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A selected ion flow tube study of the reactions of H_3O^+, NO^+ and $O_2^{+\bullet}$ with seven isomers of hexanol in support of SIFT-MS

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ABSTRACT

A selected ion flow tube, SIFT, study has been carried out of the reactions of H_3O^+, NO^+ and $O_2^{+\bullet}$ with seven structural isomers of hexanol with the common molecular formula $C_6H_{14}O$ and molecular weight 102 that are commonly met in food science studies. The main objective is to provide the kinetic data, i.e., the rate constants and the product ion branching ratios to be included in the SIFT-MS kinetics database that would allow the separate identification and quantification of these compounds. The specific compounds involved are the primary alcohols 1-hexanol, $CH_3(CH_2)_5OH$; 2-ethyl-1-butanol, $(C_2H_5)_2CHCH_2OH$; 4-methyl-1-pentanol, $(CH_3)_2CH(CH_2)_3OH$; secondary alcohols 2-hexanol, $CH_3(CH_2)_3CH(OH)CH_3$; 4-methyl-2-pentanol, $(CH_3)_2CHCH_2CH(OH)CH_3$; 3-hexanol, $CH_3(CH_2)_2CH(OH)CH_2CH_3$ and a tertiary alcohol 3-methyl-3-pentanol, $(CH_3CH_2)_2C(CH_3)OH$. The reactions of H_3O^+ proceed via dissociative proton transfer invariably producing $C_6H_{13}^+$ hydrocarbon ions (m/z 85). The reactions of NO^+ proceed predominantly via hydride ion transfer producing $C_6H_{13}O^+$ ions (m/z 101) for the primary and secondary hexanols, with a minor fragmentation channel for the primary hexanols, when a H_2O molecule is lost from the major product ion resulting in $C_6H_{11}^+$ ions (m/z 83), and a minor channel representing the process of hydroxide ion transfer producing $C_6H_{13}^+$ ions (m/z 85) for secondary alcohols. The latter reaction is also the dominant process for the tertiary alcohol. $O_2^{+\bullet}$ reacts by dissociative charge transfer in all reactions resulting in multiple product ions analogous to electron ionization. The differences in product ion branching ratios and fragmentation patterns can thus assist SIFT-MS identification of the different hexanol isomers in cases when they are not present in complex mixtures.

1. Introduction

Volatile alcohols are ubiquitous in nature and must be expected to be detected when studying the volatile organic compounds, VOCs, released by plants and animals, cell and bacterial cultures and natural foods and food products, often termed biogenic VOCs or BVOCs [1]. Selected ion flow tube mass spectrometry, SIFT-MS [2,3], has been developed for the study of such systems, with special attention being given to the real time analysis of exhaled breath [4] in which the three simplest aliphatic alcohols methanol, ethanol and propanol are readily detected unambiguously [5], except to say that a challenge is constantly met, i.e., distinguishing between isomeric forms of VOCs, already demonstrated by 1-propanol and 2-propanol [6,7]. Some progress in isomeric detection can be made by analysis gaseous samples using the three different precursor ions H_3O^+, NO^+ and $O_2^{+\bullet}$, which are available for SIFT-MS analyses, by virtue of the fact that different product ions sometimes result in the reactions of these precursor ions with the different isomers of specific compounds [8,9]. This important point will be discussed more thoroughly later in this paper in relation to the present study. However, it is clear that the numbers of possible isomeric forms of a compound increases as the (constant) molecular weight of the compound increases and then using SIFT-MS the challenge becomes increasingly difficult. Then it usually becomes necessary to exploit gas chromatography, GC, to identify isomeric forms in complex mixtures. We have previously shown how 1-propanol and 2-propanol can be separated and quantified using a combination of GC and SIFT-MS [10].

The stimulus for the present study came from the observation that an alcohol of molecular weight 102 g/mol was present in the VOCs emitted by a bacterial culture and it is easy to see that such an alcohol can have several isomeric forms with the same molecular formula $C_6H_{14}O$. Polyatomic alcohols are very common in nature and have an inevitable place in everyday life. It is thus desirable that they can be analyzed by SIFT-MS. This requires a study of the kinetics of their reactions with the precursor ions

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used in SIFT-MS, as mentioned above, and the appropriate rate constants and product ions for the reactions included in the analytical kinetics library [11]; such studies will need to be carried out as and when required. However, the list of isomeric forms can be very long and we have limited the present kinetics study to seven alcohols with the common molecular formula $C_6H_{14}O$, as given above, these being 1-, 2-, 3-hexanol; 3-methyl-3-pentanol; 4-methyl-1-pentanol; 4-methyl-2-pentanol and 2-ethyl-1-butanol. The ultimate aim of this study is be able to identify and analyze these compounds using SIFT-MS and to develop a method to obtain their absolute concentration in real time.

The alcohols chosen for this study are not arbitrarily chosen; they are mostly of biogenic origin. 2-Ethyl-1-butanol is a member of the fragrance group of branched chain saturated alcohols that are used in cosmetics and also in non-cosmetics products such as household cleaners [12]. It is also known in the field of food science as an oxidation product of cheese components released following light exposure [13]. 4-Methyl-1-pentanol is released from crushed transgenic tobacco leaves by expressing *Aspergillus niger* [14] and together with 4-methyl-2-pentanol and 1-hexanol contributes to wine flavour [15]. Their known occurrences are summarized in Table 1.

Hence, the rate constants and the product ion distributions of the reactions of these seven chosen alcohols with H_3O^+, NO^+ and $O_2^{+\bullet}$ have been studied primarily to explore this ion chemistry and to investigate the feasibility of using the kinetic information to construct database entries for their quantification using SIFT-MS. It is now well understood that quantification of compounds, M, in humid samples by SIFT-MS must involve hydrated precursor ions, e.g., $H_3O^+(H_2O)_{1,2,3}$ and $NO^+(H_2O)_{1,2}$, and hydrated product ions, e.g., $MH^+(H_2O)_{1,2}$ and $[M{-}H]^+(H_2O)_{1,2}$, that inevitably form, if accurate concentration of M is to be obtained [2,30]. These hydrates, often termed cluster ions, can be formed via three-body reactions and ligand switching reactions, and we have also determined the three-body rate constants for some of these reactions.

2. Experimental

The conventional way to study the kinetics of ion-molecule reactions at thermal energies and to provide the required rate constants (often termed rate coefficients) and product ion for use in SIFT-MS analyses is by using the selected ion flow tube technique as described previously [2,31]. The SIFT technique has been used to study numerous ion-molecule reactions in several laboratories around the world, especially recently to study the reactions of H_3O^+, NO^+ and $O_2^{+\bullet}$ with many types of organic compounds [2,8,32–35]. Current SIFT-MS instruments can readily be used for this purpose, as described previously [7,36,37], and so only the specific detail of the present experimental procedure are outlined below.

2.1. Determination of the branching ratios and the rate constants for the bimolecular reactions of H_3O^+, NO^+ and $O_2^{+\bullet}$ with the alcohols $C_6H_{14}O$

In order to determine the product ions and their branching ratios of these reactions, the headspace of weak aqueous solutions of each alcohol (purchased from Sigma–Aldrich, 97-99% purity) were prepared at 20 °C and then the humid headspace was introduced into a *Profile 3* SIFT-MS instrument (Instrument Science Limited, Crewe, UK) via a heated calibrated capillary and full scan mass spectra were acquired whilst each of the three selected precursor ions were alternately injected into the helium carrier gas in the reactor flow tube. The range of mass-to-charge ratio (m/z) was chosen as 10–160, which covered all m/z values of the expected primary product ions and any adduct (hydrated) ions that might form. For each precursor ion, five mass spectra were obtained each with a total integration time of 60 s. The major ion product ions of each reaction were identified and their count rates were precisely determined in separate experiments using the multi-ion monitoring, MIM, mode [2]. In order to determine the primary ion product branching ratios of the reactions, it is necessary to plot the percentages of the individual product ions on a linear scale as a function of the sample mixture (headspace) flow rate. This flow rate was measured by a flow meter (manufactured by Voegtlin, Aesch, Switzerland) and regulated by a Swagelok needle valve. An example of these plots is shown in Fig. 1). By extrapolating to zero sample gas/vapour flow rate (i.e., estimating the percentage at zero sample concentration) the true primary branching ratios, excluding any secondary reactions, can be obtained. The flow rate of hexanol vapour which is proportional to concentration of $C_6H_{14}O$ molecules in He carrier gas, can be most conveniently expressed in dimensionless units of the logarithm of the reduction of the precursor ion signal $\ln(I_0/I)$. Only product ions with a resulting branching ratio greater than 3% are reported in this paper.

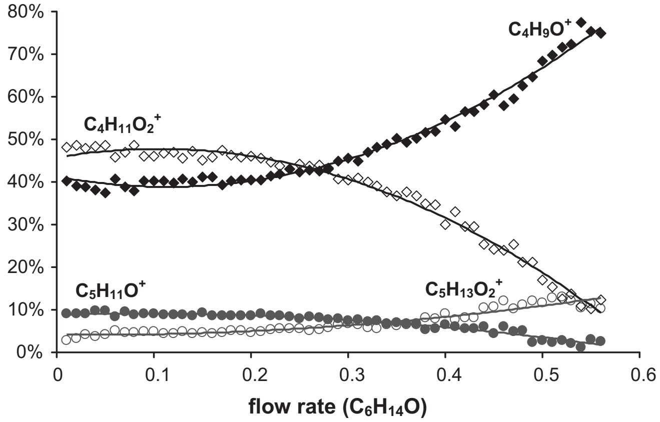

Fig. 1. Percentages of the primary ion product count rates for the reaction of $O_2^{+\bullet}$ with 3-methyl-3-pentanol as a function of the flow rate of the air/alcohol vapour mixture. The flow rate is in relative units corresponding to the rate of loss of the precursor ion count rate $\ln(I_0/I)$.

It is well established that proton transfer reactions of H_3O^+ proceed at the collisional rate, as described by the collisional rate constant k_c, when these reactions are exothermic by more than 40 kJ/mol [38]. Thus, the k_c for the reactions of H_3O^+ were calculated according to Su and Chesnavich [39] using their dipole moments [40] and polarisabilities calculated according to [41] (see Table 2). The rate constants for the reactions with NO^+ and $O_2^{+\bullet}$ (k) were then derived from their experimentally-derived decay rates relatively to that for the H_3O^+ reaction [42] by injecting all three precursors simultaneously and allowing them to react with the sample introduced at varied concentrations. The count rates of H_3O^+, NO^+ and $O_2^{+\bullet}$ were plotted on a semi-logarithmic scale as functions of the sample flow rate and the k values for the NO^+ and $O_2^{+\bullet}$ reactions were determined from the relative slopes of these plots [5]. The collisional rate constants for the NO^+ and $O_2^{+\bullet}$ reactions were also calculated according to [39]; they differ from the corresponding k_c for the H_3O^+ reactions only by virtue of the larger reduced mass of the NO^+/M and $O_2^{+\bullet}$/M systems as compared to that for the H_3O^+/M system.

In a later section we discuss the termolecular reactions of some of the product ions of the above reactions, focusing on the ion products $[M{-}H]^+$ of the NO^+ reactions following a similar procedure we adopted to determine the three-body rate constants for the reactions of protonated molecules MH^+ formed in the reactions of H_3O^+ with M, as described in detail in our previous publications [30,36,43].