefficient, k_c, which can be calculated according to the procedure given by Su and Chesnavich [6]. Numerous measurements demonstrate this fact [7,17]. To calculate k_c, the polarisability, α, and the dipole moment, μ, of the reactant molecule are required; these parameters are known for some alcohol molecules [25] and so the k_c can be obtained, but they are not known for all of the alcohols included in this study, Fortunately, however, inspection of the available data (see [25] and Table 1) reveals that the dipole moments do not vary greatly amongst the saturated aliphatic alcohols, and whilst there is a more

Table 1

Rate coefficients for the reactions of H_3O^+, NO^+ and O_2^+ with the alcohols indicated which are listed in order of their molecular weight, m, in atomic units, u (except for the aromatic, phenol). Also given are their polarisabilities, α, in units of 10^{-24} cm^3 and their permanent dipole moments in Debye, D. The values of α and μ are known for only seven of the alcohols included in this study and they are shown in regular type (taken from [25]). For the remaining ten alcohols we have estimated their μ assuming that it does change significantly with the number of carbon atoms in alcohol molecules, and their α by adopting the average values of the known polarisabilities of other organic molecules possessing the same number of carbon atoms as the alcohol concerned. Then the collisional rate coefficients, k_c, for all 51 reactions have been calculated using the parameterised trajectory formulation of Su and Chesnavich [6] and these are given in the square brackets (estimated accuracy $\pm$ 10%). 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}

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})
methanol	32	3.29	1.70	2.7 [2.7]	0.01 [2.3]	~1 [2.3]
ethanol	46	5.84	1.69	2.7 [2.7]	1.2 [2.3]	2.3 [2.3]
1-propanol	60	6.74	1.68	2.7 [2.7]	2.3 [2.3]	2.2 [2.2]
2-propanol	60	7.61	1.66	2.7 [2.7]	2.4 [2.3]	2.3 [2.3]
1-butanol	74	8.88	1.66	2.8 [2.8]	2.2 [2.3]	2.5 [2.3]
2-methyl-1-propanol	74	8.92	1.64	2.7 [2.7]	2.4 [2.3]	2.5 [2.3]
$\pm$ 2-butanol	74	*9 $\pm$ 1*	*1.65 $\pm$ 0.1*	2.7 [2.7]	1.9 [2.3]	2.1 [2.3]
2-methyl-2-propanol	74	*9 $\pm$ 1*	*1.65 $\pm$ 0.1*	2.7 [2.7]	2.0 [2.3]	2.1 [2.3]
1-pentanol	88	*10 $\pm$ 1*	*1.65 $\pm$ 0.1*	2.8 [2.8]	2.5 [2.3]	2.8 [2.3]
3-methyl-1-butanol	88	*10 + 1*	*1.65 $\pm$ 0.1*	2.8 [2.8]	2.3 [2.3]	2.1 [2.3]
3-pentanol	88	*10 $\pm$ 1*	*1.65 $\pm$ 0.1*	2.8 [2.8]	2.3 [2.3]	2.7 [2.3]
2-methyl-2-butanol	88	*10 $\pm$ 1*	*1.65 $\pm$ 0.1*	2.8 [2.8]	2.3 [2.3]	2.6 [2.3]
1-hexanol	102	*12 $\pm$ 2*	*1.65 $\pm$ 0.2*	2.9 [2.9]	2.4 [2.4]	2.6 [2.3]
1-octanol	126	*16 $\pm$ 2*	*1.65 $\pm$ 0.2*	3.1 [3.1]	2.3 [2.6]	2.3 [2.5]
2-octanol	126	*16 $\pm$ 2*	*1.65 $\pm$ 0.2*	3.1 [3.1]	2.9 [2.6]	2.5 [2.5]
menthol	154	*18 $\pm$ 2*	*1.65 $\pm$ 0.2*	3.1 [3.1]	2.6 [2.5]	2.9 [2.5]
phenol	94	11.1	1.45	12.7 [2.7]	2.0 [2.2]	1.8 [2.2]

marked variation of the polarisabilty (which increases with the molecular mass of the alcohol molecule) we can make a reasonable estimate of the unknown values of α and μ using the procedure given in the caption to Table 1. So the k_c for the H_3O^+ reactions can be calculated to a reasonable accuracy which we estimate to be $\pm$ 10%; these are listed in Table 1. (It is worth noting that the k_c for polar molecules can be much larger at low temperatures [26].)

However, as we have noted earlier, it cannot be assumed that the NO^+ and O_2^+ reactions proceed at the collisional rate and so the k for these reactions must be determined experimentally, To do this, we prepared weak mixtures (of unknown concentrations) of the alcohol vapours in cylinder air at atmospheric pressure in sealed plastic bags and used these as the reactant gases in these SIFT experiments. Then all three reactants ions involved in this study, H_3O^+,

NO^+ and O_2^+, were injected simultaneously into the SIFT (by operating the injector quadrupole at very low resolution) and the decay curves of each ion count rate as a function of the flow rate of the air/vapour mixture were obtained. The slopes of the three decay plots provided the relative k values, and since the k for the H_3O^+ reactions are assumed to be equal to k_c, the values of k for the NO^+ and O_2^+ reactions were thus obtained. Sample decay curves obtained in this way are shown in Fig. 1(a) for a case when all three reactions proceed at the collisional rate, and in Fig. 1(b) for a case when the NO^+ reaction is clearly slower than the collisional rate.

An interesting point to note is that the k_c for the reactions of different ions with a particular reactant molecule is dependent on the reduced mass of the reactant ion/reactant molecule system. Clearly, the reduced mass of the H_3O^+/
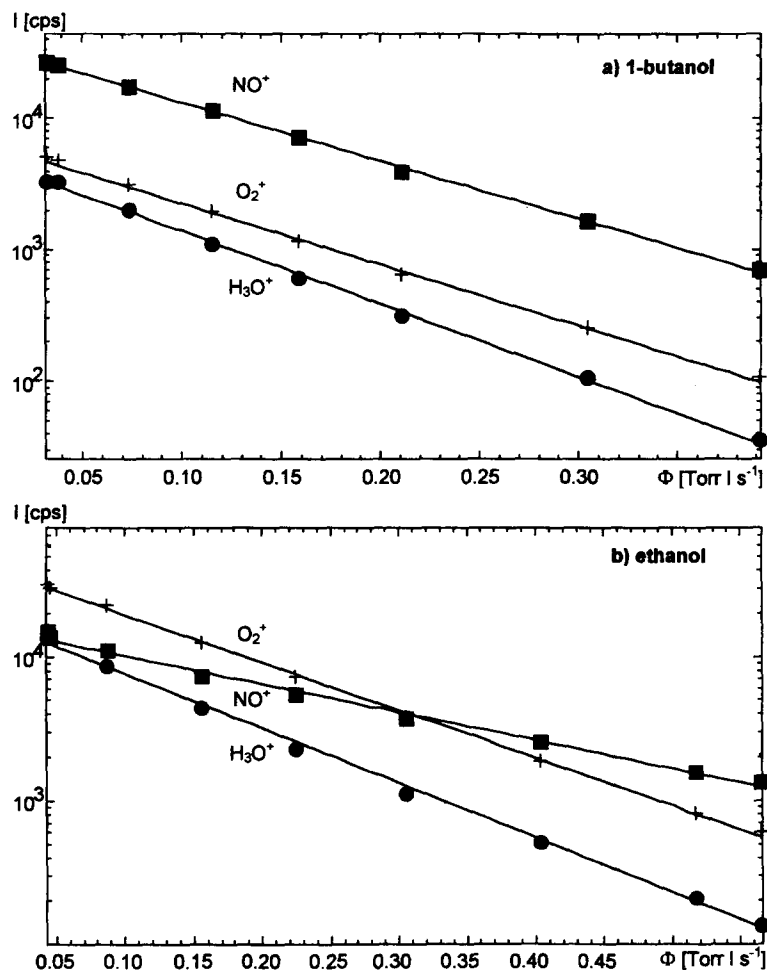
Fig. 1. Semi-logarithmic decay plots of the count rates, I (in counts per second, cps), of the simultaneously injected H_3O^+, NO^+ and O_2^+ primary ions as functions of the flow rate, Φ (in Torr.litres per second), of air containing the vapour of (a) 1-butanol and (b) ethanol. Because these three primary 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 alcohol molecules. Therefore, the slopes of these plots provide the relative rate coefficients of the reactions of the three ions with each alcohol. 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 (these values are given in Table 1). Note that the association reaction of NO^+ with ethanol is clearly slower then the corresponding H_3O^+ and O_2^+ reactions (see the text for discussion of this).

reactant molecule is somewhat less than that for the analogous NO^+ and O_2^+ systems, and this reflects in a somewhat smaller calculated k_c and (as it turns out) in the measured relative k for these reactions. This can actually be seen in the data array (see Table 1), only because almost all the NO^+ and O_2^+ reactions proceed at or close to the collisional rate.

The product ion distributions for each reaction

were obtained as described above, again using a mixture of the alcohol vapour in cylinder air, but in these experiments by injecting each reactant ion separately (operating the injector quadrupole at a sufficiently high resolution) to avoid the confusion which arises in product ion identification when the three reactants ions are injected simultaneously. The results obtained for all the rate coefficients and product ion percentages are

Table 2

Products of the reactions of the alcohols indicated with H_3O^+, NO^+ and O_2^+. The molecular formulae of the ion products listed do not necessarily represent their structures; the percentage of each ion product 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 are not well-defined. Note the production of an additional H_2O molecule in some of the H_3O^+ reactions, the production of both HNO and HNO_2 in some of the NO^+ reactions, and the several fragment ions in some of the O_2^+ reactions. Note also that NO^+ ions associate with methanol molecules and undergo charge transfer with phenol molecules (see the text for a discussion of these reactions). It is interesting to note that the oxygen-containing (carboxy) product ions invariably associate with the H_2O molecules when they are introduced into the helium carrier gas (see also [3])

Molecules	H_3O^+	NO^+	O_2^+
CH_3OH methanol	$CH_5O^+(100) + H_2O$	$NO^+.CH_3OH(100)$	$CH_4O^+(\sim50)$, $CH_3O^+(\sim50)$
C_2H_5OH ethanol	$C_2H_7O^+(100) + H_2O$	$C_2H_5O^+(100) + HNO$	$C_2H_5O^+(75)$, $C_2H_6O^+(25)$
C_3H_7OH 1-propanol	$C_3H_7^+(90) + 2H_2O$ $C_3H_9O^+(10) + H_2O$	$C_3H_7O^+(100) + HNO$	$CH_3O^+(90)$, $C_3H_6^+(10)$
2-propanol	$C_3H_7^+(80) + 2H_2O$ $C_3H_9O^+(20) + H_2O$	$C_3H_7O^+(100) + HNO$	$C_2H_5O^+(100)$
C_4H_9OH 1-butanol	$C_4H_9^+(95) + 2H_2O$ $C_4H_{11}O^+(5) + H_2O$	$C_4H_9O^+(> 95) + HNO$ $C_4H_9^+(< 5) + HNO_2$	$C_4H_8^+(80)$, $C_3H_7^+(10)$, $C_3H_6^+(5)$, $CH_5O^+(5)$
2-methyl-1-propanol	$C_4H_9^+(100) + 2H_2O$	$C_4H_9O^+(> 95) + HNO$ $C_4H_9^+(< 5) + HNO_2$	$CH_5O^+(40)$, $C_3H_6^+(20)$, $C_4H_9^+(20)$
(±)2-butanol	$C_4H_9^+(95) + 2H_2O$ $C_4H_{11}O^+(5) + H_2O$	$C_4H_9O^+(100) + HNO$	$C_2H_5O^+(60)$, $C_3H_7O^+(20)$, $C_3H_6^+(20)$
2-methyl-2-propanol	$C_4H_9^+(100) + 2H_2O$	$C_4H_9^+(100) + HNO_2$	$C_3H_7O^+(100)$
$C_5H_{11}OH$ 1-pentanol	$C_5H_{11}^+(100) + 2H_2O$	$C_5H_{11}O^+(85) + HNO$ $C_5H_9U + (10) + HNO + H_2O$ $C_5H_{11}^+(5) + HNO_2$	$C_5H_{10}^+ + (45)$, $C_3H_6^+(35)$, $C_5H_{11}^+(10)$, $C_4H_7^+(10)$
3-methyl-1-butanol	$C_5H_{11}^+(100) + 2H_2O$	$C_5H_{11}O^+(85) + HNO$ $C_5H_{11}^+(10) + HNO + H_2O$ $C_5H_{11}^+(5) + HNO_2$	$C_3H_7O^+(85)$, $C_3H_6O^+(10)$, $C_4H_9O^+(5)$
3-pentanol	$C_5H_{11}^+(100) + 2H_2O$	$C_5H_{11}O^+(90) + HNO$ $C_5H_{11}^+(10) + HNO_2$	$C_5H_{10}^+(50)$, $C_4H_9^+(20)$, $C_4H_8^+(10)$, $C_4H_7^+(10)$, $C_3H_6^+(10)$
2-methyl-2-butanol	$C_5H_{11}^+(100) + 2H_2O$	$C_5H_{11}^+(100) + HNO_2$	$C_3H_7O^+(55)$, $C_4H_9O^+(40)$, $C_5H_{11}^+(5)$
$C_6H_{13}OH$ 1-hexanol	$C_6H_{13}^+(100) + 2H_2O$	$C_6H_{13}O^+(90) + HNO$ $C_6H_{13}O^+(90) + HNO_2$	$C_4H_8^+(40)$, $C_6H_{12}^+(20)$, $C_3H_6^+(20)$, $C_5H_{10}^+(10)$, $C_3H_7^+(10)$
$C_8H_{17}OH$ 1-octanol	$C_8H_{17}^+(40) + 2H_2O$ $C_5H_{11}^+(35) + C_3H_7OH + H_2O$ $C_4H_9^+(25) + C_4H_9OH + H_2O$	$C_8H_{17}O^+(95) + HNO$ $C_5H_8^+(5) + HNO_2$	$C_6H_{12}^+(20)$, $C_5H_{10}^+(20)$, $C_6H_{11}^+(15)$, $C_4H_8^+(15)$, $C_6H_{10}^+(10)$, $C_5H_9^+(10)$, $C_8H_{16}^+(5)$, $C_5H_8^+(5)$
2-octanol	$C_8H_{17}^+(75) + 2H_2O$ $C_5H_{11}^+(15) + C_3H_7OH + H_2O$ $C_4H_9^+(10) + C_4H_9OH + H_2O$	$C_8H_{17}O^+(70) + HNO$ $C_2H_5O^+(30) + C_6H_{12} + HNO$	$C_2H_5O^+(70)$, $C_8H_{16}^+(5)$, $C_7H_{14}^+(5)$, $C_6H_{12}^+(5)$, $C_6H_{11}^+(5)$, $C_5H_{10}^+(5)$, $C_4H_8^+(5)$
$C_{10}H_{19}OH$ (±)menthol	$C_{10}H_{19}^+(100) + 2H_2O$	$C_{10}H_{19}O^+(50) + HNO$ $C_{10}H_{19}^+(50) + HNO_2$	$C_6H_9^+(40)$, $C_7H_{11}^+(15)$, $C_6H_{10}^+ + (10)$, $C_4H_7O^+(10)$, $C_7H_{12}^+(10)$, $C_{10}H_{18}^+(10)$, $C_6H_8^+(5)$
C_6H_5OH phenol	$C_6H_7O^+(100) + H_2O$	$C_6H_6O^+(100) + NO$	$C_6H_6O^+(100) + O_2$

given in Tables 1 and 2. Since the accuracy of the calculated k_c for the H_3O^+ reactions is ± 10% and the relative slopes of the decay plots such as those shown in Fig. 1 can be determined to ± 5% then the net accuracy of k for the NO^+ and O_2^+ reactions is estimated to be ± 15%.

3. Discussion of results

3.1. General comments

We will discuss the detailed results of this study in subsections which deal with the H_3O^+,

NO$^+$ and O$_2^+$ reactions separately. But first some general observations are in order.

We justifiably assume that all the H$_3$O$^+$ (proton transfer) reactions proceed at the collisional rate, with $k = k_c$, and following this assumption, inspection of the data given in Table 1 shows that the measured k are equal to their respective k_c for almost all the corresponding NO$^+$ and O$_2^+$ reactions. But the processes occurring in the reactions of these three ion species are quite different. The H$_3$O$^+$ reactions proceed via proton transfer, which for the smaller alcohols produce only the protonated molecules MH$^+$(+ H$_2$O), but which with increasing size result in only the production of the hydrocarbon ions (M − H$_2$O)$^+$(+ 2H$_2$O), i.e. H$_2$O molecules are ejected from the alcohol molecules following their protonation by the H$_3$O$^+$. The NO$^+$ reactions proceed variously via hydride ion (H$^-$) transfer producing (M − H)$^+$ ions (+ HNO) and hydroxide ion (OH$^-$) transfer producing (M − OH)$^+$ hydrocarbon ions (+ HNO$_2$). The O$_2^+$ reactions mostly proceed by charge transfer which is sufficiently exothermic to produce fragmentation of the excited (M$^+$)* ions, thus resulting in two or more product ions. We comment on these interesting processes below, 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, and that the reactions can sometimes be exploited to distinguish between the isomeric forms of some of these alcohols.

3.2. H$_3$O$^+$ reactions

All these exothermic proton transfer reactions are presumed to occur at the collisional rate with $k = k_c$. That almost all of the NO$^+$ and O$_2^+$ reactions are seen to proceed at or close to the rates of the corresponding H$_3$O$^+$ reactions (see Table 1) is strong supporting evidence that all these reactions are indeed proceeding at their collisional rates. No further comments will be made here on the kinetics of these H$_3$O$^+$ reactions; rather attention will be focused on the ion products of the reactions.
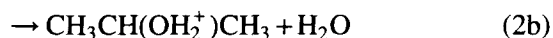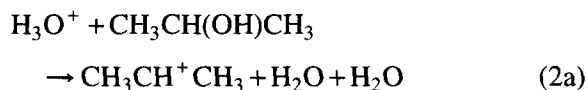
3.2.1. Methanol, CH$_3$OH, and ethanol, C$_2$H$_5$OH

These are the simplest of the reactions in this study, because both proceed by direct, nondissociative proton transfer producing only the protonated parent molecules CH$_3$OH$_2^+$ and C$_2$H$_5$OH$_2^+$ (see Table 2) as is dictated by the energetics, e.g.

$$H_3O^+ + CH_3OH \rightarrow CH_3OH_2^+ + H_2O \qquad (1)$$
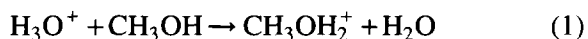
This simplifies the detection and quantification of these alcohols in air and breath. These results are in accordance with a previous study [27].

3.2.2. 1-propanol, C$_3$H$_7$OH, and 2-propanol, CH$_3$CH(OH)CH$_3$

The rate coefficients and the branching ratios for these two reactions have been previously studied as a function of the ion/molecule interaction energy in a flow-drift tube experiment [13]. Two product ions were observed for both of these reactions, the major channel in both involves H$_2$O elimination, the nascent protonated parent molecules appearing only as the minor product Thus, in the reaction of 2-propanol, i.e.

$$H_3O^+ + CH_3CH(OH)CH_3$$

$$\rightarrow CH_3CH^+CH_3 + H_2O + H_2O \qquad (2a)$$

$$\rightarrow CH_3CH(OH_2^+)CH_3 + H_2O \qquad (2b)$$

the branching ratio is 78% to 22% in favour of (2a) at thermal energy, whilst in the reaction of 1-propanol the corresponding branching ratio is 92% to 8%. The present SIFT results are essentially identical to these (see Table 2).

It is interesting to note that the available thermochemical data [28] indicates that the product ions of reaction (2b) and the corresponding C$_3$H$_7^+$ product of the 1-propanol reaction must be the iso-C$_3$H$_7^+$ isomer (as indicated), because formation of the n-C$_3$H$_7^+$ isomer is clearly

endothermic in both reactions. Clearly some rearrangement is required to form the iso-$C_3H_7^+$ isomer in the 1-propanol reaction, and this in part may explain why there is a somewhat smaller fraction of this ion formed in the reaction (compared to the 2-propanol reaction).

3.2.3. Four isomers of $C_4H_9(OH)$

The isomers are 1-butanol $CH_3CH_2CH_2CH_2OH$, 2-methyl-1-propanol $CH_3CH(CH_3)CH_2OH$, ($\pm$)2-butanol $CH_3CH_2CH(CH_3)OH$ and 2-methyl-2-propanol $C(CH_3)_3OH$. In the reactions of all four isomers, H_2O elimination is the very dominant channel, indeed, it is the only process that occurs for two of the reactions (see Table 2), e.g.

$$H_3O^+ + C(CH_3)_3OH \rightarrow C^+(CH_3)_3 + H_2O + H_2O \tag{3}$$
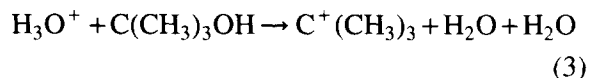
The structure of the product ion in this reaction most probably is the tertiary ion as shown, since its production is certainly exothermic (using the thermochemical data given in [28]) and no rearrangement is necessary. In the 1-butanol and 2-butanol reactions, the protonated parent molecules are minor but definite products, e.g.
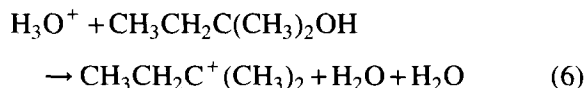
$$H_3O^+ + CH_3CH_2CH_2CH_2OH$$

$$\rightarrow C_4H_9^+ + H_2O + H_2O \tag{4a}$$

$$\rightarrow C_4H_9OH_2^+ + H_2O \tag{4b}$$
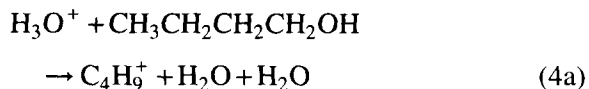
The energetics of reaction (4a) reveal that the production of n-$C_4H_9^+$ is endothermic whereas sec-$C_4H_9^+$ and tert-$C_4H_9^+$ can both be produced exothermically (by 8 kcal/mol and 25 kcal/mol respectively). Although we cannot say which of these is the actual product of the reaction, the more exothermic tert-$C_4H_9^+$ ion may be favoured (perhaps both isomers are produced).

3.2.4. Four isomers of $C_5H_{11}(OH)$ and 1-hexanol, $C_6H_{13}OH$

The isomers are 1-pentanol $C_5H_{11}OH$, 3-methyl-1-butanol $CH_3CH(CH_3)CH_2CH_2OH$,

3-pentanol $CH_3CH_2CH(OH)CH_2CH_3$, and 2-methyl-2-butanol $CH_3CH_2C(CH_3)_2OH$. In all four reactions a single product ion is observed, $C_5H_{11}^+$, indicating that H_2O is eliminated following protonation of all these alcohols, e.g.

$$H_3O^+ + C_5H_{11}OH \rightarrow C_5H_{11}^+ + H_2O + H_2O \tag{5}$$

$$H_3O^+ + CH_3CH_2C(CH_3)_2OH$$

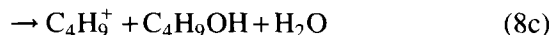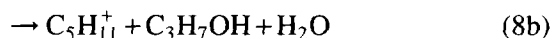$$\rightarrow CH_3CH_2C^+(CH_3)_2 + H_2O + H_2O \tag{6}$$

Although the thermochemical data for these larger ionic species is sparse, it is adequate to show [28] that reaction (5) is exothermic by about 11 kcal/mol and that the tertiary hydrocarbon ion $CH_2CH_3C^+(CH_3)_2$ could be a product of the reactions of all four of these alcohol reactions. The 1-hexanol reaction also proceeds only via H_2O elimination:

$$H_3O^+ + C_6H_{13}OH \rightarrow C_6H_{13}^+ + H_2O + H_2O \tag{7}$$
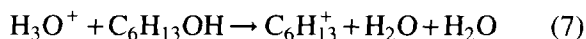
3.2.5. 1-octanol, $C_5H_{17}OH$, and 2-octanol, $C_6H_{13}CH(OH)CH_3$

On the basis of all the above data it might be assumed that the higher-order alcohols will continue to react with H_3O^+ by H_2O elimination only, but the 1-octanol and 2-octanol reactions certainly do not conform with this, three products being observed in both reactions, e.g.:

$$H_3O^+ + C_8H_{17}OH \rightarrow C_8H_{17}^+ + H_2O + H_2O \tag{8a}$$

$$\rightarrow C_5H_{11}^+ + C_3H_7OH + H_2O \tag{8b}$$

$$\rightarrow C_4H_9^+ + C_4H_9OH + H_2O \tag{8c}$$

On protonation, a fraction of the protonated molecules eject an H_2O molecule and the remainder dissociate along the carbon chain to the hydrocarbon ions and the lower-order alcohol molecules. Although the product species are the same for the reactions of both the octanol isomers, the branching ratios are clearly different (see Table 2). For the 1-octanol reaction (8) the three products are of comparable percentage

whereas for the 2-octanol reaction the H_2O elimination channel is obviously the major channel (see Table 2). These results illustrate the danger in making too wide-ranging assumptions about the way in which these and any other ion/molecule reaction may proceed.

3.2.6. Menthol, $C_{10}H_{20}O$

This well-known mint flavour compound is protonated by H_3O^+ thus:

$$H_3O^+ + \begin{array}{c} OH \\ \end{array} \rightarrow C_{10}H_{19}^- + H_2O + H_2O \qquad (9)$$
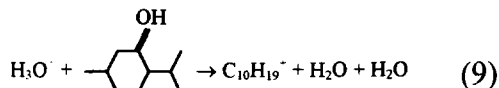
Again, the H_2O elimination process occurs which shows that this process is not restricted to the reactions of open-chain alcohols, but that it also occurs by the extraction of the OH moiety from the saturated six-member ring in menthol.

3.2.7. Phenol, C_6H_5OH

This special case of an alcohol with the OH adjacent to the aromatic ring is worthy of investigation. The reaction proceeds to produce only protonated phenol:

$$H_3O^+ + C_6H_5OH \rightarrow C_6H_5OH_2^+ + H_2O \qquad (10)$$

This is no surprise because it is the only exothermically available channel, H_2O elimination being quite endothermic (by 35 kcal/mol).

3.3. NO^+ reactions

All of these reactions (except for the methanol and ethanol reactions) proceed at or close to the collisional rate with $k = k_c$ (see Table 1). We therefore focus our interest on the products of these reactions and the reaction mechanisms. Two important and very interesting processes occur in these reactions, hydride ion transfer and hydroxide ion transfer, in which respectively an HNO molecule and an HNO_2 molecule are formed together with the appropriate carboxy ion and hydrocarbon ion (see Table 2). Because the recombination energy of NO (9.26 eV) is

low, the process of charge transfer only occurs with phenol because of its lower ionisation eneroy (8.47 eV) and not with any of the other alcohols included in this study; this is in marked contrast to the reactions of O_2^+ in which apparently charge transfer is the only process that occurs (see Table 2 and Section 3.4).

3.3.1. Methanol, CH_3OH

Bimolecular reaction processes (such as charge transfer and hydride ion transfer) are not allowed energetically and so this simplest of alcohols reacts uniquely with NO^+ ions via collisional (three-body) association under the conditions of these SIFT experiments thus:

$$NO^+ + CH_3OH + He \rightarrow NO^+.CH_3OH + He \qquad (11)$$
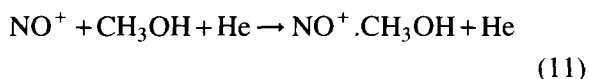
The He atoms of the carrier gas act in collisions to remove the binding energy of the cluster ion thus stabilising it against dissociation to the reactants. Thus we determine the termolecular rate coefficient to be $\sim 10^{-28}\,cm^6\,s^{-1}$ at 300 K in agreement with a previous measurement [29], although a contribution by two body radiative association cannot be ruled out entirely.

3.3.2. Ethanol and the two propanol isomers

In the ethanol reaction we see the occurrence of hydride ion, H^-, transfer, which is the most commonly occurring process in these reactions, as a glance at Table 2 confirms:

$$NO^+ + C_2H_5OH \rightarrow C_2H_4OH^+ + HNO \qquad (12)$$

In this process H^- is transferred, presumably in a tight ion/molecule complex, producing (as required by the energetics) the protonated acetaldehyde ion CH_3CHOH^+ (i.e. $(M - 1)^+$) and HNO (compare this with H^+ transfer which occurs in the H_3O^+ reaction resulting in the ion $(M + 1)^+$). Formation of the other stable structural isomer, the ion $C_2H_5O^+$, in reaction (12) is endothermic according to the data given in [28]. Reaction (11) is relatively inefficient, the measured k being only about $1/2\,k_c$, in reasonable

agreement with the results of previous studies [4,18].

The reactions of both 1-propanol and 2-propanol also proceed via H^- transfer with the production of $C_3H_7O^+$ ions which presumably are respectively the structural isomers $CH_3CH_2CH^+OH$ (19 kcal/mol exothermic) for 1-propanol and $(CH_3)_2C^+OH$ (29 kcal/mol exothermic) for 2-propanol. Formation of $CH_3CH_2CH_2O^+$ and $CH_3CHO^+CH_3$ in either of these reactions would be endothermic (by > 47 kcal/mol), thus indicating that the hydride ion is taken from the carbon atom and not from the OH group. A similar process occurs in the ethanol reaction (11).

3.3.3. Four isomers of C_4H_9OH

In this group of reactions we first see the occurrence of hydroxide ion, OH^-, transfer, and the striking result that this is the only process which occurs in the reaction of the tertiary alcohol 2-methyl-2-propanol:

$$NO^+ + (CH_3)_3COH \rightarrow (CH_3)_3C^+ + HNO_2 \quad (13)$$
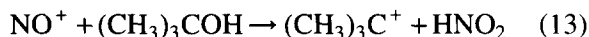
Here the tertiary hydrocarbon ion and a nitrous acid molecule are formed, as was previously observed [2,18]. However, in the reactions of the other three isomers, i.e. two primary alcohols and one secondary alcohol, hydroxide ion transfer is only a minor channel (see Table 2) and essentially only hydride ion transfer occurs, e.g.
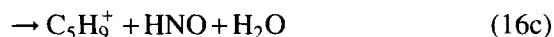
$$NO^+ + CH_3CH_2CH(OH)CH_3$$
$$\rightarrow CH_3CH_2C^+(OH)CH_3 + HNO \quad (14)$$
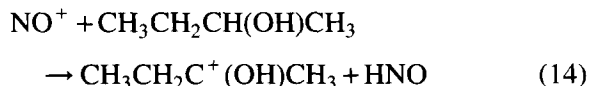
For hydroxide ion transfer to occur, the products would have to be either tert-$C_4H_9^+$ or sec-$C_4H_9^+$, because the n- and iso- structures are not accessible [28]. Again, the H^- is taken from a carbon atom, not from the OH group, probably forming $CH_3CH_2C^+(OH)CH_3$ as is indicated in reaction (14).

3.3.4. Four isomers of $C_5H_{11}(OH)$ and 1-hexanol, $C_6H_{13}OH$

Again, there is a single product of the 2-methyl-2 butanol (tertiary alcohol) reaction resulting from hydroxide ion transfer:

$$NO^+ + CH_3CH_2(CH_3)_2COH$$
$$\rightarrow CH_3CH_2(CH_3)_2C^+ + HNO_2 \quad (15)$$
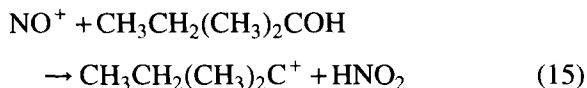
The fact that hydroxide ion transfer is only a minor reaction channel for the other three pentanol isomers is remarkably similar to the reactions of the butanol isomers in which the very dominant process is hydride ion transfer (see Table 2). However, an additional process occurs in the reactions of the primary alcohols 1-pentanol and 3-methyl-1-butanol resulting in the production of an ion at 69 u. This must be the hydrocarbon ion $C_5H_9^+$ (and not the oxygen-bearing ion $C_4H_5O^+$) because it does not cluster with water molecules when these are introduced into the carrier gas (this is a very valuable diagnostic check; see [3]). This $C_5H_9^+$ product ion could be the result of reaction (16c), i.e. hydride ion transfer (producing HNO) and H_2O ejection, or reaction (16b), i.e. OH^- transfer (producing HNO_2) followed by H_2 ejection, e.g.

$$NO^+ + C_5H_{11}OH \rightarrow C_5H_{11}O^+ + HNO \quad (16a)$$
$$\rightarrow C_5H_{11}^+ + HNO_2 \quad (16b)$$
$$\rightarrow C_5H_9^+ + HNO + H_2O \quad (16c)$$

These possibilities also apply to the 3-methyl-1-butanol reaction for which the products are essentially identical. The thermicities of the individual reaction channels are determined by the particular isomer of $C_5H_9^+$ that is formed [28]. Allowed structures of the $C_5H_9^+$ product ion are $CH_2=CHCH^+CH_2CH_3$ and $CH_3CH^+CH=CHCH_3$.

In the 1-hexanol reaction, hydride ion transfer is the very dominant process but hydroxide ion transfer is again discernible (see Table 2). Within this complete data set it seems that the primary and secondary alcohols react with NO^+ mainly
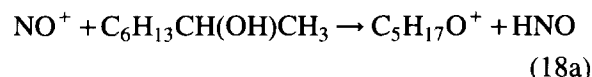
via hydride ion transfer producing HNO, whereas the tertiary alcohols react via hydroxide ion transfer producing HNO_2, a trend observed previously in chemical ionisation studies [2,15].

3.3.5. 1-octanol and 2-octanol

Hydride ion transfer is again the dominant process in both these reactions, being very dominant in the 1-octanol reaction:

$$NO^+ + C_8H_{17}OH \rightarrow C_8H_{17}O^+ + HNO \qquad (17a)$$

$$\rightarrow C_8H_{17}^+ + HNO_2 \qquad (17b)$$

However, in the 2-octanol reaction, it appears that following the hydride ion transfer the excited $(C_8H_{17}O^+)$ product ion partially dissociates at the 2–3 carbon bond producing the protonated acetaldehyde ion and a 1-hexene molecule thus:

$$NO^+ + C_6H_{13}CH(OH)CH_3 \rightarrow C_5H_{17}O^+ + HNO$$
$$(18a)$$

$$\rightarrow C_2H_4OH^+ + C_4H_9CH=CH_2 + HNO \quad (18b)$$

A corollary to this is that it seems likely that the hydride ion is extracted from the carbon chain and not from the oxygen.
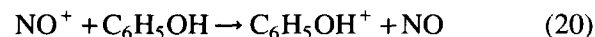
3.3.6. Menthol

Both hydride ion and hydroxide ion transfer occur with about equal probability in this reaction, again producing the carboxy ion and the hydrocarbon ion respectively:

$$NO^+ + C_{10}H_{19}OH \rightarrow C_{10}H_{19}O^+ + HNO \qquad (19a)$$

$$\rightarrow C_{10}H_{19}^+ + HNO_2 \qquad (19b)$$
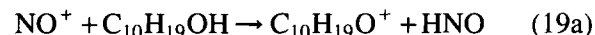
3.3.7. Phenol

This reaction is unique in this whole series in that it proceeds only via the process of charge transfer:

$$NO^+ + C_6H_5OH \rightarrow C_6H_5OH^+ + NO \qquad (20)$$

Indeed, this is the only exothermic process that can occur made possible by the low ionisation

energy of phenol (8.47 eV) which is smaller than the recombination energy of NO^+ (9.26 eV, [28]). Both hydride ion and hydroxide ion transfer in this system are endothermic processes and therefore cannot occur at the low interaction energies pertaining to a SIFT at 300 K.
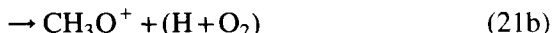
3.4. O_2^+ reactions

A glance at Table 1 shows that all these reactions proceed at or near the collisional rate ($k = k_c$). They can all be described as charge transfer reactions, although in a few cases the occurrence of other mechanisms such as H^- ion transfer (e.g. reaction (21b))and CH_3^- ion transfer (e.g. reaction (22)) cannot positively be ruled out. It is well known that some charge transfer reactions involving small reactant molecules are inefficient (i.e. $k < k_c$) [17], which is usually ascribed to the sparcity of accessible electronic states in the ionised parent molecules and thus to unfavourable Franck–Condon Factors [30–32]. However, in these polyatomic alcohols such inhibiting factors are far less likely and the reactions are efficient. In only two of the reactions (i.e. of methanol and ethanol) are the ionised parent molecule observed products. For the rest, the parent ions fragment following the charge transfer, in some cases into as many as six product channels (see Table 2) and so these are best described as dissociative charge transfer reactions. This multiple "cracking" of the reactant molecule is reminiscent of the cracking that follows electron impact ionisation (which presumably would result in even more fragment ions) and as such these O_2^+ reactions are of limited value for chemical ionisation of large molecules. However, as we will indicate, these O_2^+ reactions may have some value in distinguishing between the isomeric forms of some alcohols.

The complications in the product ion mass spectra for the reactions of the butanols, pentanols, hexanol and octanols means that it is difficult and unprofitable to discuss each reaction individually, so we will group them under a

single sub-heading and simply make a few general observations.

3.4.1. Methanol and ethanol

In both of these primary alcohol reactions the parent ion, M^+, is observed together with the appropriate $(M - H)^+$ ion, this being the CH_3O^+ ion in the methanol reaction:

$$O_2^+ + CH_3OH \rightarrow CH_3OH^+ + O_2 \qquad (21a)$$

$$\rightarrow CH_3O^+ + (H + O_2) \qquad (21b)$$

The bracket enclosing H and O_2 recognises the point that HO_2 or $H + O_2$ can be formed in this reaction (this is similarly indicated in reactions (22), (24) and (25) below). In the ethanol reaction, $C_2H_5O^+$ is the major product (see Table 2). Note that in reaction (21a) the product ion has the same mass as O_2^+ and this complicates the determination of the branching ratio for the overall reaction as has been discussed in a previous paper [4].

3.4.2. 1-propanol and 2-propanol

The 1-propanol (primary alcohol) reaction proceeds again largely with the production of CH_3O^+ (+ C_2H_5) with $C_3H_6^+$(+ H_2O) as only a minor product. However, the 2-propanol (secondary alcohol) reaction proceeds via the ejection of an end CH_3 moiety:

$$O_2^+ + CH_3CH(OH)CH_3$$

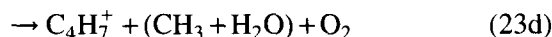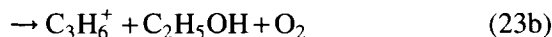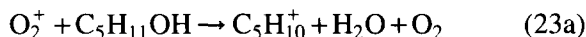$$\rightarrow CH_3CHOH^+ + (CH_3 + O_2) \qquad (22)$$
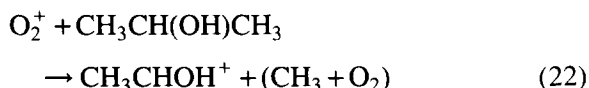
This difference in the products of the reactions with O_2^+ of these two isomers of propanol offers a way of distinguishing between them when one or both are present in a gas sample; this is also possible by exploiting the different branching ratios for the H_3O^+ reactions (see Section 3.2).

3.4.3. The $C_4H_9(OH)$, $C_5H_{11}(OH)$, $C_8H_{17}(OH)$ isomers and $C_6H_{13}OH$

Following the electron (charge) transfer to the O_2^+, the product parent ions fragment at various positions along the carbon chains producing

hydrocarbon ions along with neutral oxygen-containing moieties such as OH, H_2O and lower-order alcohols, and/or *carboxy ions* along with hydrocarbon neutral fragments. The carboxy ions partially associate with the water vapour molecules (when these are introduced into the helium carrier gas) producing the $C_nH_mO^+.H_2O$ hydrate ions, whereas the hydrocarbon ions do not. Such observations are of assistance in determining if a particular product ion is hydrocarbon or carboxy, which is particularly useful when an ion product at a given mass could be either one of these types. The detailed product distributions are given in Table 2, and do not merit detailed discussion because of their complexities. However, some general comments are in order.
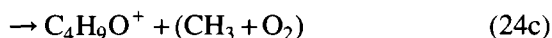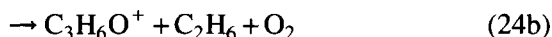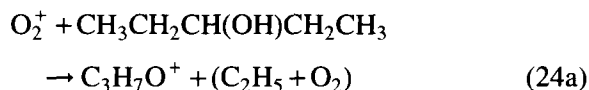
It is apparent that the reactions of the non-branched alcohols and most (but not all) of the primary alcohols result largely in hydrocarbon ions only. This is so for 1-pentanol, 3-methyl-1-butanol, 1-hexanol, 1-octanol and essentially so for 1-butanol, As an example, the 1-pentanol reaction proceeds thus:

$$O_2^+ + C_5H_{11}OH \rightarrow C_5H_{10}^+ + H_2O + O_2 \qquad (23a)$$

$$\rightarrow C_3H_6^+ + C_2H_5OH + O_2 \qquad (23b)$$

$$\rightarrow C_5H_{11}^+ + OH + O_2 \qquad (23c)$$

$$\rightarrow C_4H_7^+ + (CH_3 + H_2O) + O_2 \qquad (23d)$$

The neutral products indicated are the most likely ones, but we include the neutral products of reaction (22d) in brackets (28 kcal/mol exothermic) because we cannot be sure of them and they could be (CH_4 + OH, about 14 kcal/mol exothermic). The exception in these primary alcohol reactions is the 2-methyl-1-propanol reaction in which a carboxy ion is the major product (see Table 2) in common with the smaller alcohol reactions discussed above.

On the other hand, as can be seen in Table 2, the ion products of the reactions of the secondary alcohols, 2-butanol, 3-pentanol, 2-octanol, and

the tertiary alcohols, 2-methyl-2-propanol and 2-methyl-2-butanol are predominantly carboxy ions. For example, the 3-pentanol reaction proceeds thus:

$$O_2^+ + CH_3CH_2CH(OH)CH_2CH_3$$

$$\rightarrow C_3H_7O^+ + (C_2H_5 + O_2) \qquad (24a)$$

$$\rightarrow C_3H_6O^+ + C_2H_6 + O_2 \qquad (24b)$$

$$\rightarrow C_4H_9O^+ + (CH_3 + O_2) \qquad (24c)$$

It can be seen how in reaction (23), and indeed in the other similar reactions, how the chain cleaves at different positions. However, unusually there is only a single product ion in the 2-methyl-2-propanol tertiary alcohol reaction:
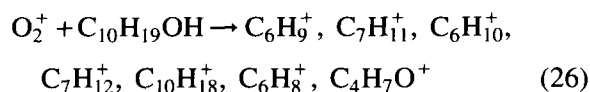
$$O_2^+ + (CH_3)_3COH \rightarrow (CH_3)_2COH^+ + (CH_3 + O_2) \qquad (25)$$
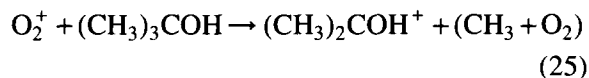
Note also that there is only a single product ion for the reactions of this alcohol with both H_3O^+ and NO^+ (see Table 2).

It is worthy of note that hydrocarbon ions are the only observed products of the 1-octanol primary alcohol reaction, whereas the major product of the 2-octanol secondary alcohol reaction is $C_2H_5O^+$ together with several minor hydrocarbon ions. Clearly, therefore, these O_2^+ reactions could be used to distinguish between these two isomers.

3.4.4. Menthol and phenol

We group these two reactions to demonstrate again the very different behaviour of the cyclic-core, non-aromatic molecule menthol, and the relatively stable aromatic molecule, phenol. Charge transfer occurs in both reactions, but whereas for the phenol the single product, parent ion is formed, $C_6H_5OH^+$, there are seven fragment ions produced in the menthol reaction:

$$O_2^+ + C_{10}H_{19}OH \rightarrow C_6H_9^+,\ C_7H_{11}^+,\ C_6H_{10}^+,$$

$$C_7H_{12}^+,\ C_{10}H_{18}^+,\ C_6H_8^+,\ C_4H_7O^+ \qquad (26)$$

This considerable fragmentation, even following

"soft" ionisation by O_2^+ (with an estimated excess energy of only 3–4 eV), forcibly demonstrates the great advantage of H_3O^+ and NO^+ in chemical ionisation compared to electron impact ionisation for which the excess energy is much greater with the consequent much greater fragmentation. Note in reaction (26) that amongst the many products, the sole carboxy ion, $C_4H_7O^+$, is only a 10% product (Table 2).

4. Concluding remarks

The results of this study reveal some interesting trends in the reactivity of alcohols with H_3O^+ and NO^+ ions. A common process in most of the H_3O^+ reactions is the elimination of an H_2O moiety following protonation producing the appropriate hydrocarbon ion. In several of these reactions only a single product ion results and in none of them are there more than three product ions.

In the NO^+ reactions, the common processes are hydride ion and hydroxide ion transfer producing identifiable products which facilitates analysis using chemical ionisation [2]. The process of hydroxide ion transfer in positive ion reactions is now well characterised, and a similar process involving the transfer of OH^- from H_3O^- to some molecules, including CO, has been observed [33]. It is very interesting that these NO^+ reactions can be used to distinguish between the primary and secondary butanol and pentanol isomers and their tertiary counterparts, the reactions of the latter isomers resulting in only the corresponding hydrocarbon ions whereas the reactions of the former isomers result largely in the appropriate carboxy ions. The analytical value of this is complemented by the fact that the hydrocarbon ions do not associate with water molecules whereas the carboxy ions do associate with water molecules very efficiently.

It is clear that O_2^+ is less useful in chemical ionisation because of the multiple products that result from their reactions with complex

molecules (see Table 2). However, O_2^+ is a very valuable precursor ion for the detection and quantification of those smaller molecules which react with neither H_3O^+ nor NO^+ such as NO and NO_2 and some fluorochlorocarbons [17].

Within the many molecules included in this study, we note the simple results of the phenol reactions in which only a single product results in each case, this being an indicator of the greater stability of the aromatic ring.

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