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A SIFT study of the reactions of H_2ONO^+ ions with several types of organic molecules

David Smith[a,*], Tianshu Wang[a], Patrik Španěl[b]

[a] Centre for Science and Technology in Medicine, School of Medicine, Keele University, Thornburrow Drive, Hartshill, Stoke-on-Trent ST4 7QB, UK
[b] V.Čermák Laboratory, J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223, Prague 8, Czech Republic

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Abstract

A selected ion flow tube (SIFT) study has been carried out of the reactions of hydrated nitrosonium ions, NO^+H_2O, which theory has equated to protonated nitrous acid ions, H_2ONO^+. One objective of this study was to investigate if this ion exhibits the properties of both a cluster ion and a protonated acid in their reactions with a variety of organic molecules. The chosen reactant molecules comprise two each of the following types—amines, terpenes, aromatic hydrocarbons, esters, carboxylic acids, ketones, aldehydes and alcohols. The reactant H_2ONO^+ (NO^+H_2O) ions are formed in a discharge ion source and injected into helium carrier gas where they are partially vibrationally excited and partially dissociated to NO^+ ions. Hence, the reactions of the H_2ONO^+ ions had to be studies simultaneously with NO^+ ions, the reactions of the latter ions readily being studied by selectively injecting NO^+ ions into the carrier gas. The results of this study indicate that the H_2ONO^+ ions undergo a wide variety of reaction processes that depend on the properties of the reactant molecules such as their ionisation energies and proton affinities. These processes include charge transfer with compounds, M, that have low ionisation energies (producing M^+), proton transfer with compounds possessing large proton affinities (MH^+), hydride ion transfer ($M–H^+$), alkyl radical ($M–R^+$), alkoxide radical transfer ($M–OR^+$), ion–molecule association (NO^+H_2OM) and ligand switching (NO^+M), producing the ions given in parentheses.

Keywords: SIFT; Nitrosohydronium ions; Protonated nitrous acid; Proton transfer; Charge transfer; Switching; Association

1. Introduction

Selected ion flow tube mass spectrometry (SIFT-MS) has been developed for the on line, real time analysis of trace gases in air and exhaled breath [1–3] with specific applications in mind, notably in medicine for clinical diagnosis and therapeutic monitoring and in physiology. The areas explored using SIFT-MS include amongst others: breath ammonia in renal failure [4,5], urine headspace analysis for bacterial infection [6] and prostate and bladder cancer [7], quantification of breath isoprene [8,9], ethanol metabolism [10], quantification of the most common normal metabolites present in breath [11,12], changes in urine headspace during ovulation [13] and acetonitrile in breath and urine related to cigarette smoking [14].

SIFT-MS utilises H_3O^+, NO^+ and $O_2{}^+$ precursor ions to chemically ionise the trace gases in the air/breath sample to the exclusion of the major air species, N_2, O_2 and CO_2 [1]. Quantitative analysis has required the construction of a large kinetics database of the reactions of these precursor ions with the wide variety of organic species that are present in polluted air and exhaled breath [2]. When the air samples are very humid, as is the case for exhaled breath, the hydrated ions $H_3O^+(H_2O)_{1,2,3}$ and $NO^+(H_2O)_{1,2}$ form from the H_3O^+ and NO^+ precursor ions in the helium carrier gas of the SIFT-MS instrument (see Section 2) and so the reactions of these cluster ions, which can act as precursor ions, need to be taken into account for accurate analyses [15–17]. This is especially important when the precursor ion is H_3O^+, because its hydrates can become the dominant ions in the carrier gas. So previously we have carried out detailed studies of the role of $H_3O^+(H_2O)_{1,2,3}$ ions, and hence the involvement of water vapour, in SIFT-MS analyses [15,16].

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[*] Corresponding author. Tel.: +44-1782-554253; fax: +44-1782-717079.
E-mail address: d.smith@bemp.keele.ac.uk (D. Smith).

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Under typical conditions for SIFT-MS analyses of breath using NO^+ precursor ions, about 10% of the NO^+ ions are converted to H_2ONO^+ ions, and their role as precursor ions must be accounted for in trace gas analyses. However, little is known about the reactivity of these ions and so we have carried out a study of their reactions with some selected organic compounds. Initially, we have chosen some neutral species that are relevant to air and breath analyses, these being alcohols, aldehydes, ketones, carboxylic acids, esters, amines, aromatic hydrocarbons and monoterpenes. We were guided in the choice of specific compounds by their reactivity with NO^+ ions, which is known from previous SIFT studies [17–23].

An additional motivation for the present study lies in the nature and importance of the H_2ONO^+ ion in other situations. It has been known for decades that this ion is an intermediate in the production of hydrated hydronium ions in the lower regions of the ionosphere [24] where it is formed by the three-body association of NO^+ ions with H_2O molecules:

$$NO^+ + H_2O + M \rightarrow H_2ONO^+ + M \qquad (1)$$

Further hydration of the NO^+H_2O ions finally results in their decomposition to hydrated hydronium ions and nitrous acid molecules, HNO_2 [24]. This is not surprising in the light of the current understanding that the structure of the product ion of reaction (1) is that of protonated nitrous acid H_2ONO^+ [25–27]. The nitrous acid molecule, HONO, is protonated on the (HON) oxygen and the resulting ion H_2ONO^+ represents just a single minimum on the potential energy surface that can lead to dissociation to H_2O and NO^+. So how does this ion react with neutral molecules, as the hydrate, $H_2O–NO^+$, by ligand switching or as protonated acid, H_2ONO^+ by proton transfer? The results of this study show that both processes can be invoked during their reactions, the dominant one depending on the properties of the reactant molecule such as its proton affinity and ionisation energy (IE). A list of the chosen molecules together with their ionisation energies and proton affinities are given in Table 1. During this study, the reactions of NO^+ ions with all the reactant molecules were re-examined in parallel in order to allow direct comparisons with the H_2ONO^+ reactions.

2. Experimental

The standard SIFT technique (and SIFT-MS) has been described in numerous publications [1–3,17–23,28] and so it is sufficient here to summarise it as follows. Precursor ions are generated in a microwave discharge ion source, mass selected by a quadrupole mass filter and then injected as selected ionic species into fast-flowing helium carrier gas. The reactant gases of interest are then introduced at controlled flow rates into the ion swarm/carrier gas where they react with the chosen precursor ion species. The loss rates of the precursor ions and the product ions of the reactions 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

Table 1
The ionisation energies (IE), in electron volts (eV), and proton affinities (PA), in kJ/mol, of the compounds included in this study, both in ascending order

Compounds	IE (eV)[a]	Compounds	PA (kJ/mol)[a]
Aniline $C_6H_5NH_2$	7.720 ± 0.002	Benzene C_6H_6	750.4
Trimethylamine $(CH_3)_3N$	7.85 ± 0.05	Acetaldehyde CH_3CHO	768.5
R-Limonene $C_{10}H_{16}$	8.3	Ethanol C_2H_5OH	776.4
Toluene $C_6H_5CH_3$	8.828 ± 0.001	Acetic acid CH_3COOH	783.7
Camphene $C_{10}H_{16}$	≤8.86	Toluene $C_6H_5CH_3$	784.0
Benzene C_6H_6	9.24378 ± 0.00007	Nitrous acid HNO_2	785.3[b]
Nitric oxide NO	9.2642 ± 0.00002	1-Butanol C_4H_9OH	789.2
Methyl benzoate $C_6H_5COOCH_3$	9.32 ± 0.04	1-Butanal C_3H_7CHO	792.7
2-Pentanone $CH_3(CH_2)_2COCH_3$	9.38 ± 0.06	Nitrous acid HNO_2	801.2[c]
Acetone CH_3COCH_3	9.703 ± 0.006	Acetone CH_3COCH_3	812
1-Butanal C_3H_7CHO	9.82 ± 0.04	*n*-Butanoic acid C_3H_7COOH	∼812[d]
1-Butanol C_4H_9OH	9.99 ± 0.05	2-Pentanone $CH_3(CH_2)_2COCH_3$	832.7
Ethyl acetate $CH_3COOC_2H_5$	10.01 ± 0.05	Ethyl acetate $CH_3COOC_2H_5$	835.7
n-Butanoic acid C_3H_7COOH	10.17 ± 0.05	Methyl benzoate $C_6H_5COOCH_3$	850.5
Acetaldehyde CH_3CHO	10.229 ± 0.0007	Aniline $C_6H_5NH_2$	882.5
Ethanol C_2H_5OH	10.48 ± 0.07	Trimethylamine $(CH_3)_3N$	948.9
Acetic acid CH_3COOH	10.65 ± 0.02	*R*-limonene $C_{10}H_{16}$	n.a.
		Camphene $C_{10}H_{16}$	n.a.

n.a.: not available.

[a] Data obtained from NIST database [32]. All IE values are evaluated, except those for *R*-limonene and camphene which are from single measurements.

[b] From [25], estimated uncertainty given as ±8 kJ/mol.

[c] From [27], basis-size effects reported as ±10 kJ/mol.

[d] Estimated from the proton affinities of acetic acid and propanoic acid [32].

reactant/product ions as their count rates are determined [2]. The FSM is primarily used to identify the product ions of individual reactions and the MIM is used to accurately determine the product ion distributions [2,17].

The focus of this study is the reactions of H_2ONO^+ ions ($m/z = 48$) and NO^+ ions ($m/z = 30$). These ions are produced in the ion source using laboratory air as the source gas. The NO^+ ions are produced in abundance, the count rate at the downstream mass spectrometer being typically 50,000 counts per second (c/s). The ions at m/z of 48 are only minor species in the ion source (they are formed predominantly by the slow three-body association of NO^+ ions with H_2O molecules [24]), so their typical count rates downstream were only about 200 c/s. In order to determine the even lower count rates of product ions to an acceptable accuracy, longer integration times than is normal in SIFT studies are required. Further to this, because the H_2ONO^+ ions are weakly bound, on injection they suffer partial dissociation to NO^+ ($+H_2O$) in collisions with the helium atoms of the carrier gas. Hence, their reactions had to be studied in parallel with the reactions of NO^+ ions that were detected at a comparable count rate. So to identify the ionic products of the H_2ONO^+ reactions those of the corresponding NO^+ reactions have to be known. The latter have been determined in previous SIFT studies, but it was simple to retune the upstream ion injection quadrupole for NO^+ ions only and to determine the product ion distributions again using the same sample of reactant neutrals. Both H_3O^+ and $O_2{}^+$ ions are also produced in abundance in the ion source, which allows these ions to be injected simultaneously with the NO^+ and H_2ONO^+ ions. Hence, the relative decay rates of all four ionic species could be determined as the reactant organic vapour is introduced into the carrier gas. This allows the absolute rate coefficients for the NO^+ and H_2ONO^+ ions to be determined using the rate coefficients for the corresponding H_3O^+ proton transfer reactions as a control, as outlined below.

The various organic vapours were introduced into the carrier gas as follows. A drop of the organic liquid is introduced into a sealable plastic bag, which is then inflated using dry cylinder air (to a volume of about 500 ml). The liquid vapour/dry air mixture is then introduced into the helium carrier gas via a variable leak (needle valve) by puncturing the bag with a hypodermic needle connected to the inlet port of the instrument. Determination of the count rates of the precursor and product ions as a function of the flow rate allows the rate coefficients and the product ion distributions for the reactions to be deduced. Clearly, the concentration of the liquid vapour in the dry air is unknown. So to determine the relative rate coefficients of the three precursor ion species with each organic vapour, we compare the decay rates of H_3O^+, NO^+, $O_2{}^+$ and H_2ONO^+ ions as the flow rate of the neutral reactant mixture 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 [29]. Hence, from the relative decay rates of the three injected ionic species, the rate coefficients for the NO^+, $O_2{}^+$ and H_2ONO^+ reactions can be determined (see the decay curves in Fig. 1). Details of this technique have been given in several papers [17–23]. This particular method has been used exclusively in these studies.

When the product ions of some of the reactions of the NO^+ ions derived from the break-up of the injected H_2ONO^+ ions were being determined, it became clear that partial charge transfer was occurring when this process is known to be slightly endothermic for ground vibronic state NO^+ ions (by virtue of the known ionisation energies of the

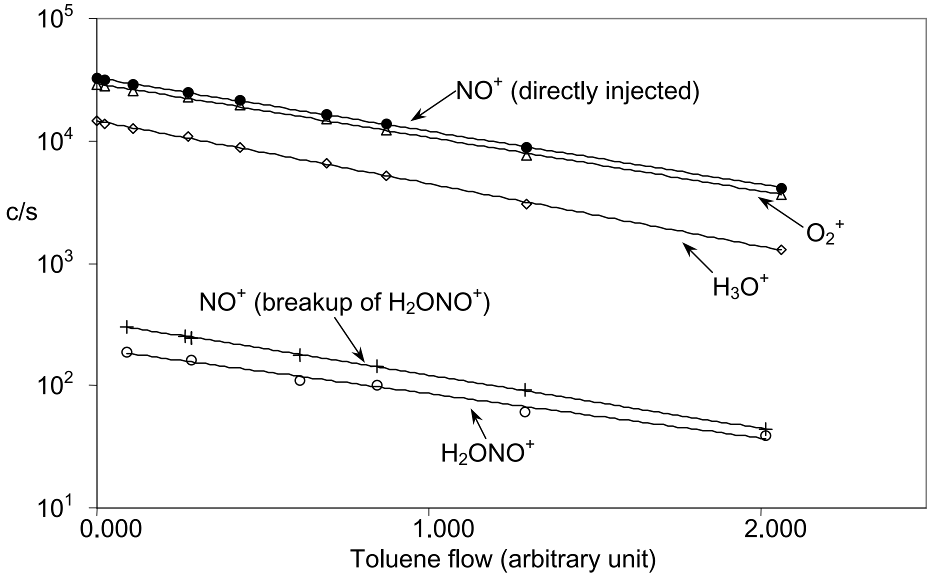

Fig. 1. Typical decay curves for the reactions of toluene with the ions indicated (see the text for further explanation).

reactant molecules; see Table 1). Further to this, it was also apparent that a similar phenomenon was occurring in some of the H_2ONO^+ reactions. The inevitable conclusion that we draw from these observations is that a fraction of both the H_2ONO^+ ions and the NO^+ ions derived from them are vibrationally excited. We assume that this excitation occurs in the collisions of the H_2ONO^+ ions with helium carrier gas atoms that induce partial break-up to NO^+ ions, as can be seen in Fig. 1. The laboratory energies of the injected ions had to be typically 40 eV to obtain sufficient current injection. Hence, the mean centre-of-mass H_2ONO^+/He energies are typically 1–2 eV, which is certainly sufficient to partially dissociate these molecular ions. So, in addition to measuring the rate coefficients and product ions in pure helium carrier gas, measurements were carried out following the introduction of some laboratory air into the carrier gas at a flow rate typical of that used for SIFT-MS analyses of ambient air [2,17]. This air is known to quench vibrationally excited NO^+ ions [30]. However, apparently, this quenching process is not so efficient for the H_2ONO^+ ions (see Section 3).

In an attempt to check the likely influence of this excitation of the precursor ions, an experiment was carried out in which the H_2ONO^+ ions were formed from injected NO^+ ions by introducing water vapour into the helium carrier gas, according to reaction (1). Unfortunately, significant amounts of the dihydrate ions $(H_2O)_2NO^+$ were also formed and these, together with the remaining (majority) NO^+ ions and the secondary reactions of the product ions of the several reactions with water molecules, rendered the data too complex to interpret with confidence. We return to this point again when we discuss the results of the reaction of H_2ONO^+ ions with toluene in the next section. Avoidance of such problems is the major reason why the SIFT method is preferred to the original flowing afterglow method for the study of ion–molecule reaction [31]. To prevent condensation of the organic vapours, the inlet lines are heated to about 100 °C. However, the reactant vapour is rapidly cooled in collisions with He carrier gas and thus the ion chemistry proceeds under thermalised conditions at 300 K. All the present studies were carried out at a helium carrier gas pressure of 0.7 Torr and at room temperature of 296–300 K.

3. Results and discussion

3.1. General comments

The reactions of NO^+ ions with all the organic species included in the present work have been studied previously using our SIFT and the results have been published in several papers [17–23]. A variety of reaction types are represented in these wide-ranging studies, which can be summarised as follows. When charge transfer is energetically allowed, that is when the IE of the reactant molecules (M) is lower than the recombination energy (RE) of the reactant NO^+ ions, it usually occurs efficiently and is either the only process or the dominant process. The IE for NO molecules, IE(NO) is 9.26 eV [32]. Charge transfer is exemplified by the reactions with amines that have low IE [21,32], e.g., trimethylamine:

$$NO^+ + (CH_3)_3N \rightarrow (CH_3)_3N^+ + NO \qquad (2)$$

The thermicity of such reactions (for ground state reactants and products) is given by $IE(NO) - IE(M)$. The molecules included in this study are listed in Table 1 in increasing order of their IE values, with IE(NO) inserted so that it can quickly be seen which reactions can energetically proceed via charge transfer. The experimentally determined values of the rate coefficients and product ions obtained for all the NO^+ reactions, which confirm the dominance of charge transfer for the lowest IE molecules [21], are given in Table 2. Specifically, charge transfer is the dominant process in the amine, terpene and aromatic hydrocarbon reactions. Extending this principle to H_2ONO^+ ions, it is reasonable to deduce that charge transfer should be energetically allowed in the reactions of these ions when their *effective* recombination energy $RE_{eff}(H_2ONO^+)$ exceeds IE(M). The $RE_{eff}(H_2ONO^+)$ is lower than IE(NO) by an amount equal to the NO^+–H_2O binding energy, which has been determined to be 0.72 eV [25–27,33]. So $RE_{eff}(H_2ONO^+)$ is 8.54 eV. In adopting this $RE_{eff}(H_2ONO^+)$ value to set the threshold for charge transfer, we tacitly assume that in this process the neutral NO and H_2O product molecules are not bound, for example:

$$H_2ONO^+ + M \rightarrow M^+ + NO + H_2O \qquad (3)$$

In the unlikely event that a weakly bound $\{NOH_2O\}$ molecule is temporarily formed, then the threshold will be increased accordingly. Theoretical studies have shown that there is a weakly bound neutral NOH_2O complex, but the binding energy is only 400 cm^{-1} (0.05 eV) [34], which barely influences the energetics of reactions such as reaction (3). Nevertheless, the results of those reactions that are close to thermoneutral must be interpreted circumspectly. If the reactant H_2ONO^+ ions possess excess vibrational energy (i.e., above thermal at 300 K) then charge transfer may become apparent in reactions for which this process is ostensibly endothermic for ground state ions. There is evidence for this in some of the reactions, as we discuss in Section 3.3.

Other reaction processes occur in the NO^+ reactions when charge transfer is energetically unfavourable. Hydride ion transfer is very common, especially in alcohol and aldehyde reactions, resulting in the formation of a neutral HNO molecule, as in the ethanol reaction [17,18]:

$$NO^+ + C_2H_5OH \rightarrow C_2H_5O^+ + HNO \qquad (4)$$

The structure of the product ion of this reaction that is allowed energetically is actually $C_2H_4OH^+$ [18] (breaking of the O–H bond is endothermic [35]), but for consistency all the product ions in the equations in this paper are given as their respective stochiometric formulae. Hydroxide ion

Table 2
Rate coefficients, *k*, and ion product distributions for the reactions of NO^+ and H_2ONO^+ with the organic compounds indicated

Compounds	$k(NO^+)$	Products from NO^+	$k(H_2ONO^+)$	Product from H_2ONO^+
Aniline $C_6H_5NH_2$	2.0 [2.3]	$C_6H_5NH_2^+$ (100)	1.8 [2.0]	$C_6H_5NH_2^+$ (100)
Trimethylamine $(CH_3)_3N$	1.8 [1.7]	$(CH_3)_3N^+$ (100)	1.4 [1.5]	$(CH_3)_3N^+$ (95), $C_3H_8N^+$ (5)
R-Limonene $C_{10}H_{16}$	2.2 [2.1]	$C_7H_8^+$ (5), $C_7H_9^+$ (4), $C_7H_{10}^+$ (3), $C_9H_{13}^+$ (2), $C_{10}H_{15}^+$ (4), $C_{10}H_{16}^+$ (82)	1.7 [1.8]	$C_{10}H_{16}^+$ (100)
Camphene $C_{10}H_{16}$	2.3 [2.1]	$C_7H_8^+$ (2), $C_7H_9^+$ (3), $C_7H_{10}^+$ (2), $C_9H_{13}^+$ (11), $C_{10}H_{16}^+$ (69), $NO^+C_{10}H_{16}$ (13)	1.6 [1.8]	$NO^+C_{10}H_{16}$ (50), $C_9H_{13}^+$ (50)
Benzene C_6H_6	1.5 [1.6]	$C_6H_6^+$ (85); $NO^+C_6H_6$ (15)	1.1 [1.4]	$NO^+C_6H_6$ (100)
Toluene $C_6H_5CH_3$	1.7 [1.8]	$C_7H_8^+$ (100)	1.2 [1.5]	$C_7H_8^+$ (100)
Methyl benzoate $C_6H_5COOCH_3$	2.0 [2.6]	$C_6H_5CO^+$ (90), $NO^+C_6H_5COOCH_3$ (10)	1.7 [2.2]	$C_6H_5CO^+$ (<5), $NO^+C_6H_5COOCH_3$ (>95), $C_6H_5COOCH_3^+$ (<2)
Ethyl acetate $CH_3COOC_2H_5$	2.4 [2.4]	$NO^+CH_3COOC_2H_5$ (90), CH_3CO^+ (10)	1.9 [2.1]	$CH_3COOC_2H_5H^+$ (15), $NO^+CH_3COOC_2H_5$ (55), $NO^+H_2OCH_3COOC_2H_5$ (30)
Acetic acid CH_3COOH	0.9 [2.2]	NO^+CH_3COOH (100)	0.6 [2.2]	$NO^+H_2OCH_3COOH$ (>95), NO^+CH_3COOH (<5)
n-Butanoic acid C_3H_7COOH	2.3 [2.4]	$NO^+C_3H_7COOH$ (50), $C_3H_7CO^+$ (50)	1.5 [2.1]	$C_3H_7COOHH^+$ (15), $NO^+C_3H_7COOH$ (70), $NO^+H_2OC_3H_7COOH$ (15)
Acetone CH_3COCH_3	1.8 [3.3]	$NO^+C_3H_6O$ (100)	1.6 [2.9]	$NO^+CH_3COCH_3$ (100)
2-Pentanone $CH_3(CH_2)_2COCH_3$	3.2 [3.2]	$NO^+CH_3(CH_2)_2COCH_3$ (100)	2.9 [2.8]	$NO^+CH_3(CH_2)_2COCH_3$ (100)
Acetaldehyde CH_3CHO	0.6 [3.2]	$C_2H_3O^+$ (100)	0.5 [2.8]	CH_3CO^+(60), NO^+CH_3CHO (40)
1-Butanal C_3H_7CHO	3.5 [3.2]	$C_4H_7O^+$ (100)	2.2 [2.7]	$C_4H_7O^+$ (>85), $C_3H_7CHOH^+$ (∼5), $NO^+C_3H_7CHO$ (∼10)
Ethanol C_2H_5OH	1.2 [2.3]	$C_2H_5O^+$ (100)	0.2 [2.1]	$CH_3CH_2OHH^+$ (100)
1-Butanol C_4H_9OH	2.7 [2.3]	$C_4H_9O^+$ (>95), $C_4H_9^+$ (<5)	1.2 [2.0]	$C_4H_9O^+$ (60), $C_4H_7^+$ (40)

Collisional rate coefficients, k_c, are given in square brackets. The k and k_c values are in unit of 10^{-9} cm^3/s. It is important to note that a fraction of the H_2ONO^+ ions are vibrationally excited (see Section 3, especially Section 3.3 concerning the H_2ONO^+/toluene reaction).

transfer is common in the carboxylic acid reactions, resulting in the formation of a neutral nitrous acid molecule HNO_2, this process often occurring in parallel with adduct formation [20], as in the *n*-butanoic acid reaction:

$$NO^+ + C_3H_7COOH \rightarrow C_3H_7CO^+ + HNO_2 \qquad (5a)$$

$$NO^+ + C_3H_7COOH \xrightarrow{He} NO^+C_3H_7COOH \qquad (5b)$$

Reaction (5b) is effectively a three-body association reaction in which an $(NO^+C_3H_7COOH)^*$ excited complex is first formed that partially dissociates (reaction (5a)) or is stabilised in collisions with helium carrier gas atoms (reaction (5b)).

The reactions of NO^+ with ketones usually involves adduct formation, but for the higher order ketones, which have IE values close to IE(NO) [19], charge transfer occurs in parallel [19]. In the present study, the re-measurement of the NO^+ reaction with 2-pentanone (by direct injection of NO^+ ions) revealed a small percentage (<4%) of charge transfer. Thus:

$$NO^+ + C_3H_7COCH_3 \rightarrow NO^+C_3H_7COCH_3 \qquad (6a)$$

$$NO^+ + C_3H_7COCH_3 \rightarrow C_3H_7COCH_3^+ + NO \qquad (6b)$$

As can be seen in Table 1, the published IE of 2-pentanone precludes a significant fraction (<1%) of these ion–molecule interactions occurring via charge transfer under fully thermalised conditions in the SIFT at 300 K. This is an indication that a minor fraction of the NO^+ ions that are injected directly into the helium carrier gas are vibrationally excited, since on the addition of air to the carrier gas the charge transfer product is absent (quenching occurs). We will return to this important point in Section 3.3, when we consider the reactions of the NO^+ ions derived from H_2ONO^+ break-up. It is clear that when all bimolecular reaction processes are endothermic, the NO^+ reactions can only occur via three-body (termolecular) adduct formation, as is the case for the acetone and acetic acid reactions (see Table 2).

How do these ideas and principles relate to the reactions of H_2ONO^+ ions? The following questions arise. Can these ions transfer protons to molecules, M, to form MH^+ ions and neutral HNO_2 molecules? Can simple ligand switching occur in which the H_2O moiety in the ion is replaced by the reactant molecule M thus forming NO^+M ions? Consideration of the details of some of the reactions included in this study reveals the answers to these questions.

3.2. *Amines and monoterpenes*

The amines have sufficiently low IE that charge transfer is possible and indeed occurs in their reactions with both NO^+ and H_2ONO^+, so nothing new can be described. The H_2ONO^+ ions apparently behave in the charge transfer reactions as lower energy NO^+ ions that release their H_2O ligand in the reactions. The NO^+ reactions with the terpenes proceed via charge transfer that results in partial dissociation, but the parent cations, $C_{10}H_{16}^+$, are the major product ions [23], as can be seen in Table 2. The reaction of H_2ONO^+ ions with limonene leads exclusively to the parent cation, the lower energy of this ion compared to NO^+ apparently preventing fragmentation. Charge transfer is predicted to be endothermic by about 0.3 eV in the H_2ONO^+/camphene reaction by virtue of the somewhat greater IE of camphene (see Table 1) and, indeed, the parent cation is not produced. In this case, the reaction proceeds via parallel ligand switching and CH_3 abstraction. Thus:

$$H_2ONO^+ + C_{10}H_{16}(\text{camphene}) \rightarrow NO^+C_{10}H_{16} + H_2O \tag{7a}$$

$$H_2ONO^+ + C_{10}H_{16}(\text{camphene}) \rightarrow C_9H_{13}^+ + CH_3NO + H_2O \tag{7b}$$

Alkyl radical abstraction reactions like (7b) are common when NO^+ reacts with several monoterpenes, including camphene, as our recent detailed study of the reactions of 11 monoterpenes has indicated [23]. Using the available thermochemical data [35], it is seen that reaction (7b) is exothermic by >64 kJ/mol. So, in this case, the reactant ion behaves both like a bare NO^+ ion and as a hydrate in which the H_2O ligand is replaced by a camphene molecule. More examples of this dual behaviour can be seen in Table 2.

3.3. Benzene and toluene

The IE of benzene is very close to that of NO [32] (see Table 1). This allows near-thermoneutral charge transfer to occur in the NO^+/benzene reaction and the proximity of the IE values assists the parallel partial formation of the adduct $(NO–C_6H_6)^+$ ions [17,22]. Charge transfer is, therefore, endothermic by about 0.7 eV in the reaction of vibrationally relaxed H_2ONO^+ ions with benzene and ligand switching is seen to occur exclusively, producing $NO^+C_6H_6$ ions. That ligand switching occurs rapidly indicates that the $NO^+–C_6H_6$ binding energy exceeds that of $NO^+–H_2O$ [33]. The IE of toluene (8.82 eV) is lower than that of NO and so charge transfer is facile in the NO^+/toluene reaction resulting in the parent cation as the only product ion, as has been observed in our previous study [22].

However, charge transfer between ground vibronic state H_2ONO^+ and toluene molecules is endothermic by 0.28 eV, yet $C_7H_8^+$ is seen to be the major product ion. This is surely due to excess vibrational energy in the H_2ONO^+ reactant ions and, as we will see in Sections 3.4 and 3.6, there is more evidence for this excitation from the ion products of other reactions. As indicated previously, the generation of this vibrational energy is most probably in the collisions of the H_2ONO^+ ions with helium atoms that partially dissociate them to NO^+. The energy of the $v = 1$ stretching vibration of the $(H_2ON–O)^+$ bond is 0.29 eV [27], which corresponds to the endothermicity of the toluene reaction. Thus, if this vibrational state is significantly populated and it survives in multiple collisions with helium atoms of the carrier gas, then it can drive the otherwise endothermic charge transfer reaction. It is well known from detailed SIFT studies that bare NO^+ ions can retain vibrational energy in helium [30] and so it is not unreasonable to consider that vibrational excitation can be retained in the N–O bond of the H_2ONO^+ ions against multiple helium atom collisions. The decay curves for the reactions with toluene of both H_2ONO^+ and NO^+ (for comparison) are shown in Fig. 1. Note the perfect linearity of the decay curve for injected NO^+ ions (and the H_3O^+ and O_2^+ ions) at the much higher count rates and the scatter about the lines for the NO^+ ions obtained from the break-up of H_2ONO^+ ions that are inevitably at much lower count rates. Notwithstanding the scatter, the H_2ONO^+ line is not noticeably curved. This is an indicator that either predominantly one reactant species is present in the swarm, in this case the vibrationally excited H_2ONO^+ ions, or that the ground state ions also react at or near the collisional rate, which is forbidden energetically for charge transfer. These data show that the H_2ONO^+/toluene reaction proceeds just a little more slowly than the upper-limit collisional rate (see Table 2).

As mentioned above, if the neutral products remain bound as (H_2ONO) following the charge transfer, then about 50 meV of energy is provided and the endothermicity of the charge transfer is reduced correspondingly, but it is still about 0.23 eV. In order to gain further understanding of the toluene reaction with H_2ONO^+ ions, we attempted to study it by forming the H_2ONO^+ ions from NO^+ ions that had been injected into the helium carrier gas. On the addition of toluene the $NO^+C_7H_8$ ion was clearly seen, the signal level being correlated with the signal level of the NO^+H_2O ion. The conclusion we draw from this observation is that ligand switching occurs in which the C_7H_8 toluene molecule replaces the H_2O molecule in the *ground* state NO^+H_2O ions, whereas for the *vibrationally excited* ion charge transfer occurs. These results illustrate a very interesting point that we have observed in many reactions (notably those of NO^+ with ketones [19]), which is that when charge transfer is energetically allowed it dominates over both ion–molecule association and ligand switching. This further emphasises the fact that the injected H_2ONO^+ ions are mostly vibrationally excited.

3.4. Methyl benzoate and ethyl acetate

Charge transfer between NO^+ ions and methyl benzoate is endothermic by 0.06 eV (see Table 1) and so their reaction proceeds largely via OCH_3 abstraction with a smaller (10%) adduct formation channel [20] (see Table 2). The proximity of the IE values for NO and $C_6H_5COOCH_3$ can promote adduct formation, as discussed previously. Charge transfer is endothermic by 0.7 eV for ground state reactant ions in the H_2ONO^+/methyl benzoate reaction, yet the parent cation is seen as a minor product (<2%). These parent cations are most probably produce from an impurity ion reaction (e.g., $NO^+(v)$), but in any event such is within the uncertainty in the determination of the product distributions. If the minor fraction of parent cations is ignored, the reaction proceeds along two channels only:

$$H_2ONO^+ + C_6H_5COOCH_3 \rightarrow NO^+C_6H_5COOCH_3 + H_2O \tag{8a}$$

$$H_2ONO^+ + C_6H_5COOCH_3 \rightarrow C_6H_5CO^+ + CH_3NO_2 + H_2O \tag{8b}$$

The major channel is ligand switching (reaction (8a)), the minor parallel channel being OCH_3 abstraction. Because the H_2ONO^+ reactant ions possess some vibrational energy, the ion product distribution given in Table 2 maybe somewhat different to that for ground state reactant ions. This comment applies to all the reactions included in this study. However, we do not expect the small amount of excess vibrational excitation in the H_2ONO^+ ions to dramatically influence their reactivity when their ground state ion reactions are significantly exothermic.

The first example of proton transfer is seen in the ethyl acetate reaction, this process occurring in parallel with both adduct formation and ligand switching:

$$H_2ONO^+ + CH_3COOC_2H_5 \rightarrow NO^+CH_3COOC_2H_5 + H_2O \tag{9a}$$

$$H_2ONO^+ + CH_3COOC_2H_5 \rightarrow NO^+H_2OCH_3COOC_2H_5 \tag{9b}$$

$$H_2ONO^+ + CH_3COOC_2H_5 \rightarrow CH_3COOC_2H_5H^+ + HNO_2 \tag{9c}$$

The proton transfer channel is clearly exothermic (see Table 1), but is still a minor channel in this reaction (see Table 2). We also see the first example of the association of H_2ONO^+ ions with a molecule (reaction (9b)). This indicates that this reaction proceeds via the formation of excited $(NO^+H_2OCH_3COOC_2H_5)^*$ adduct ions, which can be partially stabilised in helium atom collisions and partially separate along the two bimolecular channels, the major channel being ligand switching. This reaction well indicates the peculiar nature of this interesting ion.

3.5. Acetic acid and n-butanoic acid

NO^+ ions react with *n*-butanoic acid producing both $NO^+C_3H_7COOH$ adduct ions and $C_3H_7CO^+$ ions ($+HNO_2$ as a result of hydroxide ion transfer) in equal proportions [20], whereas in the acetic acid reaction only adduct formation occurs, hydroxide ion transfer being endothermic. Charge transfer is endothermic in both reactions, as can be seen by a glance at Table 1. In the H_2ONO^+ reactions with both acetic and *n*-butanoic acids, ligand switching and adduct formation occur (see Table 2). Proton transfer is also observed in the *n*-butanoic acid reaction, but this process is endothermic in the acetic acid reaction (see the list of proton affinities in Table 1). Ligand switching is the major channel in the H_2ONO^+/butanoic acid reaction; note the similarity of this reaction to the corresponding ethyl acetate reaction (Table 2). It is interesting that H_2ONO^+/M adduct ions are formed only with the carboxylic compounds (acetic and butanoic acids and ethyl acetate) amongst those compounds included in this study. We have no convincing explanation for this behaviour and more experiments need to be carried out to further investigate this.

3.6. Acetone and 2-pentanone

In the reaction of NO^+ with both these ketones, the only process that is observed is adduct formation, this being the common process in the several NO^+/ketone reactions that we have studied previously [19]. Although charge transfer is endothermic in both reactions, a small fraction of the parent cation was observed when the NO^+ derived from the break-up of H_2ONO^+ ions reacted with 2-pentanone. This again indicates that these NO^+ ions are partially vibrationally excited, those in their first vibrational state being able to charge transfer with the 2-pentanone molecule, which has an IE only slightly greater than IE(NO) (see Table 1). Since both charge transfer and proton transfer are endothermic in the reactions of ground vibronic state H_2ONO^+ ions with these two ketones, reactions occur via the only exothermic routes available, i.e., ligand switching producing $NO^+CH_3COCH_3$ and $NO^+C_3H_7COCH_3$ adduct ions.

3.7. Acetaldehyde and 1-butanal

These aldehydes react with NO^+ only via hydride ion transfer producing $(M–H)^+$ ions [19], as can be seen in Table 2. The acetaldehyde reaction is relatively inefficient, the rate coefficient for the reaction being only about 20% of the collisional rate. An ion cyclotron resonance study also showed that this reaction is inefficient [36]. The H^- ion must be abstracted from the C(H)=O grouping, since abstraction from the CH_3 grouping is very endothermic. The exothermicity of this reaction is only 0.7 eV and barriers may be present. However, the reactions of these aldehydes with H_2ONO^+ ions are more complex. The acetaldehyde reaction proceeds via parallel hydride ion transfer and ligand switching and the reaction is inefficient proceeding at a rate of about 15% of its collision rate. The hydride ion transfer reaction is apparently endothermic by 3 kJ/mol, which is sufficient to inhibit this process at a temperature of 300 K. That the parallel switching reaction is also slow implies that the $NO^+–CH_3CHO$ bond is comparable in strength to that of the $NO^+–H_2O$ bond. Hydride ion transfer in the 1-butanal reaction is exothermic by 18 kJ/mol and this is the major process that occurs in this efficient reaction for which three product ions are observed:

$$H_2ONO^+ + C_3H_7CHO \rightarrow C_4H_7O^+ + HNO + H_2O \quad (10a)$$

$$H_2ONO^+ + C_3H_7CHO \rightarrow NO^+C_3H_7CHO + H_2O \quad (10b)$$

$$H_2ONO^+ + C_3H_7CHO \rightarrow C_3H_7CHOH^+ + HNO_2 \quad (10c)$$

Ligand switching also occurs and additionally a minor proton transfer channel is evident, this process being exothermic according to the proton transfer ladder given in Table 1.

3.8. Ethanol and 1-butanol

The reaction of NO^+ with ethanol proceeds via hydride ion (H^-) transfer only and the reaction is relatively slow, perhaps implying that barriers are involved. H^- transfer is also the major process in the NO^+/1-butanol reaction, but a minor hydroxide ion (OH^-) transfer product is also evident (producing $C_4H_9{}^+$ ions; see Table 2). OH^- transfer dominates the reactions of NO^+ with tertiary alcohols, as our previous study has shown [17,18]. This reaction has been studied using ion cyclotron resonance with very similar results ([36] and also see [18]).

The reactions of H_2ONO^+ ions with these alcohols are the most unusual and challenging of all the reactions in this study. The ethanol reaction is very slow and the only product is that due to proton transfer, $C_2H_5OH_2{}^+$. When proton transfer is slow, the implication is that it is not greatly exothermic. A previous study has shown that the minimum difference in the PA of the donor and acceptor molecules for fast proton transfer to occur is 15–20 kJ/mol [37]. On this evidence alone, the present experimental data would indicate that the PA of nitrous acid is closer to the lower value given in Table 1 of 780 kJ/mol rather than the higher value of 801 kJ/mol. Hydroxide ion transfer is exothermic by only 1 kJ/mol and is not observed. Adduct formation has not been observed in any of the many reactions of NO^+ ions with alcohols that we have studied [18], presumably because hydride ion and hydroxide ion transfer are often significantly exothermic and facile for the larger alcohols. Establishing that $C_2H_5OH_2{}^+$ was the product of this reaction was complicated by the fact that the NO^+ ions that were simultaneously present reacted with ethanol to produce $C_2H_5O^+$ ions, and these reacted rapidly with ethanol to produce $C_2H_5OH_2{}^+$ also. Hence, careful kinetic modelling of the secondary chemistry was required to prove that the product of the slow H_2ONO^+/ethanol reaction was indeed $C_2H_5OH_2{}^+$.

The H_2ONO^+/1-butanol reaction is difficult to understand. These SIFT experiments indicate that two product ions result:

$$H_2ONO^+ + C_4H_9OH \rightarrow C_4H_9O^+ + HNO + H_2O \quad (11a)$$

$$H_2ONO^+ + C_4H_9OH \rightarrow C_4H_7{}^+ + (H_2O + HNO) + H_2O \quad (11b)$$

However, all our efforts to establish the thermicity of reaction (11b) indicate that for all the likely structures of the $C_4H_7{}^+$ ion, and for any acceptable configurations of the neutral products, the production of $C_4H_7{}^+$ ions is endothermic. This is so even when its structure is $CH_3CH_2CH{=}CH^+$, this ion having the lowest heat of formation of the isomers for which thermochemical data are available [35]. However, a potentially more stable structure, $CH_3CH{=}CHCH_2{}^+$, is possible, for which thermochemical data are not available. We tentatively suggest that the reaction proceeds via the formation of $(C_4H_9O^+)^*$ excited ions (reaction (11a) is exothermic by at least 13 kJ/mol [35]), which then partially decomposes in the multiple collisions that they suffer with helium atoms as they pass along the SIFT. This reaction remains intriguing and is deserving of a more thorough study. An interesting suggestion concerning the origin of the $C_4H_7{}^+$ ions was made by one of the referees, who questioned if the 1-butanol vapour could be partially dehydrated to butene (C_4H_8) in the heated feed line via which the air/butanol mixture is introduced. This suggestion has caused us some thought. The reactant mixture only spends about a millisecond in the heated feed line before entering the carrier gas, which is held at room temperature and in which the feed gas is quickly cooled. We have seen no evidence for this phenomenon previously for unstable compounds and thus we are sceptical that it could be the origin of the $C_4H_7{}^+$ ions. Also, these ions are not seen as products when NO^+ reactant ions are used.

4. Concluding remarks

This study has revealed the very unusual nature of the H_2ONO^+ ion. Several types of processes occur in its reactions with a range of organic molecules. These are charge transfer with organic compounds, M, that have low ionisation energies (producing M^+ ions), proton transfer with compounds possessing large proton affinities (MH^+), hydride ion transfer $(M–H)^+$, alkyl radical $(M–R)^+$ and alkoxide radical $(M–OR)^+$ transfer, ion–molecule association (H_2ONO^+M) and ligand switching (NO^+M). In each of the ethyl acetate, *n*-butanoic acid and 1-butanal reactions, three different processes occur in parallel (see Table 2). These observations answer the questions posed earlier, since they reveal that H_2ONO^+ ions react like both hydrated nitrosonium ions and protonated nitrous acid.

It must be stated again that the experimental data shows that the reactant H_2ONO^+ ions studied in these experiments are partially vibrationally excited, most probably as a result of the collisions they suffer with the helium atoms of the carrier gas on injection. This vibrational energy was not readily removed by the addition of air (N_2 and O_2 molecules) to the helium carrier gas, which is known to quench vibrational excitation in NO^+ ions [30]. So the kinetic data summarised in Table 2 may be somewhat different for the reactions of ground vibronic state ions, especially for those reactions that are close to thermoneutral, such as the toluene reaction.

If kinetic data are desired for the reactions of these remarkable ions in their ground vibronic states, vibrational excitation must be avoided during the injection procedure, but this would require much lower injection energies, which currently leads to unacceptably low precursor ion signals. A possible approach would be to use a flowing afterglow ion source [38,39], which would surely be a richer source of H_2ONO^+ ions.

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