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A selected ion flow tube, SIFT, study of the reactions of H_3O^+, NO^+ and $O_2{}^+$ ions with a series of diols

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Abstract

A selected ion flow tube study has been carried out of the reactions of H_3O^+, NO^+ and $O_2{}^+$ with 1,2-ethanediol (ethylene glycol), 1,2- and 1,3-propanediol, 1,2-, 1,3- and 1,4-butanediol, 1,5-pentanediol, 1,2-cyclopentanediol and 2-thioethanol (or 2-mercapto-ethanol, $HOCH_2CH_2SH$). The reactions of these species with H_3O^+ ions are assumed to proceed via exothermic proton transfer, their rate coefficients, k, being equal to the calculated collisional rate coefficients, k_c. On this basis, the experimental k values for most of the NO^+ and $O_2{}^+$ reactions are also close to their respective k_c values, although the k values for three of the NO^+ reactions are measurably smaller than their k_c values. In the H_3O^+ reactions the protonated parent ions, MH^+, are always minor product ions. $(MH–H_2O)^+$, resulting from the loss of H_2O from the nascent MH^+ ions being the major product ions. Three-body rate coefficients are derived for the association reactions of these product ions with water molecules. The most common process that occurs in the NO^+ reactions is hydride ion transfer producing $(M–H)^+$ ions, but for the 1,4-butanediol and 1,5-pentanediol reactions, hydride ion transfer and parallel H_2O elimination occur. The $O_2{}^+$ reactions all lead to multiple product ions, which must result from very diverse fragmentation processes. The value to selected ion flow tube mass spectrometry of these kinetic data is briefly alluded to. (Int J Mass Spectrom 218 (2002) 227–236)

Keywords: SIFT; Diols; Proton transfer; Charge transfer; Association; Dissociation

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1. Introduction

Our continued development of the quantitative selected ion flow tube mass spectrometry, SIFT-MS, [1–3] and its use in various fields (e.g., in medicine [4–6], animal husbandry [7,8] cell biology [9] and environmental science [10]) requires a continuous extension of the database of ion–molecule reaction kinetics on which the analyses depend [11–13]. In this regard, we have carried out detailed selected ion flow tube, SIFT, studies of the reactions of the precursor ions H_3O^+, NO^+ and $O_2{}^+$ that are used in the chemical ionisation of the trace gases in air samples with a wide variety of organic and inorganic compounds [14–25]. One class we have studied is the monoalcohols that are met in many media of interest, including human breath [26], above in vitro cell cultures [27] and in environmental air. To analyse alcohols in these media has required the detailed SIFT studies of the reactions of the above precursor ions with primary, secondary and tertiary alcohols that we carried out in the early stages of SIFT-MS development [15]. These studies revealed

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that the protonation of alcohols by H_3O^+ rarely resulted in the formation of stable parent protonated alcohol molecules, MH^+, but rather that the nascent $(MH^+)^*$ excited ions mostly dissociate releasing water molecules, thus leaving the corresponding hydrocarbon ions. However, in this regard, the H_3O^+ reactions of methanol and ethanol are exceptions in that the stable protonated alcohols are their only products [15,28]. The reactions of NO^+ with alcohols largely proceed via hydride ion transfer producing the appropriate $(M–H)^+$ ion (and an HNO molecule) and hydroxide ion transfer producing the appropriate hydrocarbon ion (and an HNO_2 molecule) [15]. These relatively simple reactions and the readily identifiable product ions facilitate SIFT-MS analyses of these alcohols. Further to this, the production in these H_3O^+ and NO^+ reactions of hydrocarbon ions, which do not efficiently associate with water molecules [25,29], eases the potential analytical difficulties that are sometimes met in SIFT-MS due to the large amount of water present in some media to be analysed (particularly breath) [30].

Recently, in pursuit of our growing interest in the molecular emissions from normal and abnormal cell cultures in vitro using SIFT-MS [27], we have found the need to understand the reactions of diols with the chosen precursor ions referred to above. Hence, we have now carried out a SIFT study of the reactions of H_3O^+, NO^+ and $O_2{}^+$ with 1,2-ethanediol (ethylene glycol), 1,2- and 1,3-propanediol, 1,2-, 1,3- and 1,4-butanediol, 1,5-pentanediol, 1,2-cyclopentanediol and 2-thioethanol (or 2-mercapto-ethanol, $HOCH_2CH_2SH$). The last compound is often used in cell culture media to reduce disulphide bonds [31]. As we will see, there are similarities and some differences in the mechanisms of these reactions when compared with the corresponding reactions of the monoalcohols. The implications of these observations to SIFT-MS are briefly discussed and assessed.

2. Experimental

We have described the well-known SIFT technique and the way in which we determine the rate coefficients and ion product distributions for the reactions of H_3O^+, NO^+ and $O_2{}^+$ ions with organic compounds in several previous publications [14,15], so it is only necessary to allude to the technique here. Because of the “sticky” nature of these diols (and many other organic compounds) and the lack of data on their vapour phase physical properties, it is not easy to measure the flow rates of their neat vapours into the carrier gas of the SIFT instrument, as is normally carried out to determine rates coefficients [32]. Rather, in these circumstances, we place a small drop of the (often-viscous) diol liquid into a sealed plastic bag and then inflate it with dry cylinder air. Then the air/diol vapour mixture (of unknown concentration) is introduced into the helium carrier gas/precursor ion swarm of the SIFT via a flow meter in the usual way. Because we do not know the absolute flow rate of the diol vapour, we cannot determine the rate coefficients, k, of the reactions directly. However, we can justifiably assume that the k for the proton transfer reactions of H_3O^+ with the diols are exothermic and proceed at their collisional rates, because the proton affinities (PAs) of alcohols invariably exceed the proton affinity of water molecules [33]. Their collisional rate coefficients, k_c, can be calculated if the polarisabilities and the dipole moments of the reactant diols are known or can be estimated. The collisional rate coefficients, k_c, for all reactions have been calculated using the parameterised trajectory formulation of Su and Chesnavich [34]. The rate coefficients, k, for the NO^+ and $O_2{}^+$ reactions can be obtained by comparing the decay rates of the H_3O^+, NO^+ and $O_2{}^+$ ions as they are injected together into the carrier gas of the SIFT. Here, these ions react with the diol as the air/diol mixture is introduced into the helium carrier gas at a measured (variable) flow rate. On the assumption that all the H_3O^+ reactions proceed at the respective collisional rates [35], the rate coefficients, k, for the NO^+ and $O_2{}^+$ reactions have been experimentally derived from the relative decay rates of the three ion species. The estimated absolute and relative uncertainties in these calculated rate coefficients are ±30 and ±15%, respectively. More detailed explanations of this approach are given in our previous publications [9,15,16].

The ion products of the reactions are determined by introducing the H_3O^+, NO^+ and O_2^+ ion species individually into the carrier gas and by scanning the downstream analytical mass spectrometer over an appropriate range. When the products for each reaction have been established, the percentage product distributions are determined using the multi-ion monitoring (MIM) mode [12] of the analytical mass spectrometer, i.e., by switching and dwelling on each product ion.

In SIFT-MS analyses of moist air samples such as breath, it is important to know if any of the product ions, R^+, of the analytical reactions undergo association with water molecules [36]. To investigate if any of the R^+ ions reacted with water molecules, controlled amounts of an air/water vapour mixture were introduced into the carrier gas whilst monitoring the R^+ ions using the MIM mode (see Fig. 1). The rate coefficients for these association reactions can be estimated

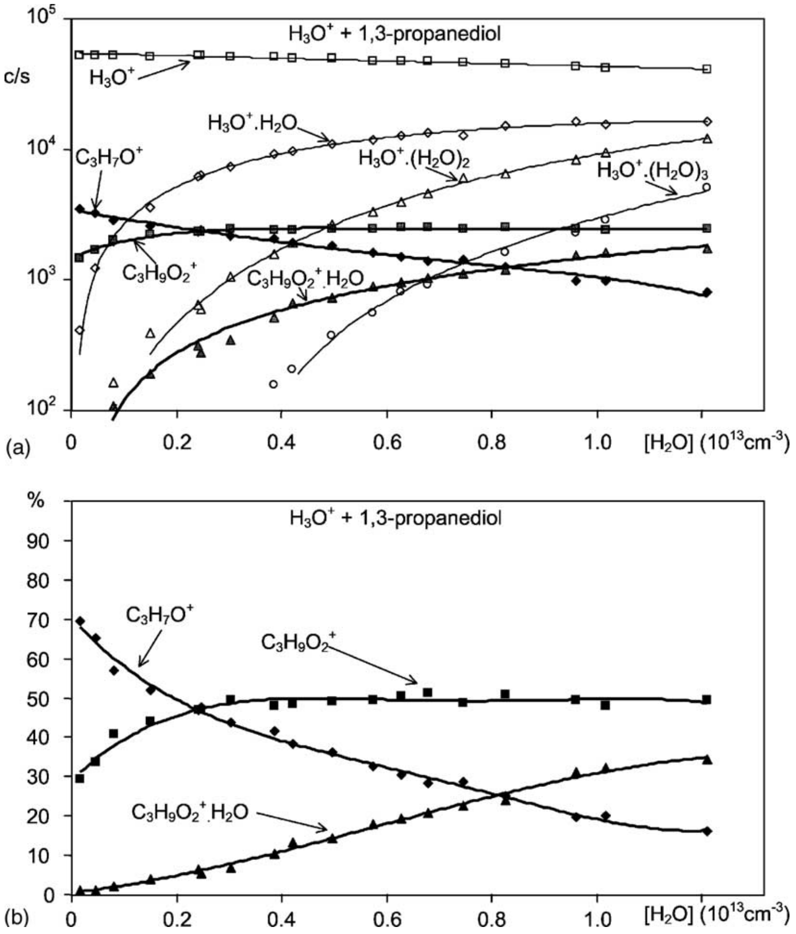

Fig. 1. Experimental SIFT data tracing the ion chemistry that occurs when H_3O^+ ions are injected into the helium carrier gas into which a small steady flow of 1,3-propanediol and variable flows of water vapour are introduced. (a) The decay curves. Count rates for the precursor and product ions indicated are plotted on a semilogarithmic scale as a function of the number density of water molecules $[H_2O]$ in the carrier gas. Note that the $C_3H_9O_2^+$ ions are both primary products of the reaction of H_3O^+ with 1,3-propanediol and also products of the association reaction of $C_3H_7O^+$ with H_2O. Analysis of these kinetic data provides the value of the three-body rate coefficient for this association reaction. (b) Percentages of the product ions count rates as a function of $[H_2O]$. Note that in the limit of zero $[H_2O]$ these percentages converge towards the true branching ratio (product ion distribution) for the reaction of H_3O^+ with 1,3-propanediol.

from the dependencies of the $[R^+{\cdot}H_2O]/[R^+]$ count rate ratios on the H_2O molecule number density in the carrier gas as is calculated from the distribution of the H_3O^+ ions and its hydrates $H_3O^+{\cdot}(H_2O)_{1,2,3}$. This procedure has been discussed previously in a paper on the influence of humidity on SIFT-MS analysis [36] and it has been used recently in our studies of aldehyde [25] and alkene reactions [14]. The true branching ratios for the primary H_3O^+/diol reactions are obtained in the absence of water vapour by the commonly used extrapolation procedure [32] indicated in Fig. 1b.

3. Results

3.1. Rate coefficients for the H_3O^+, NO^+ and $O_2{}^+$ reactions

As indicated above, it is a simple procedure to establish the relative rate coefficients for the H_3O^+, NO^+ and $O_2{}^+$ reactions with each of the diol species from the relative decay rates of the ions. However, for SIFT-MS analysis it is necessary to know the absolute rate coefficients and for this we first assume that the H_3O^+ reactions proceed at their collisional rates with $k = k_c$ [35]. As noted above, to calculate the respective k_c it is necessary to know the polarisabilities, α, and the dipole moments, μ, of the reactant diols [34]. Unfortunately, the value of μ is known only for 1,2-ethanediol [37]. For the remaining diols, we have estimated their α and μ (shown in Table 1 in italics) by adopting the values for similar alcohol molecules. This is acceptable, because the variability of these parameters within a series is not great. However, this procedure does place a larger than usual uncertainty of ±30% on the theoretical and hence the experimentally derived values of the rate coefficients. The calculated collisional rate coefficients, k_c, and the derived rate coefficients, k, for the NO^+ and $O_2{}^+$ reactions are listed in Table 1.

As can be seen, the k values for the NO^+ and $O_2{}^+$ reactions are at or close to their respective k_c values. The only significant exceptions are those for the NO^+ reactions with 1,2-ethanediol, 1,3-propanediol and 1,3-butanediol, the k values for which are clearly somewhat lower than their respective k_c values. A possible explanation for this is that these reactions probably proceed via the formation of the adduct ions $(NO^+{\cdot}M)^*$, which undergo partial unimolecular decomposition back to the initial reactants NO^+ and

Table 1
Rate coefficients for the reactions of H_3O^+, NO^+ and $O_2{}^+$ with the diols indicated

Molecule	m (Da)	α[a] ($10^{-24}\,cm^3$)	μ[a] (D)	k_c (H_3O^+) ($10^{-9}\,cm^3\,s^{-1}$)	k[b], k_c (NO^+)[b] ($10^{-9}\,cm^3\,s^{-1}$)	k[b], k_c ($O_2{}^+$)[b] ($10^{-9}\,cm^3\,s^{-1}$)
1,2-Ethanediol	62	5.7	2.28	[3.2]	1.7 [2.7]	2.7 [2.7]
1,2-Propanediol	76	*7.7 ± 1.0*	*2.43 ± 0.3*	[3.5]	2.8 [2.9]	2.7 [2.8]
1,3-Propanediol	76	*7.7 ± 1.0*	*2.43 ± 0.3*	[3.5]	1.6 [2.9]	2.4 [2.8]
1,2-Butanediol	90	*9.7 ± 1.0*	*2.58 ± 0.3*	[3.7]	2.3 [3.1]	2.3 [3.0]
1,3-Butanediol	90	*9.7 ± 1.0*	*2.58 ± 0.3*	[3.7]	1.1 [3.1]	3.3 [3.0]
1,4-Butanediol	90	*9.7 ± 1.0*	*2.58 ± 0.3*	[3.7]	2.6 [3.1]	2.6 [3.0]
1,5-Pentanediol	104	*11.7 ± 1.0*	*2.73 ± 0.3*	[3.9]	–[c] [3.2]	–[c] [3.2]
1,2-Cyclopentanediol	102	*10.1 ± 1.0*	*3.31 ± 0.3*	[4.4]	2.8 [3.6]	3.3 [3.5]
2-Thioethanol	78	*7.7 ± 0.5*	*2.2 ± 0.3*	[3.2]	2.8 [2.7]	2.7 [2.6]

Also given are their molecular weights, m, in Daltons (Da), their polarisabilities, α, in units of $10^{-24}\,cm^3$ and their permanent dipole moments, μ, in Debye (D). The collisional rate coefficients, k_c, calculated using the parameterised trajectory formulation of Su and Chesnavich [34] are given in square brackets.

[a] The known α and μ values [37] are shown in regular type. The estimated α and μ are shown in italics.

[b] The rate coefficients, k, for the NO^+ and $O_2{}^+$ reactions are experimentally derived by the procedure described in Section 2. The absolute and relative uncertainties in these calculated rate coefficients are ±30 and ±15%, respectively.

[c] The vapour pressure of 1,5-pentanediol is insufficient to allow a significant decay of the ion signals, and therefore these rate coefficients could not be derived.

M before collisional stabilisation or decomposition to the $(M–H)^+$ and HNO products can occur. Hence, the k values are somewhat less than their k_c values. Note in the 1,2-ethanediol reaction that the adduct ion $NO^+\cdot M$ is an observed minor product.

3.2. The H_3O^+ reactions

Without exception, these reactions proceed via the formation of a protonated parent molecule, MH^+, a fraction of which remain intact, but most of which dissociate with the ejection of an H_2O molecule (in one case two H_2O molecules; see below) as exemplified by the 1,2-ethanediol reaction:

$$H_3O^+ + HOCH_2CH_2OH \rightarrow C_2H_7O_2{}^+ + H_2O \qquad (1a)$$

$$\rightarrow C_2H_5O^+ + 2H_2O \qquad (1b)$$

In all these reactions, the dissociative channels are very much in the majority (see Table 2). The mechanism of water elimination from protonated diols is well understood following a recent chemical ionisation mass spectrometry study [38], where the structures of the product ions of protonated diols have been identified using the NR-MS technique. Thus, the product of reaction (1b) is protonated acetaldehyde. Also, on the basis of the thermochemical data and ab initio calculations' [38], there is an activation barrier of 99 kJ mol^{-1} for dissociation (H_2O elimination) of the lowest energy state of protonated 1,2-ethanediol. This activation energy is available in reaction (1b) by virtue of the difference between the proton affinities of H_2O and $HOCH_2CH_2OH$ which is (815.9–691) = 124.9 kJ mol^{-1}. Formation of the cyclic ether in this reaction is not allowed energetically, but from the data given in [38], both the open-chain aldehyde and the cyclic ether structures are energetically accessible for the $(MH–H_2O)^+$ ions formed following protonation of both 1,3-propanediol and 1,4-butanediol by H_3O^+.

In the reaction of the lone cyclic diol included in this limited study, a minor additional channel that results from the elimination of two H_2O molecules from the nascent $(C_5H_{11}O_2)^{*+}$ ion is observed. This produces the $C_5H_7{}^+$ hydrocarbon ion. Thus, the five-membered ring apparently remains intact and the product ion presumably is protonated cyclopentadiene (PA = 835 kJ mol^{-1} [33]). This cyclopentenyl cation has high stability due to its aromatic nature and it is the lowest energy isomer of $C_5H_7{}^+$ [39].

It is interesting to note that following protonation of the 2-thioethanol only the more exothermic elimination of H_2O occurs and H_2S elimination is not observed. The sum of the heats of formation of the observed products ($C_2H_4SH^+ + H_2O$) and those products that *would* result from H_2S elimination, i.e. ($C_2H_4OH^+ + H_2S$), differ only by 12.5 kJ mol^{-1} (assuming acetaldehyde-like structures for the ions) [39,40]. And so it is unlikely that simple energetics are controlling the exit channel for this reaction. Presumably, therefore, it is energy barriers that determine that only H_2O and not H_2S elimination occurs.

An interesting aspect of this ion chemistry relates to the reactivity of the product ions with H_2O molecules. Clearly, should the product $(MH–H_2O)^+$ ions associate with H_2O molecules then ions with the same m/z as MH^+ would be produced. This association does occur in all cases. So the branching ratios into the dissociative and non-dissociative channels need to be established in the absence of water vapour in the helium carrier gas, because its presence would falsely enhance the fraction of the product MH^+ ions. To estimate the potential contribution that this association process can make to the enhancement of the MH^+ ions, the three-body association reactions of the $(MH^+–H_2O)$ ions with H_2O molecules, e.g.,

$$C_2H_5O^+ + H_2O + He \rightarrow C_2H_7O_2{}^+ + He \qquad (2)$$

were studied by adding controlled amounts of water vapour to the helium carrier gas while simultaneously observing the loss of the H_3O^+ precursor ions and the production of $H_3O^+\cdot H_2O$ ions due to the analogous association reaction:

$$H_3O^+ + H_2O + He \rightarrow H_3O^+ \cdot H_2O + He \qquad (3)$$

A typical set of experimental data is shown in Fig. 1a. From such data, the rate coefficient for reaction (2) and the analogous reactions involving the other diol reaction products have been estimated from

Table 2
Product ions and their percentage (in brackets) and the associated neutral products for the reactions of H_3O^+ and NO^+ with diols indicated

Molecule	Product ions		
	H_3O^+	NO^+	O_2^+
1,2-Ethanediol, $C_2H_6O_2$	$C_2H_7O_2^+$ (35%) + H_2O $C_2H_5O^+$ (65%)[a] + $2H_2O$	$C_2H_6O_2{\cdot}NO^+$ (10%) $C_2H_5O_2^+$ (90%) + HNO	$C_2H_6O_2^+$ (15%) CH_5O^+ (50%) CH_3O^+ (35%) CH_4O^{+}[j]
1,2-Propanediol, $C_3H_8O_2$	$C_3H_9O_2^+$ (5%) + H_2O $C_3H_7O^+$ (95%)[b] + $2H_2O$	$C_3H_7O_2^+$ (100%) + HNO	$C_3H_8O_2^+$ (5%) $C_3H_7O^+$ (5%) $C_2H_5O^+$ (85%) CH_4O^+ (5%)
1,3-Propanediol, $C_3H_8O_2$	$C_3H_9O_2^+$ (30%) + H_2O $C_3H_7O^+$ (70%)[c] + $2H_2O$	$C_3H_7O_2^+$ (100%) + HNO	$C_3H_8O_2^+$ (10%) $C_3H_7O^+$ (60%) $C_3H_6O^+$ (20%) $C_2H_6O^+$ (5%) $C_2H_5O^+$ (5%)
1,2-Butanediol, $C_4H_{10}O_2$	$C_4H^{11}O_2^+$ (5%) + H_2O $C_4H_9O^+$ (95%)[d] + $2H_2O$	$C_4H_9O_2^+$ (100%) + HNO	$C_3H_7O^+$ (75%) $C_3H_6O^+$ (20%) $C_2H_5O_2^+$ (5%)
1,3-Butanediol, $C_4H_{10}O_2$	$C_4H_{11}O_2^+$ (10%) + H_2O $C_4H_9O^+$ (90%)[e] + $2H_2O$	$C_4H_9O_2^+$ (100%) + HNO	$C_4H_9O_2^+$ (5%) $C_4H_8O^+$ (30%) $C_3H_7O_2^+$ (10%) $C_3H_5O^+$ (10%) $C_2H_3O^+$ (45%)
1,4-Butanediol, $C_4H_{10}O_2$ (PA = 915.6 kJ mol^{-1})	$C_4H_{11}O_2^+$ (10%) + H_2O $C_4H_9O^+$ (90%)[f] + $2H_2O$	$C_4H_9O_2^+$ (40%) + HNO $C_4H_7O^+$ (60%) + HNO + H_2O	$C_4H_9O_2^+$ (5%) $C_4H_9O^+$ (5%) $C_4H_8O^+$ (15%) $C_4H_7O^+$ (20%) $C_3H_6^+$ (15%) $C_2H_4O^+$ (40%)
1,5-Pentanediol, $C_5H_{12}O_2$	$C_5H_{13}O_2^+$ (10%) + H_2O $C_5H_{11}O^+$ (90%)[g] + $2H_2O$	$C_5H_{11}O_2^+$ (5%) + HNO $C_5H_9O^+$ (95%) + HNO + H_2O	$C_5H_9O^+$ (10%) $C_5H_8^+$ or $C_4H_4O^+$ (30%) $C_4H_8^+$ (35%) $C_3H_5O^+$ (20%) $C_2H_4O^+$ (5%)
1,2-Cyclopentanediol, $C_5H_{10}O_2$	$C_5H_{11}O_2^+$ (2%) + H_2O $C_5H_9O^+$ (94%)[h] + $2H_2O$ $C_5H_7^+$ (4%) + $3H_2O$	$C_5H_9O_2^+$ (100%) + HNO	$C_5H_{10}O_2^+$ (13%) $C_5H_9O_2^+$ (2%) $C_5H_9O^+$ (8%) $C_5H_8O^+$ (51%) $C_5H_9^+$ or $C_4H_5O^+$ (6%) $C_4H_8^+$ or $C_3H_4O^+$ (9%) $C_4H_7^+$ or $C_3H_3O^+$ (11%)
2-Thioethanol, C_2H_6OS	$C_2H_7OS^+$ (5%) + H_2O $C_2H_5S^+$ (95%)[i] + $2H_2O$	$C_2H_6OS{\cdot}NO^+$ (5%) $C_2H_4SNO^+$ (60%) $C_2H_6OS^+$ (10%) $C_2H_4S^+$ (25%)	$C_2H_6OS^+$ (5%) $C_2H_4S^+$ (55%) CH_4S^+ (25%) CH_3S^+ (10%) CH_3O^+ (5%)

The major product ions are listed for the O_2^+ reactions, but the uncertain neutral products are not given. The three-body rate coefficient for the association reactions of water with the product ions are as follows: (a) 2.2×10^{-27} cm^6 s^{-1}; (b) 4.4×10^{-27} cm^6 s^{-1}; (c) 1.8×10^{-27} cm^6 s^{-1}; (d) 3.6×10^{-27} cm^6 s^{-1}; (e) 2.0×10^{-27} cm^6 s^{-1}; (f) 4.4×10^{-27} cm^6 s^{-1}; (g) 5.2×10^{-27} cm^6 s^{-1}; (i) $<0.1 \times 10^{-27}$ cm^6 s^{-1}; (j) CH_4O^+ overlaps with O_2^+ at *m/z* 32 and thus it cannot be excluded as a product in any of these reactions.

the known rate coefficient for reaction (3), which is $5.8 \times 10^{-28}\,\mathrm{cm^6\,s^{-1}}$ at 298 K [41] under these SIFT conditions (helium pressure of 0.7 Torr at a temperature of 300 K). These three-body rate coefficients are given in the footnote to Table 2. It is seen that these association reactions are several times faster than reaction (3). This is consistent with expectations in that the rates of three-body reactions tend to increase with the binding energy of the product ions and with the complexity of the reacting species [42].

It must be appreciated that ligand switching reactions of the kind indicated by reaction (4) may contribute to the production of MH^+ hydrates:

$$H_3O^+ \cdot H_2O + M \rightarrow MH^+ \cdot H_2O + H_2O \qquad (4)$$

Since these binary reactions generally proceed at the collisional rate they must always be considered. We have described in detail how such reactions are accounted for in a recent paper [30]. We conclude that the ligand switching reactions are responsible for only a small fraction of the $MH^+{\cdot}H_2O$ hydrates that are observed in these diol reactions.

Interestingly, the three-body reaction of H_2O molecules with the $C_3H_7O^+$ product ion of the 1,3-propanediol (protonated aldehyde structure) is clearly slower than the corresponding reaction of the isomeric $C_3H_7O^+$ product of the reaction of the asymmetrical 1,2-propanediol. This implies that these two $C_3H_7O^+$ product ions have different structures. Thus, the $C_3H_7O^+$ product of the 1,2-propanediol reaction with H_3O^+ may have a cyclic ether structure. Also, the product ions of the water elimination channels resulting from the H_3O^+ proton transfer reactions of the three butanediol isomers have different three-body rate coefficients for their association reactions with H_2O implying that these product ions have different structures.

Apparently, hydration of these ions does not stop with the formation of the monohydrates, since the dihydrate ions also appear on the product ion spectra. However, the third hydrate of protonated 1,2-propanediol is only weakly bound according to a recent high-pressure ion source equilibrium study [43]. As discussed earlier, it must be recognised that hydrated ions can also be produced in switching reactions of the kind:

$$\begin{aligned} &H_3O^+ \cdot (H_2O)_{1,2,3} + M \\ &\quad\rightarrow MH^+ \cdot (H_2O)_{1,2} + (1\ \mathrm{or}\ 2)H_2O \qquad (5) \end{aligned}$$

The hydrated hydronium ions $H_3O^+{\cdot}(H_2O)_{1,2,3}$ inevitably form when water is added to the helium carrier gas and so these switching reactions must occur to some extent.

Unexpectedly, the $C_2H_5S^+$ ion product that results from the elimination of H_2O from protonated 2-thioethanol does not hydrate to a significant extent, unlike the equivalent $C_2H_5O^+$ product ion of the 1,2-ethanediol reaction. This is probably because the binding energy of this $C_2H_5S^+$ ion to H_2O is smaller than that of the $C_2H_5O^+$ ion to H_2O (by about $50\,\mathrm{kJ\,mol^{-1}}$ according to the rules given in [44,45]).

3.3. The NO^+ reactions

A glance at Table 2 reveals that these reactions mostly proceed via hydride ion (H^-) transfer, which requires the formation of a “tight” complex. We, therefore, postulate that these reactions proceed firstly via the formation of the adduct ions $NO^+{\cdot}M$, which then dissociate to the observed products. However, in only the 1,2-ethanediol and the 2-thioethanol reactions are the adduct ions seen as (minor) stable products. The 1,2- and 1,3-propanediol, 1,2- and 1,3-butanediol and the 1,2-cyclopentanediol reactions proceed exclusively via H^- transfer, but the 1,4-butanediol and 1,5-pentanediol reactions proceed via parallel H^- transfer and H^- transfer together with H_2O elimination, e.g.:

$$NO^+ + HO(CH_2)_4OH \rightarrow {C_4H_9O_2}^+ + HNO \qquad (6a)$$

$$\rightarrow {C_4H_7O_2}^+ + HNO + H_2O \qquad (6b)$$

It is possible in these longer chain diol reactions that H_2O elimination results from cyclodehydration [46] of the product ions producing more stable structures, especially when the OH groups are on the end carbons, but we have no experimental or theoretical evidence to support this suggestion.

The 2-thioethanol reaction is more complex, four product ions being evident:

$$NO^+ + HOCH_2CH_2SH(+He) \rightarrow C_2H_6OSNO^+(+He) \quad (7a)$$

$$\rightarrow C_2H_4SNO^+ + H_2O \quad (7b)$$

$$\rightarrow C_2H_6OS^+ + NO \quad (7c)$$

$$\rightarrow C_2H_4S^+ + H_2O + NO \quad (7d)$$

Reaction (7a), which reveals the formation of the adduct ion, is a very minor channel, while reaction (7b) which, in effect, is the result of H_2O elimination from the adduct ion, is the major channel (see Table 2). Additionally, charge transfer (reaction (7c)), occurs because the ionisation energy (IE) of 2-thioethanol (9.1 eV [47]) is lower than that of NO (9.26 eV [47]). Remarkably, the charge transfer product ion also apparently undergoes dissociation by eliminating an H_2O molecule (reaction (7d)). We cannot say if the latter reactions occur sequentially or if this is a concerted reaction in which the observed product ions and the associated neutrals separate simultaneously from the excited adduction.

It is worthy of note that when laboratory air is added to the helium carrier gas (increasing the total pressure from 0.7 Torr to about 0.78 Torr) the adduct ion becomes a larger fraction of the product ions, as does the ion resulting from the elimination of H_2O from the adduct ion (reaction (7b)). These enhancements are at the expense of the charge transfer and dissociative charge transfer reactions (7c) and (7d). It is well known that N_2 and O_2 molecules are more efficient at stabilising nascent ion–molecule complexes [42], and this clearly happens in these reactions. Thus, the enhanced energy extraction diminishes the fraction of the charge transfer channels that presumably are the least exothermic of these product channels. Unfortunately, there is no thermochemical data to substantiate this hypothesis.

3.4. The O_2^+ reactions

Even though ionisation by O_2^+ ions is relatively “soft”, multiple products are produced, as can be seen by a glance at Table 2. The mass spectra of the product ions are not very different than the corresponding mass spectra produced by 70 eV electron impact, some of which are given in the NIST database [48]. It is futile to attempt to interpret these product ion mass spectra in detail. It is sufficient to note the obvious, which is that following the exothermic charge transfer reactions, the nascent parent ions, M^+, fragment at various bonds along the carbon skeleton. The nature of some of the product ions also indicates that H atoms also migrate between carbon atoms before dissociation of the parent ion occurs. In the case of the cyclic diol reaction all the ionic products cannot be positively identified (see Table 2) and it cannot be ascertained if ring opening occurs (without further experiments such as collisional dissociation studies). What is clear is that the multiple ionic products of these O_2^+ reactions means that O_2^+ ions are unsuitable as precursor ions for SIFT-MS analyses of mixtures containing diols.

4. Concluding remarks

The reactions of H_3O^+ with all the diols included in this study result in two products, the protonated parent ions, MH^+, which are always in the minority, and $(MH–H_2O)^+$ ions that result from the loss of H_2O from the nascent MH^+ ions. This is also the case for the reactions of the smaller monoalcohols [15], but for the longer chain monoalcohols, H_2O loss occurs exclusively leaving hydrocarbon ions as the single products of these reactions. These ion products of these diol reactions associate with H_2O molecules, whereas the hydrocarbon product ions of the monoalcohol reactions do not, which simplifies the quantification of the latter alcohol species using SIFT-MS.

The most common process that occurs in the NO^+ reactions with the diols is hydride ion transfer producing $(M–H)^+$ ions as are also produced in the NO^+/monoalcohol reactions [15]. Also, in the latter reactions parallel hydroxide ion transfer occurs producing (M–OH)$^+$ hydrocarbon ions, a process that is not seen in the NO$^+$/diol reactions. However, in the 1,4-butanediol and 1,5-pentanediol reactions, hydride ion transfer and parallel H_2O elimination occur, the latter representing the major product channel in both reactions (see Table 2). As is commonly the case, there are multiple productions in the $O_2{}^+$ reactions with these diols and this means that $O_2{}^+$ ions cannot be used to effect in SIFT-MS analyses of these species.

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