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A selected ion flow tube study of the reactions of H_3O^+, NO^+ and $O_2^{+\bullet}$ with some phenols, phenyl alcohols and cyclic carbonyl compounds in support of SIFT-MS and PTR-MS

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Abstract

We have carried out a selected ion flow tube (SIFT) study of the reactions of H_3O^+, NO^+ and $O_2^{+\bullet}$ with the following 10 compounds: 2-hydroxyphenol, 2-, 3- and 4-methylphenol (*o*-, *m*- and *p*-cresol, respectively), 4-ethylphenol, 1-phenylmethanol (benzyl alcohol), 1- and 2-phenylethanol, 1,4-benzoquinone and cyclohexanone. The primary purpose of this work was to extend the kinetics database to allow these compounds (M), to be analysed in air by selected ion flow tube mass spectrometry (SIFT-MS). The initial step in all the H_3O^+ reactions is exothermic proton transfer to produce MH^+ ions, which are observed as the only products for seven of the ten reactions, but for the three aromatic alcohols, H_2O molecule elimination occurred from the nascent MH^+ ions producing the corresponding hydrocarbon ion. This is an essential point to recognise when exploiting proton transfer to analyse these compounds using SIFT-MS and proton transfer reaction mass spectrometry, PTR-MS. NO^+ reacts with six of the compounds via non-dissociative charge transfer producing M^+ ions and this is a valuable route to their analysis by SIFT-MS. In the case of the NO^+/quinone reaction, adduct formation occurs giving NO^+M product ions, whilst for the remaining three reactions two or more ion products were formed. All the $O_2^{+\bullet}$ reactions proceeded via charge transfer with multiple ion products in most cases. A sample analysis is carried out to indicate the value of simultaneous use of both H_3O^+ and NO^+ precursor ions to analyse a mixture containing some of these compounds.

Keywords: Proton transfer; Charge transfer; Phenols; Phenyl alcohols; SIFT-MS; PTR-MS

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1. Introduction

Since the advent of selected ion flow tube mass spectrometry (SIFT-MS), which is an analytical method primarily intended for the real-time, on-line analysis of the trace gases on air, and especially exhaled breath [1–4], and the headspace of biological liquids (urine [5–8], blood, cell cultures in vitro [9,10]), a continuous effort has been made to build and extend the required kinetics database. This has involved the study of the rate coefficients and product ion distributions for the reactions of H_3O^+, NO^+ and $O_2^{+\bullet}$, the commonly used precursor ions for SIFT-MS analyses [1–3], with a wide variety of organic and inorganic compounds at thermal energies using the selected ion flow tube method [11–21]. These in-depth studies have not only provided the essential kinetics data for SIFT-MS, but also contributed to the body of knowledge on ion-molecule reaction processes. Thus, it is seen that the large fraction of reactions of H_3O^+ with organic molecules proceeds rapidly via exothermic proton transfer [11,12,22], a focus of this special issue. An exception to this trend is the reactions of *n*-alkanes with H_3O^+ in which the protonated *n*-alkanes are not observed [17], presumably because the proton affinities (PA) of the *n*-alkanes are less than the PA of the H_2O molecule. This renders proton transfer endothermic at the thermal energies (300 K) of most SIFT experiments. It is

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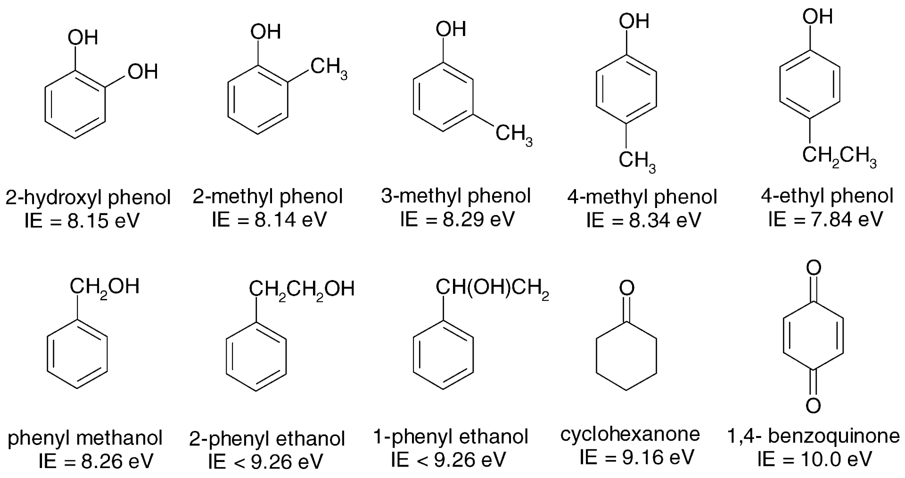
interesting to note that H_3O^+ reactions with the longer chain *n*-alkanes proceed via ion-molecule association producing H_3O^+/alkane adduct ions [17].

Appreciation of these general trends is especially relevant to the proton transfer reaction mass spectrometry, PTR-MS, analytical technique [23,24], where proton transfer from H_3O^+ occurs under supra thermal conditions in a drift tube. Thus, the small amounts of additional energy involved in the H_3O^+/neutral interaction could seriously influence the kinetics of those reactions that are close to thermoneutral such as the reactions of H_3O^+ with formaldehyde [6,25] and hydrogen sulphide [26].

A special feature of SIFT-MS is the facility to rapidly switch between the H_3O^+, NO^+ and $O_2^{+\bullet}$ precursor ions, which allows the analysis of a given gas mixture, including exhaled breath, by all three ions effectively simultaneously. This allows species to be analysed that are not accessible using H_3O^+ ions, especially small inorganic molecules such as NO and NO_2 that are well analysed using $O_2^{+\bullet}$ precursor ions [27]. Further to this, the parallel analysis of mixtures with two or three of the precursor ions provides important checks on the proper identification and quantification of compounds within the mixture [12].

Much effort has been made to obtain a thorough understanding of the reactions of the precursor ions with the ubiquitous aliphatic (open chain) oxygen containing organic compounds, especially alcohols [13], aldehydes [14], carboxylic acids [15] and ketones [14,28]. The kinetics database for these compounds is now quite extensive, but it is being extended as and when required [29,30]. The SIFT studies reveal that, except for methanol and ethanol, protonation of the alcohols in the H_3O^+/aliphatic monoalcohol reactions results in the elimination of an H_2O molecule from the nascent protonated alcohol and the production of the corresponding hydrocarbon ion [13]. Similarly, protonation of diols results in H_2O elimination, but in this case the product ion obviously retains an oxygen atom, which influences their subsequent ion chemistry [31]. Partial H_2O elimination also occurs when most aldehydes and carboxylic acids are protonated by H_3O^+ and this must be taken into account for the accurate analyses of these compounds in SIFT-MS analyses and other methods that exploit proton transfer such as PTR-MS [32]. Where doubt arises in the identification of these compounds using H_3O^+ precursor ions, NO^+ precursor ions can additionally be used for SIFT-MS analyses. These reactions largely proceed via hydride ion transfer (aliphatic alcohols [13] and aldehydes [14]), hydroxide ion transfer and parallel association (carboxylic acids [15]) and association (ketones [14,20]). The reactions of these compounds with the more energetic $O_2^{+\bullet}$ precursor ions usually results in multiple product ions [13–15], especially for the longer chain compounds, and this means that $O_2^{+\bullet}$ is not a very useful precursor ion for their analyses in mixtures, but can be used to identify individual compounds according to their characteristic fragmentation patterns.

To date, we carried out few studies of the reactions of aromatic compounds with H_3O^+, NO^+ and $O_2^{+\bullet}$ (except hydrocarbons [17]), principally because they are not so obviously present in exhaled breath or above urine and blood. However, it has recently been indicated that *p*-cresol, or 4-methylphenol, exists in the serum of patients with kidney disease [33]. So we have initiated a study of the ion chemistry of aromatic hydroxy and carbonyl compounds in order to expand our kinetics database. Thus, in this paper, we report the results of a SIFT study of the reactions of H_3O^+, NO^+ and $O_2^{+\bullet}$ with the compounds given in Fig. 1, viz. 2-hydroxyphenol, 2-, 3- and 4-methylphenol, 4-ethylphenol, 1-phenylmethanol, 1- and 2-phenylethanol, 1,4-benzoquinone and cyclohexanone. The ion chemistries of other isomers of these compounds were not studied because they are solids having prohibitively low vapour pressures. We also show SIFT-MS spectra for a mixture of some of these compounds in order to illustrate some major features of their analyses.



2-hydroxyl phenol IE = 8.15 eV
2-methyl phenol IE = 8.14 eV
3-methyl phenol IE = 8.29 eV
4-methyl phenol IE = 8.34 eV
4-ethyl phenol IE = 7.84 eV
phenyl methanol IE = 8.26 eV
2-phenyl ethanol IE < 9.26 eV
1-phenyl ethanol IE < 9.26 eV
cyclohexanone IE = 9.16 eV
1,4- benzoquinone IE = 10.0 eV

Fig. 1. The structures of the compounds involved in this study. The ionisation energies (IE), when known, are also included [39].

2. Experimental

The standard SIFT technique has been described in numerous publications [1–3,12,34] so it is sufficient here to summarise it as follows. The precursor ions H_3O^+, NO^+ and $O_2^{+\bullet}$ are generated in a discharge ion source, mass selected by a quadrupole mass filter and then injected as selected ionic species into fast-flowing helium carrier gas in a flow tube. All the reactant compounds included in this study are either liquids or low melting point solids at room temperature. Their vapours (above the liquid or solid) supported in dry air in a sealable plastic bag are then introduced at controlled flow rates into the ion swarm/carrier gas by puncturing the bag with a hypodermic needle connected to the inlet port of the SIFT instrument. The loss rates of the precursor ions and the resulting product ions are determined by a downstream quadrupole mass spectrometer. This can be operated either in the full scan mode (FSM) over a predetermined *m*/*z* range to obtain a spectrum of the reactant and product ions or in the multi-ion mode (MIM) in which the spectrometer is switched and dwells on selected reactant/product ions as their count rates are determined [2]. The FSM is primarily used to identify the product ions of the reactions and the MIM is used to accurately determine product ion distributions.

Determination of the count rates of the precursor and product ions allows the rate coefficients and the product ion distributions to be deduced. The concentrations of the reactant compound vapours in the dry air are unknown. So the relative rate coefficients for the reactions of the three precursor ion species with each compound are determined by measuring the relative decay rates of the H_3O^+, NO^+ and $O_2^{+\bullet}$ ions, simultaneously injected into the carrier gas, as the compound/dry air sample flow rate is varied. The H_3O^+ reactions invariably proceed via exothermic proton transfer, which are known to occur at their respective collisional rates, the rate coefficients for which are calculable using the known [35] (or estimated) polarisabilities and dipole moments of the reactant molecules [36]. Hence, from the relative decay rates of the three injected ionic species the rate coefficients for the NO^+ and $O_2^{+\bullet}$ reactions can be determined. Details of this technique have been given in several papers [12–18]. This relative method has been used exclusively in these studies.

Additionally, in order to support SIFT-MS analyses, the rate coefficients and the ion product distributions were determined under three different conditions: (i) using dry helium carrier gas, i.e. with only the compound/dry air mixture entering the carrier gas; (ii) with laboratory air (relative humidity about 1.5%) also introduced into the carrier gas at a flow rate typical of that used for SIFT-MS analyses of ambient air and exhaled breath (about 2 ml/s at standard atmospheric pressure [1]); and (iii) with humid air (relative humidity about 6%) introduced at this same flow rate obtained above liquid water held near 37 °C to simulate exhaled breath. These extra experiments were carried out to study the influence of water vapour on the production of the hydrates of the product ions of these reactions, because in SIFT-MS analyses any hydrates must be included in the product ion sum to obtain accurate analyses [37]. We pay some attention to the formation of these hydrates in the discussion that follows.

As always, to prevent condensation of water vapour and the reactant compounds, the sample inlet lines are heated to about 100 °C. All the present studies were carried out at a helium carrier gas pressure of 100 Pa at room temperature (296–300 K).

3. Results and discussion

The calculated collisional rate coefficients, k_c, for the H_3O^+, NO^+ and $O_2^{+\bullet}$ reactions together with the experimentally-derived rate coefficients, *k*, for the NO^+ and $O_2^{+\bullet}$ reactions and the percentage product distributions for all 30 reactions are given in Table 1. As can be seen, the *k* values for the NO^+ and $O_2^{+\bullet}$ reactions are all very close to their respective k_c values, which is beneficial for SIFT-MS analyses of these compounds. We now discuss the product distributions for the reactions of groups of similar compounds.

3.1. 2-Hydroxyphenol, 2-, 3-, 4-methylphenol and 4-ethylphenol

The reactions of H_3O^+ with all five compounds (M), proceed via non-dissociative proton transfer producing only the protonated parent molecule MH^+ (as observed previously for the phenol reaction [13]). The reaction of the methyl phenol isomers proceed thus:

$$H_3O^+ + HOC_6H_4CH_3 \rightarrow C_7H_9O^+ + H_2O \quad (1)$$

It is well known that the OH group in phenols is acidic and that the carbon-oxygen bond is much stronger in phenols than in alcohols [38]. Thus, protonation most probably occurs on the aromatic ring rather than on the OH group and so H_2O elimination does not occur. This simplifies the analysis of these compounds using SIFT-MS. However, the present experiments showed that when water vapour is present in the helium carrier gas (as introduced in the humid sample to be analysed), the monohydrate and sometimes much smaller fractions of the dihydrate of the MH^+ product ions, viz. $MH^+(H_2O)_{1,2}$ ions, appear. These can be formed in three-body association reactions, thus:

$$MH^+ + H_2O + He \rightarrow MH^+H_2O + He \quad (2)$$

They may also be formed in ligand switching reactions of the kind:

$$H_3O^+(H_2O)_n + M \rightarrow MH^+(H_2O)_{n-1} + 2H_2O \quad (3)$$

where *n* is 1, 2 or 3. The hydrated hydronium ions are inevitably formed in the carrier gas when humid samples such as exhaled breath are introduced [37]. An interesting point is that the three protonated methylphenol isomers and

Table 1

Rate coefficients (*k*), and ion product percentages (in parentheses) for the reactions of H_3O^+, NO^+ and $O_2{}^+$ with the compounds indicated

Molecule	α^a 10^{-24} (cm^3)	μ^a (D)	H_3O^+		NO^+		$O_2{}^+$	
			Product	[k_c]	Product	k [k_c]	Product	k [k_c]
2-Hydroxyphenol,$C_6H_6O_2$	*12 ± 2*	*1.5 ± 0.3*	$C_6H_6O_2H^+$ (100)	[2.7]	$C_6H_6O_2{}^+$ (100)	2.3 [2.3]	$C_6H_6O_2{}^+$ (100)	2.2 [2.2]
2-Methylphenol, C_7H_8O	*13 ± 2*	*1.5 ± 0.3*	$C_7H_8OH^+$ (100)	[2.8]	$C_7H_8O^+$ (100)	2.2 [2.3]	$C_7H_8O^+$ (100)	2.2 [2.3]
3-Methylphenol, C_7H_8O	*13 ± 2*	*1.5 ± 0.3*	$C_7H_8OH^+$ (100)	[2.8]	$C_7H_8O^+$ (100)	2.0 [2.3]	$C_7H_8O^+$ (100)	2.1 [2.3]
4-Methylphenol, C_7H_8O	*13 ± 2*	*1.5 ± 0.3*	$C_7H_8OH^+$ (100)	[2.8]	$C_7H_8O^+$ (100)	2.2 [2.3]	$C_7H_8O^+$ (100)	2.2 [2.3]
4-Ethylphenol, $C_8H_{10}O$	*13 ± 2*	*1.5 ± 0.3*	$C_8H_{10}O^+H$ (100)	[2.8]	$C_8H_{10}O^+$(100)	2.4 [2.3]	$C_7H_7O^+$ (60) $C_8H_{10}O^+$ (40)	2.4 [2.2]
Phenylmethanol, C_7H_8O	*13 ± 2*	*1.5 ± 0.3*	$C_7H_7{}^+$ (100)	[2.8]	$C_7H_7{}^+$ (10) $C_7H_7O^+$ (40) $C_7H_8O^+$ (50)	2.3 [2.3]	$C_6H_7{}^+$ (20), $C_7H_7{}^+$ (5) $C_7H_8{}^+$ (5), $C_7H_7O^+$ (25) $C_7H_8O^+$ (45)	2.3 [2.3]
2-Phenylethanol, $C_8H_{10}O$	*15 ± 2*	*1.5 ± 0.3*	$C_8H_9{}^+$ (100)	[2.9]	$C_8H_9O^+$ (10) $C_8H_{10}O^+$ (90)	2.3 [2.4]	$C_7H_7{}^+$ (20), $C_7H_8{}^+$ (75) $C_8H_{10}O^+$ (5)	2.4 [2.4]
1-Phenylethanol, $C_8H_{10}O$	*15 ± 2*	*1.5 ± 0.3*	$C_8H_9{}^+$ (100)	[2.9]	$C_7H_7{}^+$(10), $C_8H_9{}^+$(40) $C_8H_{10}{}^+$(30),$C_8H_9O^+$(5) $C_8H_{10}O^+$ (15)	2.2 [2.4]	$C_6H_7{}^+$ (5), $C_7H_7{}^+$ (20) $C_7H_6O^+$(20) $C_8H_9O^+$ (5)	2.3 [2.4]
1,4-Benzoquinone, $C_6H_4O_2$	14.5	0	$C_6H_4O_2H^+$ (100)	[2.2]	$NO^+C_6H_4O_2$ (100)	1.2 [1.8]	$C_5H_4O^+$(20), $C_4H_2O_2{}^+$ (5) $C_6H_4O_2{}^+$ (75)	1.8 [1.8]
Cyclohexanone, $C_6H_{10}O$	*12 ± 2*	*2.8 ± 1*	$C_6H_{10}OH^+$ (100)	[4.0]	$C_6H_{10}O^+$ (35) $NO^+C_6H_{10}O$ (65)	3.3 [3.3]	$C_2H_4{}^+$ (5), $C_4H_7{}^+$ (5) $C_5H_9{}^+$ (10) $C_5H_7O^+$(5)	3.2 [3.2]

Note.: Collisional rate coefficients [k_c], are given in square brackets. The k and [k_c] values are in units of 10^{-9} cm^3 s^{-1}.

[a] Estimated values of polarisability, α, and dipole moment, μ, are shown in italics. The single known value of α is from reference [35].

protonated ethylphenol clearly form a monohydrate, with the dihydrate being barely discernible in the product ion spectrum, yet the protonated 2-hydroxyphenol clearly forms both mono and dihydrate ions. As more water vapour is introduced, the dihydrate becomes more abundant than the monohydrate in the carrier gas. Regardless as to the formation route for $MH^+(H_2O)_{1,2}$ hydrates, they must be included in SIFT-MS analyses as product ions [37].

The reaction of NO^+ with all five compounds proceeds via non-dissociative charge transfer producing the parent cations, M^+, thus:

$$NO^+ + HOC_6H_4CH_3 \rightarrow C_7H_8O^{+\bullet} + NO^\bullet \quad (4)$$

Obviously, the ionisation energies, IE, of all these compounds must be lower than IE(NO) which is 9.26 eV [39]. The IE values that are known are given in Fig. 1. On addition of humid air to the carrier gas the M^+ ions are seen to form monohydrates only, these becoming an increasing fraction of the product ions as the water vapour in the carrier gas is increased. We conclude that NO^+ ions are also very useful in the analysis of these compounds (see later).

The reactions of $O_2^{+\bullet}$ with these compounds are also relatively simple. They proceeding via charge transfer that is non-dissociative forming only the parent cation like reaction (4) that is except for the 4-ethylphenol, which results in two product ions, thus:

$$O_2^{+\bullet} + HOC_6H_4C_2H_5 \rightarrow C_8H_{10}O^{+\bullet} + O_2 \quad (5a)$$

$$O_2^{+\bullet} + HOC_6H_4C_2H_5 \rightarrow C_7H_7O^+ + CH_3^\bullet + O_2 \quad (5b)$$

It is most likely that reaction (5b) involves the loss of $CH_3^\bullet$ from the ethyl group. The product ions of each of these reactions form monohydrates only, including both product ions of reaction (5). This relatively simple ion chemistry also allows $O_2^{+\bullet}$ to be used as the precursor ion for SIFT-MS analyses of these compounds.

3.2. 1-Phenylmethanol, 1- and 2-phenylethanol

The reactions of these three alcohols with H_3O^+ proceed via exothermic proton transfer to produce the excited $(MH^+)^*$ nascent ions, which then dissociate losing an H_2O molecule leaving the hydrocarbon ion, e.g.:

$$H_3O^+ + C_6H_5CH_2OH \rightarrow C_7H_7^+ + H_2O + H_2O \quad (6)$$

The stable protonated molecules, MH^+ are not seen at all, indicating that H_2O loss is spontaneous. However, when water vapour is introduced into the carrier gas, both the monohydrate and dihydrate ions of MH^+ are seen. These must be formed from the $H_3O^+(H_2O)_{1,2,3}$ ions by switching reactions of the kind indicated by reaction (3). The higher order water clusters $H_3O^+(H_2O)_{2,3}$ become more abundant in the carrier gas as the water vapour increases as do the dihydrates of the MH^+ ions.

As can be seen in Table 1, the NO^+ and $O_2^{+\bullet}$ reactions with these molecules result in three or more product ions except for the NO^+ reaction with 2-phenylethanol, which results mostly in the parent cation. This means that the IE of 2-phenylethanol is less than IE(NO), i.e. 9.26 eV. Since the reactions of NO^+ with both phenylmethanol and 1-phenylethanol result in a fraction of their parent cations, this also indicates that the IE values of these compounds also are less than or very close to 9.26 eV. Inspection of Table 1 shows that several well-known reaction mechanisms are occurring in parallel as, for example, in the phenylmethanol reaction:

$$NO^+ + C_6H_5CH_2OH \rightarrow C_7H_8O^{+\bullet} + NO^\bullet \quad (7a)$$

$$NO^+ + C_6H_5CH_2OH \rightarrow C_7H_7O^+ + HNO \quad (7b)$$

$$NO^+ + C_6H_5CH_2OH \rightarrow C_7H_7^+ + HNO_2 \quad (7c)$$

Thus, reaction (7a) is charge (electron) transfer, (7b) is hydride ion (H^-) transfer and (7c) is hydroxide ion (OH^-) transfer. There are numerous examples of the occurrence of these reaction processes in NO^+ reactions with several types of organic compounds [12–18]. The relative complexities of these ion chemistries make NO^+ and $O_2^{+\bullet}$ unlikely precursor ions for analysis of these compounds.

3.3. 1,4-Benzoquinone and cyclohexanone

The reactions of H_3O^+ with these compounds proceed via direct proton transfer producing only the protonated parent molecules, MH^+, which efficiently form their monohydrates in the presence of water vapour, but little or no dihydrates. The formation of the monohydrates is so efficient that these MH^+H_2O ions represent more than 90% of the product ion spectrum when laboratory air is introduced into the helium carrier gas. This behaviour is reminiscent of that of protonated ketones that efficiently form monohydrates [28,40]. Clearly, the presence of only small amounts of water vapour influences the product ion distribution when H_3O^+ is used to analyse these types of compounds, but this can readily be accounted for in SIFT-MS analyses [37].

The reactions of NO^+ with these compounds is reminiscent of the well-understood NO^+/ketone ion chemistry in which adduct formation and charge transfer are the dominant processes [14,20]. Since the IE of 1,4-benzoquinone at a value of 10.0 eV [39] is greater than IE(NO), charge transfer cannot occur and this reaction proceeds only via fast ($k \sim 2/3k_c$) three-body association forming $NO^+C_6H_4O_2$ ions (see Table 1). The efficiency of this reaction, similar to the efficiency of the association of NO^+ with aliphatic ketones [28], indicates that the binding energy of NO^+ to $C_6H_4O_2$ is relatively large and that the lifetime of the nascent reaction complex is long with respect to the collisional frequency of ions with atoms of helium carrier gas. However, the proximity of the IE of cyclohexanone (=9.16 eV; [39]) to IE(NO) allows for parallel charge transfer and association to occur, thus:

$$NO^+ + C_6H_{10}O \rightarrow (NO^+C_6H_{10}O)^* \rightarrow C_6H_{10}O^{+\bullet} + NO^\bullet \quad (8a)$$

$$NO^+ + C_6H_{10}O \rightarrow (NO^+C_6H_{10}O)^* + He \rightarrow NO^+C_6H_{10}O + He \quad (8b)$$

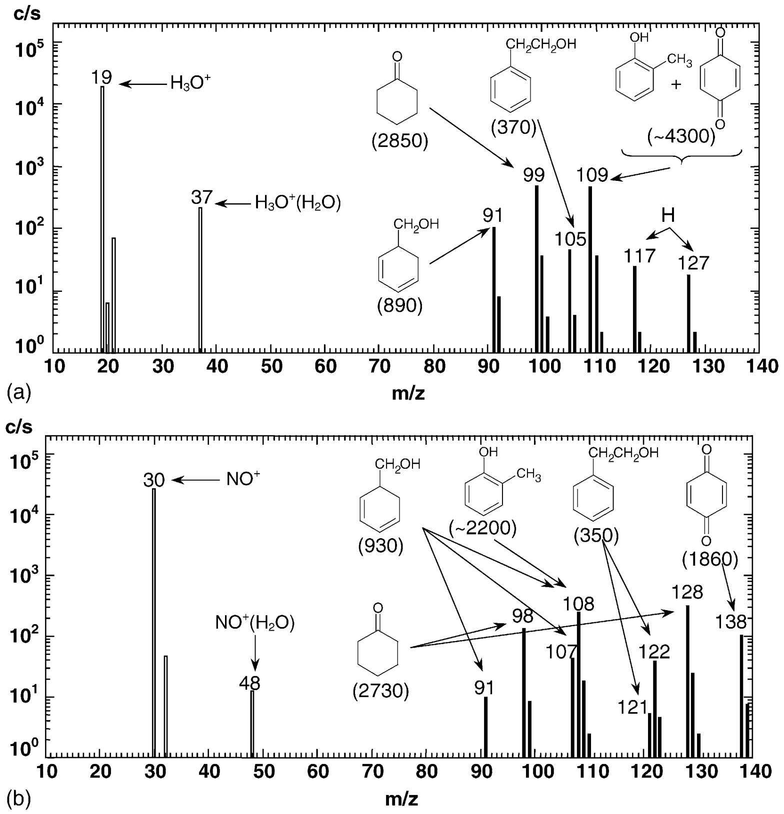


Fig. 2. FSM spectra obtained using (a) H_3O^+ precursor ions and (b) NO^+ precursor ions when a mixture of the vapours of the indicated compounds in dry air is flowed into the helium carrier gas. The numbers in parentheses are their concentrations in parts per billion as derived from MIM data for the same mixture (see the text). The ions indicated by H in panel (a) are the monohydrates of the ions at *m*/*z* values of 99 and 109.

Clearly, the efficiency of adduct formation as indicated by reaction (8b) is dependent on the helium carrier gas pressure. At the pressure of 100 Pa at which these experiments were performed, adduct formation is the dominant process (see Table 1). The importance of the energy decrement (IE(M) − IE(NO)) in determining the relative importance of charge transfer and adduct formation in NO^+/ketone reactions has been discussed in detail in a recent paper [28]. NO^+ is a useful precursor ion for SIFT-MS analyses of ketones and also quinones.

Again, the $O_2^{+\bullet}$ charge transfer reactions with these compounds result in multiple product ions, especially so for the vulnerable cyclohexanone structure. The product ions so formed are also seen on their 70 eV electron impact mass spectra that are readily available in the NIST database [41].

3.4. Sample analyses using H_3O^+ and NO^+ precursor ions simultaneously

To demonstrate the power of SIFT-MS using both H_3O^+ and NO^+ precursor ions in combination for the analysis of a given air sample, we carried out the following experiment. Small amounts of 2-methylphenol and 1,4-benzoquinone (both solids at room temperature) and phenylmethanol, 2-phenylethanol and cyclohexanone (all liquids) were introduced into a sealed plastic bag, which was then inflated with dry cylinder air. These five compounds were chosen from the ten because they all have appreciable vapour pressures at room temperature. The air/vapour mixture was then introduced into the carrier gas of the SIFT-MS instrument and FSM spectra were obtained using both H_3O^+ and NO^+ precursor ions. These spectra are shown in Fig. 2. MIM data of the observed precursor and product ions were also obtained on the same mixture in order to obtain reliable quantification of the relative partial vapour pressures of the individual compounds. The partial pressures given in Fig. 2 were obtained using the rate coefficients and product ion distributions for the individual reactions as given in Table 1. Three of the five compounds, M, are unambiguously identified using H_3O^+ ions, these being the cyclohexanone and 2-phenylethanol (MH^+ at *m*/*z* values of 99 and 105, respectively) and phenylmethanol ($(MH\text{-}H_2O)^+$ at *m*/*z* of 91). However, both the 2-methylphenol and 1,4-benzoquinone (having a common molecular weight of 108 Da) produce MH^+ ions at the same *m*/*z* value of 109 and so only the sum of their partial pressures can be obtained.

This dilemma can be resolved using NO^+ precursor ions. 2-Methylphenol and 1,4-benzoquinone react differently with NO^+ ions, the 2-methylphenol undergoes charge transfer producing $M^{+\bullet}$ only at *m*/*z* of 108, whereas 1,4-benzoquinone reacts to form only the adduct ion NO^+M at *m*/*z* of 138. Of the other three compounds in the mixture, 2-phenylethanol produces mostly $M^{+\bullet}$ ions at *m*/*z* of 122, phenylmethanol undergoes dissociative charge transfer and cyclohexanone undergoes parallel association and charge transfer. Hence, these reactions result in the multiple products given in Table 1. However, these three compounds can be quantified using one of their product ions and the appropriate scaling factors (branching ratios).

4. Concluding remarks

The kinetic data obtained by this SIFT study has extended the SIFT-MS database to include some phenols and phenyl alcohols. It has also clearly demonstrated that for three phenyl alcohols, proton transfer results predominantly in dissociation of the protonated parent compounds. This is well known to occur for most aliphatic alcohols [13] and now it is seen to be so for these phenyl alcohols. Obviously, this must be appreciated when attempting to analyse air containing these compounds using proton transfer reaction as is used for PTR-MS [23,32] and for SIFT-MS [1–3] when using H_3O^+ precursors. This study also demonstrates the value of charge transfer reactions and association reactions using NO^+ precursor ions for trace gas analysis.

Many compounds in air samples can be analysed to good precision by SIFT-MS using either H_3O^+ or NO^+ precursor ions [12]. However, we have demonstrated by a simple analysis of an air/compound mixture that it is sometimes useful to use both these precursor ions in combination to analyse a given sample. In some cases, this approach can resolve ambiguities resulting from the presence of isomers (and the like) that result in product ions at the same *m*/*z* values when using either H_3O^+ or NO^+ precursor ions only. In some cases it is helpful also to use $O_2{}^+$ precursor ions [12].

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